

Symmetry and Condensed Matter Physics

A Computational
Approach

Michael El-Batanouny and Frederick Wooten

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Symmetry and Condensed Matter Physics

Unlike existing texts, this book blends for the first time three topics in physics: symmetry, condensed matter physics, and computational methods, into one pedagogical textbook. It includes new concepts in mathematical crystallography; experimental methods capitalizing on symmetry aspects; nonconventional applications such as Fourier crystallography, color groups, quasi-crystals and incommensurate systems; and concepts and techniques behind the Landau theory of phase transitions.

The textbook adopts and develops a computational approach to the application of group theoretical techniques to solving symmetry-related problems. This dramatically alleviates the need for intensive calculations, even for the simplest systems, usually found in the presentation of symmetry. Writing computer programs helps the student achieve a firm understanding of the underlying concepts, and sample programs, based on Mathematica[®], are presented throughout the book.

Containing over 150 exercises, this textbook is ideal for graduate students in condensed matter physics, materials science, and chemistry. Solutions and computer programs are available online at www.cambridge.org/9780521828451.

MICHAEL EL-BATANOUNY is a Professor in the Department of Physics at Boston University. His research area is experimental surface physics and he has written numerous papers on solid state physics and surface physics.

FREDERICK WOOTEN (1928–2004) was Professor of Physics and Chair of the Department of Applied Science at the University of California, Davis. He is the author of *Optical Properties of Solids* and numerous articles in the fields of solid state physics and materials science.

Symmetry and Condensed Matter Physics

A Computational Approach

M. El-Batanouny

Boston University

F. Wooten

University of California, Davis



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This book is dedicated to my loving wife Gloria, to the memory of
my parents Maurice and Hayat, and to my sister Nagwa. (ME)

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Preface

Pedagogical presentation and analysis of the symmetry aspects of physical systems in terms of group theoretical concepts and methodology has been evolving over the past six or seven decades, since the pioneering textbooks by Weyl and Wigner first appeared. This constantly evolving pedagogy has resulted in over a hundred textbooks on the subject. The impetus behind these efforts has stemmed from the general recognition of the invaluable role that the application of such methodology plays in determining and predicting the properties of a physical system.

Symmetry concepts provide a very useful means for systematizing the description of a physical system in terms of its energy and momentum, and other relevant physical quantities. Furthermore, the incipient methodologies furnish a very efficient framework for classifying its physical states, and a crucial machinery for simplifying the intervening numerical applications of physical laws. By means of the irreducible representations of its symmetry group, one can classify physical states and particles in a logical way and establish selection rules, which predict restrictions on possible transitions between different physical states. The use of symmetry also simplifies numerical calculations, for example, in solving the Schrödinger equation for condensed matter systems. Moreover, from the symmetry properties of a physical system, one can make conclusions about the values of measurable physical quantities, and, conversely, one can trace a symmetry group of a system from observed regularities in measured quantities. There is also an intimate connection between symmetry, invariance and dynamical laws.

Despite all these merits, the application of symmetry methods has been seriously hampered by the need for painstaking and tedious calculations, even when dealing with the simplest group symmetries. This drawback has led many students and practitioners in the area of condensed matter physics to shy away from learning the fundamentals of this invaluable discipline.

In the recent past, a number of new ideas, techniques and approaches have emerged that have yet to be incorporated in textbooks on symmetry. We believe that the adoption of these novel aspects within a new pedagogical approach would dramatically simplify existing instructional procedures, remove the cumbersome calculational barriers that tend to severely limit the scope of examples and exercises, and provide a conduit for elucidating and unifying seemingly diverse aspects under one umbrella. We attempt to implement such an approach in this book, and present the necessary tools for its application in diverse areas in condensed matter physics.

One of the novel features characterizing this book and setting it apart from others is that it adopts and develops at the outset a computational approach to the theory of finite groups and its applications in physics. A computational approach to group theory has several significant advantages. First, it eliminates traditional difficulties encountered in problem solving. Second, it provides an alternative pedagogical process whereby a student would learn the material through writing computer programs: A logical prerequisite for program writing is that the student must have acquired a detailed understanding of the material at hand!

The modern basis for computational methods in group and representation theories dates from the 1960s, with the development of computer algorithms for generating permutation groups and studying their structure, and with the introduction of John Dixon's method for the *exact* calculation of "characters" of finite groups, which can be easily implemented on a computer. Currently, there are at least two computational systems that are well suited for the analysis of symmetry groups: GAP and MAGMA; they can be accessed through the web. However, here we shall follow the methods proposed by Stig Flodmark and Esko Blokker. These authors, recognizing the importance and utility of Dixon's method, developed computer algorithms and programs to implement Dixon's exact character method, and to use the results to construct the corresponding unitary irreducible matrix representations.

We develop the underlying ideas, algorithms and methodology for such calculations in the first seven chapters. The reader is first exposed to the relevant conceptual aspects, then introduced to corresponding computational algorithms, and instructed in methods for implementing these algorithms into programs and subroutines. We find that *Mathematica*, because of its capability to handle symbolic and combinatorial manipulations, provides a natural and convenient environment for the development of such programs. So, the main instructions in the computational approach will be based on the language of *Mathematica*. However, every student will be encouraged to develop programs in any language he or she is comfortable with. Our versions of all the *Mathematica*-based computational programs will be posted on a website, together with data files relevant to space- and point-groups.

Our work is intended to make the computational approach to group theory available to a wider audience. It is aimed at students in the physical sciences: physics, chemistry, materials science and, possibly, some disciplines in engineering. We also have in mind the working professional who would like to learn the subject or who already knows it but is unfamiliar with the modern computational approach.

In addition to adopting computational techniques, we introduce and develop several concepts that have, at best, been marginally treated in textbooks on symmetry, to date.

We develop the ideas of group actions on systems and their decomposition into orbits and strata. We demonstrate and stress the fundamental relevance of the study of the corresponding orbit space and of the set of strata to physical problems. For example, we demonstrate how the notions of the *star of the wavevector*, which appears in the theory of representations of space-groups, of *Wyckoff positions*, which are encountered in crystallography, and of images of the order-parameter of a phase transition are all manifestations of orbits. Thus, we inadvertently apply these concepts to different domains of condensed matter physics, without realizing that they are actually decompositions into orbits and strata made under different names, and, in fact they should be unified under

one umbrella. Thus, linear representations, which are engendered by group action on a basis set, are just a particular case of group actions. Group actions are introduced in Chapter 6. Subsequently, their use and appearance are stressed when appropriate.

In Chapter 6, we also introduce the concept of symmetry-projection operators and develop the computational tools for their construction, using their hermiticity and idempotency properties to cast the corresponding matrices into the form of a simple eigenvalue problem.

In Chapter 8, we introduce the notions of subgroups, cosets, normal subgroups, product groups, Kronecker products, and Clebsch–Gordan series; and end by presenting techniques for determining the Clebsch–Gordan coefficients. In Chapter 9, we explore the processes of induction and subduction of irreducible representations (Irreps) and the concept of compatibilities relating these Irreps.

In Chapter 10, we present a long and comprehensive exposé of crystallography. The novel feature of this chapter is the detailed presentation of concepts in mathematical crystallography. These include a detailed discussion of arithmetic holohedries and classes, as well as Bravais classes, classification of space-groups with respect to affine conjugations, site-symmetries, and Wyckoff positions and sets. Another unique feature of this chapter is a section on Fourier crystallography, which is one of the two methods used to study the symmetries of quasi-crystals in Chapter 18. In Chapter 11, we develop the machinery for determining the Irreps of symmorphic and nonsymmorphic space-groups.

In Chapter 12, we introduce time-reversal symmetry, and discuss the concepts of double-groups. We include in this chapter a long section on color, or Shubnikov, groups and another section detailing the construction of corepresentations. The section on the color groups includes dichromatic (black and white) point-groups, lattices and space-groups. It also discusses the extension of these concepts to polychromatic symmetries. Another section on crystal-field theory is presented and extended to cover the case of dichromatic symmetry. We end this chapter with a detailed discussion of the manifestation of time-reversal symmetry in transport properties, which is elegantly cast in the Onsager reciprocity relations.

The remaining chapters, 13–18, are dedicated to applications in diverse fields of condensed matter physics. We have extended the applications beyond the usual topics taken up in most texts on the subject. In Chapter 13 we develop the theory of tensors, present techniques for the construction of symmetry-adapted tensors, and finally present a catalog of the different material tensors. We end this chapter with an exposé of tensor fields and their relation to symmetry projection operators.

Chapter 14 develops the basic principles of the electronic structure of solids and methods for computation. The final section presents how the special features of the electronic structure of magnetically ordered systems can be viewed and classified in terms of corepresentations. Chapter 15 develops methods for computing and classifying the dynamical properties of solids and solid surfaces.

Chapter 16 is dedicated to the discussion of symmetry-based experimental techniques such as neutron and atom scattering, angle-resolved photoemission, and Raman spectroscopy.

The Landau theory of phase transitions is discussed in detail in Chapter 17. Applications to commensurate–incommensurate and magnetic phase transitions are given. A long section is devoted to methods of construction of the *Landau free energy*, including ones based on the theory of invariant polynomials, group action, and order-parameter image groups.

Finally, Chapter 18 addresses the fundamental aspects of the symmetry of quasi-crystals and incommensurate systems. The symmetries of these systems are developed along two tracks. First, the concepts of hyperspace symmetries and their projection onto the natural lower-dimensional spaces are presented. Second, the application of the techniques of Fourier space crystallography, developed in Chapter 10, are discussed.

The main emphasis, throughout this book, is on exposing the *conceptual* building blocks of this mathematical theory of symmetry. Consequently, we frequently skip over long detailed mathematical proofs which can be found in a multitude of textbooks. Instead, we point the reader to references where such proofs are clearly presented. Moreover, in contrast to previous texts on the subject, the different aspects of group theory are presented wherever they are needed rather than being lumped into one single exposé. This has the merit of associating a certain aspect of the theory with a tangible physical attribute. Thus, for example, we defer the introduction of cosets and invariant subgroups till we discuss space-groups, where they find immediate application.

Our interest throughout is in clarity and simplicity rather than elegance. We have striven to meet the needs of the beginner who must work through the gory details of many simple examples, much as we ourselves did in trying to learn the subject matter. We do not wish to hide these details in compact mathematical notation.

1

Symmetry and physics

1.1 Introduction

The application of *group theory* to study physical problems and their solutions provides a formal method for exploiting the simplifications made possible by the presence of symmetry. Often the symmetry that is readily apparent is the symmetry of the system/object of interest, such as the three-fold axial symmetry of an NH_3 molecule. The symmetry exploited in actual analysis is the symmetry of the Hamiltonian. When alluding to symmetry we usually include geometrical, time-reversal symmetry, and symmetry associated with the exchange of identical particles.

Conservation laws of physics are rooted in the symmetries of the underlying space and time. The most common physical laws we are familiar with are actually manifestations of some universal symmetries. For example, the homogeneity and isotropy of space lead to the conservation of linear and angular momentum, respectively, while the homogeneity of time leads to the conservation of energy. Such laws have come to be known as universal conservation laws. As we will delineate in a later chapter, the relation between these classical symmetries and corresponding conserved quantities is beautifully cast in a theorem due to Emmy Noether.

At the day-to-day working level of the physicist dealing with quantum mechanics, the application of symmetry restrictions leads to familiar results, such as selection rules and characteristic transformations of eigenfunctions when acted upon by symmetry operations that leave the Hamiltonian of the system invariant.

In a similar manner, we expect that when a physical system/object is endowed with special symmetries, these symmetries forge conservation relations that ultimately determine its physical properties. Traditionally, the derivation of the physical states of a system has been performed without invoking the symmetry properties, however, the advantage of taking account of symmetry aspects is that it results in great simplification of the underlying analysis, and it provides powerful insight into the nature and the physics of the system. The mathematical framework that translates these symmetries into suitable mathematical relations is found in the theory of groups and group representations. This is the subject we will try to elucidate throughout the chapters of this book.

Let us begin with a tour de force, exploring the merits of invoking symmetry aspects pertinent to familiar but simple problems. We start by reminding ourselves of the trivial example of using symmetry, or asymmetry, to simplify the evaluation of an integral.

Consider

$$\int_{-b}^{+b} \sin x \, dx = 0.$$

We *know* this to be true because $\sin x$ is an odd function; $\sin(-x) = -\sin(x)$. In evaluating this integral, we have taken advantage of the asymmetry of its integrand. In order to cast this problem in the language of symmetry we introduce two mathematical operations: I , which we will identify later with the operation of inversion, and which, for now, changes the sign of the argument of a function, i.e. $I f(x) = f(-x)$; and E , which is an identity operation, $E f(x) = f(x)$. This allows us to write

$$\int_{-b}^{+b} \sin x \, dx = \int_0^b (E + I) \sin(x) \, dx = \int_0^b (1 + (-1)) \sin(x) \, dx = 0.$$

Figure 1.1 shows schematically the plane of integration, with $\oplus$ and $\ominus$ indicating the sign of the function $\sin x$.

We may introduce a more complicated integrand function $f(x, y)$, and carry the integration over the equilateral triangular area shown in Figure 1.2.

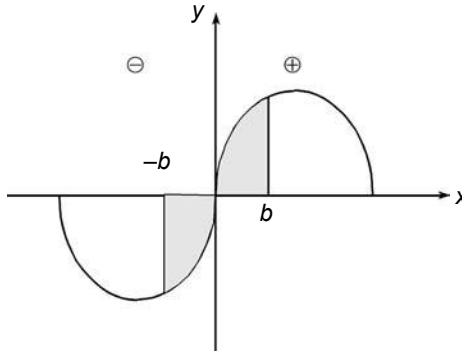


Fig. 1.1. The asymmetric function $\sin x$.

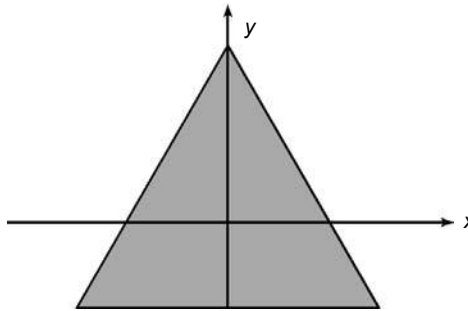


Fig. 1.2. Integration domain.

Making use of the 3-fold symmetry of the triangle, which includes rotations by multiples of $2\pi/3$, as well as reflections shown in Figure 1.3, we write the integral in the form

$$\int_{\text{triangle}} f(x, y) dx dy = \int_{\text{wedge}} (E + O_{(2\pi/3)} + O_{(4\pi/3)} + \sigma_1 + \sigma_2 + \sigma_3) \times f(x, y) dx dy,$$

where the O s represent counterclockwise rotations by the angle specified in the suffix, and the σ s are defined in Figure 1.3. Now, if the function $f(x, y)$ possesses a symmetry which can be associated with that of the triangle, as for example shown in Figure 1.4, the integral vanishes.

Later, we will see how to reach similar conclusions in the case of selection rules, for example, where the situation may be much more complicated.

Next, we present a simple example to demonstrate how to invoke symmetry to simplify the solution of dynamical problems. We consider a system of two masses and three springs as illustrated in Figure 1.5. Assume both masses to be equal to m and that all springs have the force constant κ . In that case, the Hamiltonian, which is the

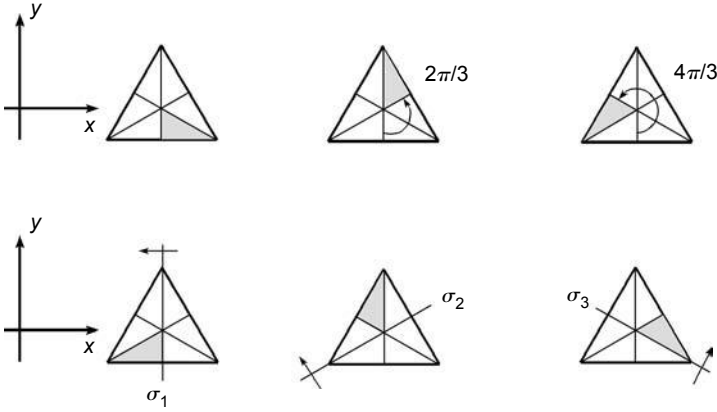


Fig. 1.3. Symmetry operations of an equilateral triangle.

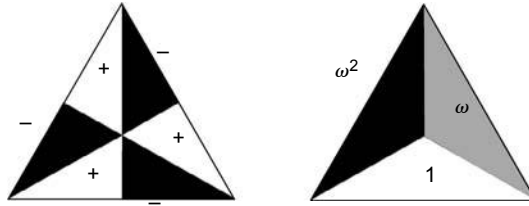


Fig. 1.4. Some possible symmetries of $f(x, y)$ on an equilateral triangle.

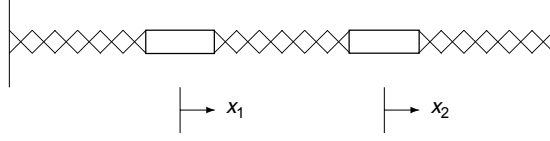


Fig. 1.5. A two-mass system with inversion symmetry about the center point.

total energy of the system,

$$\mathcal{H} = \sum_{i=1}^2 \left[\frac{p_i^2}{2m} + \frac{\kappa}{2} x_i^2 \right] + \frac{\kappa}{2} (x_2 - x_1)^2,$$

is invariant under the operation of *inversion*. That is, an inversion of the system through the mid-plane, which takes $x_1 \mapsto -x_2$ and $x_2 \mapsto -x_1$, leaves the Hamiltonian invariant.

A lengthy normal mode analysis shows that the energy eigenvectors are

$$\begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} 1 \\ -1 \end{pmatrix}.$$

This means there are two distinct modes of vibration, one in which the masses move in opposite directions and by equal amounts and one in which the masses move in the same direction and by equal amounts.

We can exploit the symmetry of this problem to obtain the same result, but with much less effort. Let I be the inversion operator. Since the Hamiltonian is invariant under the inversion operation, I commutes with H and thus the eigenvectors of I are also the eigenvectors of H . Writing the displacements x_1 and x_2 as the components of a vector $\mathbf{u}$ we have

$$I\mathbf{u} = I \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = \begin{pmatrix} -x_2 \\ -x_1 \end{pmatrix}. \quad (1.1)$$

If the vector $\mathbf{u}$ is an eigenvector of I then we have

$$I\mathbf{u} = \begin{pmatrix} -x_2 \\ -x_1 \end{pmatrix} = \lambda \mathbf{u}, \quad (1.2)$$

where λ is the eigenvalue, and applying the inversion operation once more we obtain

$$\begin{aligned} I^2\mathbf{u} &= \lambda^2\mathbf{u} \\ &= I(I\mathbf{u}) = I \begin{pmatrix} -x_2 \\ -x_1 \end{pmatrix} = \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = \mathbf{u}. \end{aligned} \quad (1.3)$$

Thus $\lambda^2 = 1$, and the eigenvalues of I are $\lambda = \pm 1$, with corresponding eigenvectors

$$\mathbf{u}_1 = \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad \text{and} \quad \mathbf{u}_2 = \begin{pmatrix} 1 \\ -1 \end{pmatrix}, \quad (1.4)$$

which are identical to those of the Hamiltonian. They describe the displacement amplitudes of the masses during normal mode vibrations and are either even or odd with respect to the inversion symmetry.

We learn that for a classical system with a symmetric one-dimensional potential $V(x)$, the eigenfunctions are of either odd or even parity, and we have seen how this knowledge can be used to simplify finding the solution to a problem. Quantum systems are generally much more complicated. Except for a few important but relatively simple systems, such as the hydrogen atom, the harmonic oscillator, and the Kronig–Penney model for a periodic lattice, most problems in quantum mechanics must be solved numerically.

Because the calculations are often long and tedious, and much effort is devoted to numerical methods, accuracy becomes a concern. Fortunately, some simplifications based on *symmetry* can be *rigorously* made. These usually involve the construction of *symmetry projection operators*, which are, in turn, based on the concept of *irreducible representations* (Irreps) and their characters. We will develop the ideas of *characters* and *representations* in Chapters 3–5. Here we state only that they play an all-important role in group theory.

We will present in Chapters 5 and 7 exact computational procedures for the calculation of matrix Irreps and characters using a method proposed by John Dixon in 1967. However, we stress here only that all the important quantitative symmetry information can be obtained with the aid of simple computer calculations.

1.2 Hamiltonians, eigenfunctions, and eigenvalues

A typical problem in condensed matter physics involves the determination of the physical states of a system given its Hamiltonian or its free energy. Consequently, the symmetry we need to exploit is, generally, that of the Hamiltonian. The application of symmetry will then require the definition of the corresponding operators and the specification of the rules of the action of these operations. Since a Hamiltonian can be defined on the configuration space of the physical system, we define a symmetry operation as a transformation effected on this configuration space. An example is the inversion operator I , which effects a vector transformation

$$\mathbf{r} \mapsto -\mathbf{r}.$$

Other typical operations are reflections, rotations, and translations. We write the transformation involving a symmetry operator $\hat{O}$ as

$$\hat{O} \mathcal{H} \hat{O}.$$

We start by collecting the symmetry operations that leave the Hamiltonian $\mathcal{H}$ *invariant*, i.e. those whose action leaves $\mathcal{H}$ unchanged. We designate this set of operations the *symmetry group*¹ of $\mathcal{H}$. If $\hat{O}$ is such an operator, then

$$\hat{O} \mathcal{H} \hat{O}^\dagger = \mathcal{H} \tag{1.5}$$

or

$$\hat{O} \mathcal{H} = \mathcal{H} \hat{O}. \tag{1.6}$$

Thus, if $\hat{O}$ leaves the Hamiltonian invariant, it must commute with the Hamiltonian. But what is the effect on an eigenfunction belonging to $\mathcal{H}$? We have

$$\mathcal{H} \Psi_i = E_i \Psi_i \tag{1.7}$$

¹ The word group will be justified in Chapter 2.

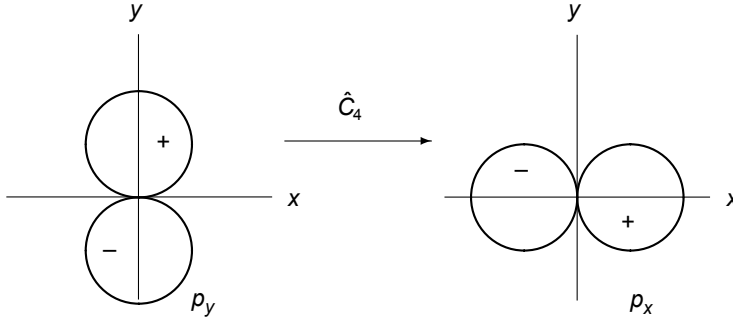


Fig. 1.6. $\hat{C}_4$ acting on p_y produces p_x .

which, when operated on by $\hat{O}$, gives

$$\hat{O}(\mathcal{H}\Psi_i) = \hat{O}(E_i\Psi_i). \quad (1.8)$$

Since the symmetry operator $\hat{O}$ commutes with $\mathcal{H}$, as described by (1.6), we obtain

$$\mathcal{H}(\hat{O}\Psi_i) = E_i(\hat{O}\Psi_i), \quad (1.9)$$

and we see that if Ψ_i is an eigenfunction, $\hat{O}\Psi_i$ is also an eigenfunction of the same Hamiltonian with the same eigenvalue E_i .

From quantum mechanics it is known that two commuting operators share a common set of eigenfunctions. Here we learn that by operating on an eigenfunction with a symmetry operator we generate another eigenfunction belonging to the same eigenvalue.

A pictorial example of the generation of a new eigenfunction with a symmetry operator is shown in Figure 1.6, it depicts the generation of a p_x -orbital by operating on a p_y -orbital with a $\pi/4$ rotation about the z -axis.

This example illustrates that the symmetry operators also act on functions defined on configuration space.²

All functions generated by the successive application of the operator $\hat{O}$ and all other symmetry operators of the system form a degenerate manifold in the Hilbert space of the Hamiltonian. The family of functions forming the basis of this manifold is classified by some characteristic symmetry properties, which distinguish it from other classes or families of functions in the Hilbert space.

To illustrate this property of generating distinct families of functions in Hilbert space, we consider the consequence of space isotropy, which is encountered under many guises

² A note on *function-space operators*

Function-space operators are generally denoted by a “hat” over the symbol for the operator, as in $\hat{O}$. This is not formally necessary in that it is possible to infer the nature of the operator by its context. If an operator acts on a function it is a function operator. Thus, sometimes, to reduce clutter, it may be convenient to not use a hat. Indeed, we do not use a hat over the Hamiltonian, which operates on wavefunctions. However, prudent practice is to use the hat for emphasis, since there are subtle differences in the action of a function operator on the coordinate variables of a function and the action of a configuration-space operator on the coordinates of a physical entity. This will be made clear in later sections of this chapter.

in mechanics, electromagnetics, and quantum mechanics. It is manifest in the family of functions we know as *spherical harmonics*, Y_l^m , which form disjoint subspaces denoted by the index l , each subspace l has dimension $2l + 1$.³

Since isotropy means invariance under arbitrary infinitesimal rotations, it implies that a system with such symmetry should be invariant under all possible rotation operations. In quantum mechanics, isotropic symmetry of a system implies that all such operations should commute with its Hamiltonian, and thus their application to the eigenfunctions of the Hamiltonian should reveal the degeneracy within each spherical harmonic manifold in its Hilbert space.

In classical mechanics and electromagnetics, as well as in quantum mechanics, the closure of the different manifolds is demonstrated by the well-known *addition theorem* of Legendre polynomials. In essence these relations express the fact that pure angular rotations of, for example, p -states about their origin result in another p -state and thus do not alter the angular characteristics of the eigenfunction. Similar rotations of a dipole produce only other dipoles, not other multipoles.

The existence of a set of classes of symmetries to which symmetrized functions distinctly belong in isotropic space, that is, the *spherical harmonics*, is not an isolated case. It is the general feature for any underlying configurational symmetry. For example, the homogeneity of space leads to the natural adaptation of *plane-wave* functions as a distinct set for classifying symmetrized functions in this configuration space. The symmetry classes associated with a given symmetry group are conventionally known as its *irreducible representations*.

Another example may be found in quantum systems for which the symmetry of indistinguishability among a set of particles leads to two distinct and disjoint classes of wavefunctions which are commonly referred to as fermion and boson wavefunctions, or particle systems. To underscore the connection between the symmetry and the nature of the allowed states of such systems let us review the argument behind this well-established classification. The indistinguishability of the particles requires that the associated Hamiltonian should not change when two particles are exchanged, that is, $\mathcal{H}$ is invariant under such an exchange, or *permutation*, operation. If we denote the operator associated with a two-particle permutation operation by $\hat{P}_{12}$, we may write

$$\hat{P}_{12} \mathcal{H} \Psi = \mathcal{H} \hat{P}_{12} \Psi = E \hat{P}_{12} \Psi. \quad (1.10)$$

Now, the commutation of $\hat{P}_{12}$ with $\mathcal{H}$ requires that they share common eigenfunctions. If we consider the eigenfunctions of $\hat{P}_{12}$, we have

$$\hat{P}_{12} \Psi = \lambda \Psi, \quad (1.11)$$

which means the exchange operation leaves the state unchanged apart from a multiplicative, possibly complex, factor λ . A second application of $\hat{P}_{12}$ returns the system to its original configuration, so that

$$\hat{P}_{12}^2 \Psi = \lambda^2 \Psi = \Psi, \quad (1.12)$$

³ In electromagnetics the spherical harmonics describe monopole, dipole, quadrupole, ... fields, and in atomic physics they are manifest as $s, p, d, \dots$ states. Indeed, the structure of the periodic table of the elements is a consequence of the three-dimensional isotropic character of space.

hence

$$\lambda^2 = 1 \quad (1.13)$$

or $\lambda = \pm 1$, thus establishing *two distinct classes of eigenstates* of a Hamiltonian describing a set of indistinguishable particles, namely, those that transform even and those that transform odd under the permutation or particle-exchange operation.

1.2.1 Examples of symmetry and conservation laws

Translation and conservation of linear momentum

Given a classical system's Hamiltonian $\mathcal{H}(x, p)$, where x and p are conjugate coordinate and momentum variables, we write the canonical equations of motion as

$$\begin{aligned} \dot{x} &= \frac{\partial \mathcal{H}}{\partial p}, \\ \dot{p} &= -\frac{\partial \mathcal{H}}{\partial x}. \end{aligned}$$

If the system is invariant under arbitrary translations, then the r.h.s of the second equation vanishes and the linear momentum p is conserved. When the system is treated quantum mechanically, we define the translation operator corresponding to an infinitesimal displacement dx as

$$R(dx) x = x + dx,$$

and, as we will show in Section 1.3, its action on function-space is given by

$$\hat{R} |\psi(x)\rangle = |\psi(x - dx)\rangle = |\psi(x)\rangle - i \frac{p}{\hbar} dx |\psi(x)\rangle,$$

so that the operator $\hat{R}$ can be expressed as

$$\hat{R} = \exp \left(-i \frac{p dx}{\hbar} \right). \quad (1.14)$$

If the Hamiltonian is invariant under such operations, then

$$[\hat{R}, \mathcal{H}] = 0. \quad (1.15)$$

Using Heisenberg's equation of motion and substituting (1.14), we obtain

$$\frac{d}{dt} \langle p \rangle = \frac{1}{i\hbar} \langle [p, \mathcal{H}] \rangle = 0. \quad (1.16)$$

Inversion and parity conservation

Consider a system which remains invariant under the inversion operation, i.e.

$$[\hat{I}, \mathcal{H}] = 0, \quad (1.17)$$

then we find that it also commutes with the time-translation operator

$$\hat{U}(t_2, t_1) = \exp \left[-i \frac{\mathcal{H}(t_2 - t_1)}{\hbar} \right] \Rightarrow [\hat{I}, \hat{U}] = 0.$$

Since $\hat{I}$ commutes with $\mathcal{H}$, they have simultaneous eigenfunctions, such that

$$\hat{I} | \psi(t_1) \rangle = \lambda_1 | \psi(t_1) \rangle. \quad (1.18)$$

Since $\hat{I}^2$ is the identity, λ_1 assumes the values ± 1 only, and we obtain

$$\begin{aligned} \hat{I} | \psi(t_2) \rangle &= \hat{I} \hat{U}(t_2, t_1) | \psi(t_1) \rangle = \hat{U}(t_2, t_1) \hat{I} | \psi(t_1) \rangle \\ &= \lambda_1 \hat{U}(t_2, t_1) | \psi(t_1) \rangle = \lambda_1 | \psi(t_2) \rangle. \end{aligned} \quad (1.19)$$

1.3 Symmetry operators and operator algebra

We introduced earlier the idea that symmetry operators may act on Hamiltonians as well as functions, and that these actions can be regarded as transformations in configuration space. Here, we shall give a detailed exposé of these ideas, and establish some concepts and conventions needed in order to be self-consistent in applying symmetry operations to physical applications of group theory.

1.3.1 Configuration-space operators

Configuration space is the real physical space in which physical objects move, i.e. where we define classical particle trajectories and quantum mechanical wavefunctions and probabilities. Operators acting in this space are known as *configuration-space operators*. Now, we consider a point object P, a particle in this space, located at position $\mathbf{r}$ with respect to the reference axes, as shown in Figure 1.7. If the object is translated by a vector $\mathbf{t}$, it will arrive at the new position defined by the vector $\mathbf{r}'$ with respect to the axes such that

$$\mathbf{r}' = \mathbf{r} + \mathbf{t}. \quad (1.20)$$

We can thus define an *active operator* t_A , and its inverse t_A^{-1} such that

$$\begin{aligned} t_A \mathbf{r} &= \mathbf{r} + \mathbf{t} \\ t_A^{-1} \mathbf{r} &= \mathbf{r} - \mathbf{t}. \end{aligned} \quad (1.21)$$

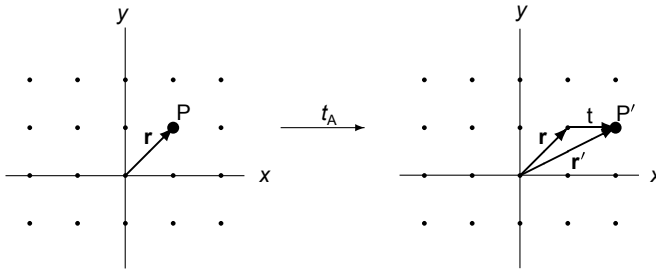


Fig. 1.7. Active operator t_A translates the point body P from $\mathbf{r}$ to $\mathbf{r}'$.

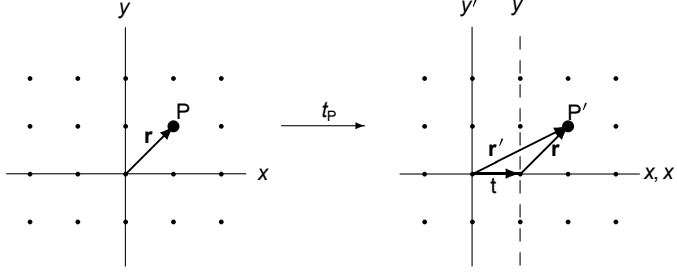


Fig. 1.8. Passive operator t_P translates the coordinate system by $-\mathbf{t}$.

We show a grid of equivalent points in configuration space because we have in mind, say, a crystal structure in which all the grid points correspond to atomic positions. In such a case, moving one point (atom) P of a body (a crystal) moves *all* the points. The space is infinite, as is the (idealized) crystal. In Figure 1.7, we show the identical fixed coordinate system twice in order to see the before and after pictures.

Now consider instead the effect of the *passive operator*, t_P , which translates the coordinate axes by $-\mathbf{t}$ while keeping the point object fixed, as in Figure 1.8. Then the new position of the point P after the translation is still given by

$$t_P \mathbf{r} = \mathbf{r}' = \mathbf{r} + \mathbf{t}, \quad (1.22)$$

but the interpretation is different. The new position is with reference to the new x', y' coordinate system. The operator t_P has the inverse effect from that of t_A .

Likewise, rotation operations can be either passive or active, bearing inverse relations to each other.

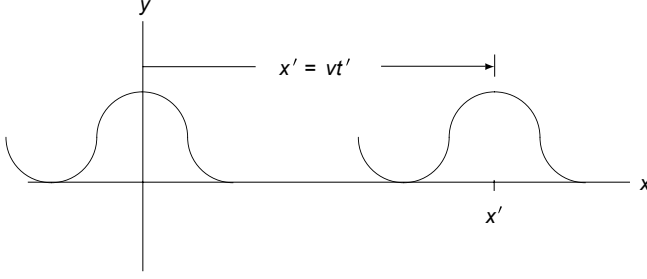
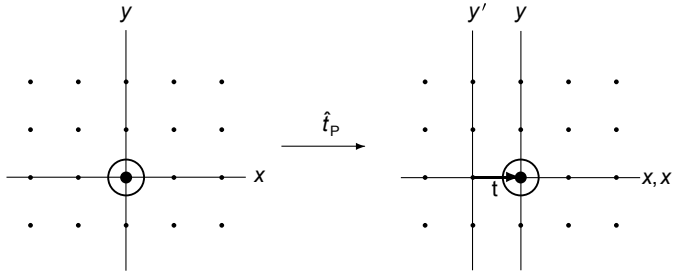
1.3.2 Function-space operations

We have alluded to a connection between configuration-space operators and function-space operators. As a prelude to showing that a coordinate transformation in configuration space *induces* a transformation of the function defined on it, we consider the case of a traveling wave. This contains the basic physics and mathematics in a familiar and easily understood situation.

Consider a transverse wave of shape $f(x, t)$ traveling with positive velocity along the x -axis, as shown in Figure 1.9. If we are to deal with the wave motion quantitatively, we need a mathematical description of the shape of the wave moving as a whole. We assume no damping or dispersion, so the shape remains unchanged, and any point on the wave may be taken as a reference point. We will follow the motion of the wave peak. To describe an amplitude that remains constant, although its position moves to the right with increasing time, we need a function of the general form

$$f(x, t) = f(x - vt). \quad (1.23)$$

With a function of this form, as t increases, x also increases, but the increase in x is exactly compensated for in the argument of f by the term $-vt$, so that the argument is

Fig. 1.9. Profile of a traveling wave at $(x, t) = (0, 0)$ and at (x', t') .Fig. 1.10. Function operator $\hat{t}_P$ generates a new function.

unchanged: There is an inverse relation between transformations in configuration space (the wave moving to the right with velocity v) and transformations in function-space (the argument of the function being translated to the left by $-vt$).

Now consider a function that describes the contour of an atomic orbital. We take that function to be a circle centered on the atom at the origin of the coordinate system in Figure 1.10 and given by the equation

$$x^2 + y^2 = c^2 \quad (1.24)$$

or

$$f(x, y) = (c^2 - x^2)^{1/2}. \quad (1.25)$$

The transformation t_P translates the x, y coordinate system such that the point with coordinates (x, y) in that system has coordinates (x', y') in the translated coordinate system, as given by

$$\begin{aligned} x' &= x + t, \\ y' &= y. \end{aligned} \quad (1.26)$$

Along with this transformation of coordinates is a change in the description of the function (the atomic orbital) associated with the lattice point. It is now described as

$$f'(x') = y' = (c^2 - (x' - t)^2)^{1/2}, \quad (1.27)$$

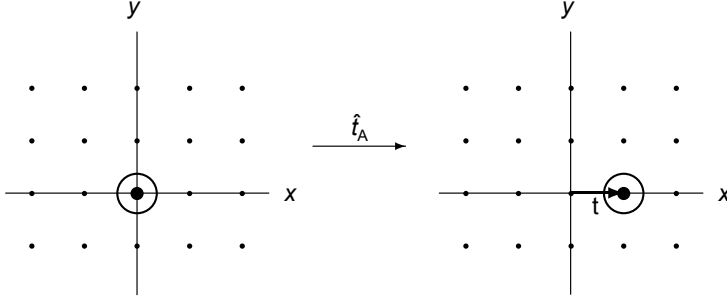


Fig. 1.11. $\hat{t}_A$ generates a new function.

as can easily be verified. Here, we are viewing the *same* function from two different coordinate systems. We have $f(x)$ as the function in the x, y coordinate system and $f'(x')$ in the x', y' coordinate system, but the physical point (the atom) has not moved, only a coordinate shift has been made. We describe it as a new function in Figure 1.10 only in the sense that it has a new functional form in the new coordinate system.

There is an alternative viewpoint, and it is the one we will use. That is to recognize $f'(x')$ as a new function and treat it as being generated by the action of a *function operator* $\hat{t}_A$ acting on the original function $f(x)$, as illustrated in Figure 1.11.

From this viewpoint we want to know the function operator that generates the new function $f'(x')$ induced by the transformation in configuration space. Just as in the treatment of a wave traveling to the right, as in Figure 1.9, we write the new function in terms of the one fixed coordinate system, but include a coordinate shift to keep the value of the new function, centered at the new coordinates, equal to the value of the original function centered on the original coordinates. Thus we have

$$\hat{t}_A f(x) = f(t_A^{-1}x) = (c^2 - (x - t)^2)^{1/2}. \quad (1.28)$$

In this *active* description, $\hat{t}_A f$ is a new function that is defined in terms of (1.23). That is, we cannot define the function operator directly, but only in terms of its action on the original function, taking account of the inverse action on the coordinates in the argument of the function by means of the operation $t_A^{-1}x$.

These are important concepts, to which we will return in Chapter 3, after first becoming familiar with the basic elements of group theory and symmetry operations in Chapter 2.

Example 1.1

From (1.25), the value of the function $f(x)$ at $x = 0$ is

$$f(0) = \pm c.$$

The new function, $\hat{t}_A f(x)$, evaluated at the new coordinate $x = t$, is, from (1.28),

$$\begin{aligned}\hat{t}_A f(x) &= (c^2 - (x - t)^2)^{1/2} \\ &= (c^2 - (t - t)^2)^{1/2} \\ &= \pm c,\end{aligned}$$

illustrating that the new function $\hat{t}_A f(x)$ evaluated at the new transformed coordinates equals the original function $f(x)$ evaluated at the original coordinates.

1.3.3 Operator algebra

Here we wish to consider two important but not always immediately obvious properties of operator algebra.

Suppose we were to operate on the product of two functions $f(x) * g(x)$. How do we carry out the operation $\hat{R}(f(x) * g(x))$? The meaning of $\hat{R}$ is that it operates on the *whole space* on which the functions $f(x)$ and $g(x)$ are defined. Thus the whole space for *both* functions must be transformed, giving

$$\hat{R}(f(x) * g(x)) = \hat{R}f(x) * \hat{R}g(x). \quad (1.29)$$

Another tricky bit of algebra is the application of one function-space operator after another. It must be done with great care. The general definition of the product of operators of any type requires that, in the present case,

$$\hat{R}\hat{S}f(x) = \hat{R}(\hat{S}f(x)), \quad (1.30)$$

which means that $\hat{R}$ is applied on the function $\hat{S}f$ of x , the functional symbol being enclosed in brackets for emphasis. That is, $\hat{S}f$ is itself a new function, obtained by operating on $f(x)$ with $\hat{S}$. We could write this new function as

$$\hat{S}f(x) = g(x). \quad (1.31)$$

Then

$$\begin{aligned}\hat{R}\hat{S}f(x) &= \hat{R}g(x) = g(R^{-1}x) \\ &= \hat{S}f(R^{-1}x) \\ &= f(S^{-1}R^{-1}x) \\ &= f((RS)^{-1}x).\end{aligned} \quad (1.32)$$

Thus if $RS = T$, then

$$\hat{R}\hat{S}f(x) = f((RS)^{-1}x) = f(T^{-1}x) = \hat{T}f(x), \quad (1.33)$$

whence

$$RS = T \mapsto \hat{R}\hat{S} = \hat{T}, \quad (1.34)$$

which is the very important *isomorphism* of the multiplication rules of function-space and configuration-space operators.

1.4 Point-symmetry operations

Point-symmetry operations are performed about a *fixed point* in configuration space. They include rotations about an axis passing through the point, reflections through planes containing the point, and inversions through the point. These operations are unitary, i.e.

$$\hat{O}\hat{O}^\dagger = \hat{O}^\dagger\hat{O} = \hat{1} \quad (\text{the identity operator in matrix form}).$$

In the following we describe the various point-symmetry operations and introduce their commonly used notations. The Schoenflies notation is given first, followed by the International (or Hermann–Mauguin) notation in parentheses.

Our interest here is in point-groups, for which the Schoenflies notation is usually used. However, the Hermann–Mauguin symbols can also describe the far more complicated symmetry of crystals and space-groups. We will revisit Hermann–Mauguin notation in Chapter 10.

- (i) **Identity** E , for *einheit*, (1) This operation leaves an object fixed or rotated by 2π about some axis.
- (ii) **Proper rotations** $C_n^k(n)$ An object is rotated $2k\pi/n$ clockwise about an axis that passes through the fixed point. The axis of highest order n , if unique, is designated as the principal axis. It is usually taken as the z -axis. The remaining axes are usually labeled by primes or by x or y if they coincide with either the x - or y -axes. In three-dimensional Euclidean space, the rotation of a vector $\mathbf{r}$ by $2k\pi/n$ about the z -axis is defined by the rotation matrix

$$C_n^k \equiv R(2k\pi/n) = \begin{bmatrix} \cos(2k\pi/n) & \sin(2k\pi/n) & 0 \\ -\sin(2k\pi/n) & \cos(2k\pi/n) & 0 \\ 0 & 0 & 1 \end{bmatrix}. \quad (1.35)$$

These matrices have a *determinant* of +1 and satisfy the unitarity property

$$\begin{aligned} C_n^k C_n^{k\dagger} &= \begin{bmatrix} \cos(2k\pi/n) & \sin(2k\pi/n) & 0 \\ -\sin(2k\pi/n) & \cos(2k\pi/n) & 0 \\ 0 & 0 & 1 \end{bmatrix} \\ &\times \begin{bmatrix} \cos(2k\pi/n) & -\sin(2k\pi/n) & 0 \\ \sin(2k\pi/n) & \cos(2k\pi/n) & 0 \\ 0 & 0 & 1 \end{bmatrix} = E. \end{aligned} \quad (1.36)$$

The discreteness of molecular and crystallographic systems limits n to integer values in these cases. For molecules, in principle, there is no restriction on n . However, a crystal lattice restricts the values of n to 1, 2, 3, 4, and 6.

The symbols used to denote the allowed n -fold rotation axes in two- and three-dimensional space lattices are shown in Figure 1.12. Note the absence of five-fold symmetry, as well as symmetries higher than six-fold.

The restriction can be verified as follows. If a lattice is composed of equilateral m -sided polygons, the angle subtended by two sides at a vertex is

$$(m-2)\frac{\pi}{m}, \quad \text{with } m \geq 3,$$

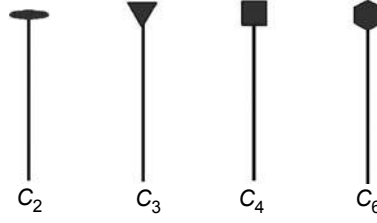


Fig. 1.12. Symbols for rotation axes.

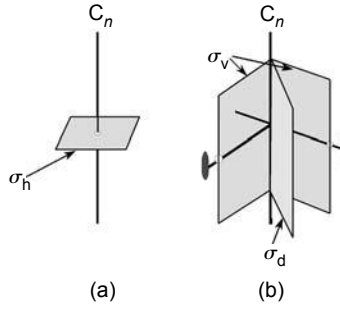


Fig. 1.13. Reflection operations.

since $m < 3$ is not a physically meaningful polygon. Because a symmetry rotation about the vertex must leave the lattice unchanged, we have

$$\frac{2\pi}{n} = \frac{(m-2)\pi}{m}, \quad \text{or} \quad n = \frac{2m}{m-2}, \quad (1.37)$$

which yields, for integer n ,

$$\begin{aligned} m &= 3, 4, 6, \\ n &= 6, 4, 3. \end{aligned} \quad (1.38)$$

A lattice of (nonequilateral) rectangles provides $n = 2$.

In order to change the orientation of a rotation axis one has to employ a unitary operator transformation

$$C'_n = RC_nR^\dagger. \quad (1.39)$$

- (iii) **Reflection operations** Reflection operations are illustrated in Figure 1.13. Part (a) shows reflection through a plane perpendicular to a principal axis σ_h ($1/m$). When the rotation axis is along the z -direction, σ_h is defined by the matrix

$$\sigma_h = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}. \quad (1.40)$$

Part (b) shows reflection through a plane containing a principal axis $\sigma_v(m)$. If the plane bisects the angle between two 2-fold axes perpendicular to a principal axis, the reflection is denoted by $\sigma_d(m)$.

- (iv) **Inversion** I ($\bar{1}$) Inversion takes a spatial vector $\mathbf{r}$ into $-\mathbf{r}$. In three-dimensions it is defined by the matrix

$$I = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}. \quad (1.41)$$

Example 1.2

In order to change the orientation of a C_n rotation axis along the z -axis to one along the x -axis we choose R to be a counterclockwise rotation of $\pi/2$ about the y -axis. Thus,

$$\begin{aligned} C_n^x &= \begin{bmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} \cos(2\pi/n) & \sin(2\pi/n) & 0 \\ -\sin(2\pi/n) & \cos(2\pi/n) & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{bmatrix} \\ &= \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos(2\pi/n) & -\sin(2\pi/n) \\ 0 & \sin(2\pi/n) & \cos(2\pi/n) \end{bmatrix}. \end{aligned}$$

- (v) **Improper rotations** $S_n(\bar{n})$ Improper rotations consist of proper rotations C_n followed by reflections σ_h , with symbols as shown in Figure 1.14.

An improper rotation is defined by

$$S_n = C_n \sigma_h = \sigma_h C_n. \quad (1.42)$$

Since $\sigma_h^2 = E$, we find that

$$S_n^k = C_n^k, \quad \text{for even } k. \quad (1.43)$$

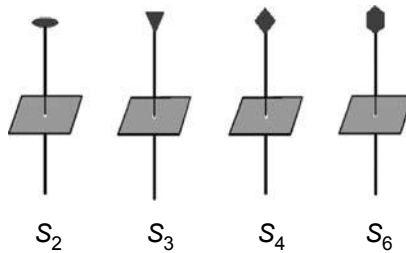


Fig. 1.14. Improper rotations.

Another interesting property of improper rotation-reflection operations is that

$$S_2 = C_2\sigma_h = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = I, \quad (1.44)$$

or $C_2I = \sigma_h$, which we use to obtain

$$\begin{aligned} S_3 &= C_3C_2I = C_6^5I = IC_6^{-1}, \\ S_4 &= C_4C_2I = IC_4^3 = IC_4^{-1}, \\ S_6 &= C_6C_2I = IC_6^4 = IC_3^{-1}. \end{aligned}$$

1.5 Applications to quantum mechanics

We now consider, briefly, two applications of group theory to quantum mechanics, in order to give a bit more insight into the physical applications of group theory before immersing ourselves in the details of group theory itself. The first application concerns selection rules; the second is the simplification of the search for eigenfunctions in complicated systems.

Selection rules determine which transitions between eigenstates are allowed by the application of a given perturbation operator to the system. They are concerned with the vanishing or nonvanishing of matrix elements (integrals) associated with operators representing external perturbations. The integrals may be evaluated analytically or numerically, whichever is more feasible, in order to determine whether a transition is allowed or not. However, we may notice that these integrals have the general form

$$\int F(\mathbf{r}) d\mathbf{r} = \int F(R^{-1}\mathbf{r}) d(R^{-1}\mathbf{r}) = \int F(R^{-1}\mathbf{r}) d\mathbf{r}, \quad (1.45)$$

where the last step in (1.45) follows because the orthogonal matrices that describe transformations between orthogonal coordinate systems are such that the absolute value of the determinant of the orthogonal transformation matrix must be unity, that is, $|\det R| = 1$. This means that lengths and angles are preserved in the transformation so that, in this case, the volume element $d(R^{-1}\mathbf{r})$ equals the volume element $d\mathbf{r}$.

Example 1.3

A one-dimensional configuration space may have reflection symmetry about a given point. F may be even or odd with respect to the reflection operation associated with this symmetry,

$$\begin{aligned} F^+(-x) &= F(x), \\ F^-(-x) &= -F(x), \end{aligned} \quad (1.46)$$

thus, as we know from freshman calculus,

$$\int_{-\infty}^{\infty} F^-(x) dx = 0; \quad \int_{-\infty}^{\infty} F^+(x) dx \neq 0. \quad (1.47)$$

Another way to arrive at this simple result is to invoke the reflection symmetry operation $\hat{\sigma}$ to the integrand F , such that

$$\hat{\sigma}F(x) = F(-x).$$

Taking the symmetry point as the origin we obtain

$$\int_{-\infty}^{\infty} F(x) dx = \int_0^{\infty} [F(x) + \hat{\sigma}F(x)] dx, \quad (1.48)$$

which leads to the same result as using (1.47). We designate F^+ to be *invariant* under the operation of reflection in one dimension.

Thus we find, once again, that if we consider a one-dimensional oscillator, its eigenstates can be classified into two groups under the reflection operation: odd or even. The oscillator may be subjected to an external perturbation, κx , which has a dipolar or vector character, in that it is an odd function under the reflection operator. The transition probabilities are then evaluated through the integral

$$\int_{-\infty}^{\infty} \psi_f^*(x) (\kappa x) \psi_i(x) dx, \quad (1.49)$$

where ψ_i and ψ_f are the initial and final states, respectively. This integral can be cast in the form of (1.48), namely,

$$\begin{aligned} \int_{-\infty}^{\infty} \psi_f^*(x) (\kappa x) \psi_i(x) dx &= \int_0^{\infty} [\psi_f^*(x) (\kappa x) \psi_i(x) + \hat{\sigma}(\psi_f^*(x) (\kappa x) \psi_i(x))] dx \\ &= \int_0^{\infty} [\psi_f^*(x) (\kappa x) \psi_i(x) + \psi_f^*(\sigma^{-1}x) (\kappa \sigma^{-1}x) \psi_i(\sigma^{-1}x)] dx, \end{aligned} \quad (1.50)$$

which vanishes when both ψ_i and ψ_f are either odd or even.

The second example we consider is the simplification of the search for eigenvalues. We start by considering the commutation relation $\hat{R}\mathcal{H} = \mathcal{H}\hat{R}$ written in a matrix representation based on eigenfunctions of $\hat{R}$, where $\hat{R}$ is a symmetry operator much like the operator $\hat{t}_A$ that we considered earlier. Then,

$$\sum_j \hat{R}_{ij} H_{jk} = \sum_j H_{ij} \hat{R}_{jk} \quad (1.51)$$

with

$$\hat{R}|j\rangle = c_j|j\rangle. \quad (1.52)$$

Imposing a requirement of orthonormality for the set of eigenstates $|j\rangle$ of $\hat{R}$,

$$\hat{R}_{ij} = \langle i|\hat{R}|j\rangle = \langle i|c_j|j\rangle = c_j \delta_{ij}. \quad (1.53)$$

Thus, the summation in (1.51) reduces to a single term, yielding

$$\hat{R}_{ii} H_{ik} = H_{ik} \hat{R}_{kk}, \quad (1.54)$$

which can be rewritten as

$$(\hat{R}_{ii} - \hat{R}_{kk}) H_{ik} = 0. \quad (1.55)$$

This simple result is of great significance. If i and k refer to different eigenvalues of $\hat{H}$, then $c_i \neq c_k$, and $H_{ik} = 0$. This means we will often be able to limit our considerations to different classes of functions separately. That is, because there are no off-diagonal elements of H connecting functions of different symmetry ($H_{ik} = 0$), we will be able, for example, to limit the search for eigenfunctions that diagonalize the Hamiltonian operator by making our search separately within the classes of functions having different eigenvalues of $\hat{H}$.

Group theory is particularly helpful in simplifying large matrices by converting the large matrix into one of block diagonal form, with the elements in each of the smaller blocks belonging to eigenfunctions of the same symmetry. Thus, for example, we will find 3×3 and 5×5 blocks associated with p-orbitals and d-orbitals, respectively.

Our goal is to be able to utilize group theory in the computational solution of physical problems. The intellectual pleasure that derives from the intrinsic elegance of the theory is a bonus. The practical reward that comes from learning group theory from a computational viewpoint is the ability to solve large problems on a computer, problems whose solution would not be feasible using the traditional tools of paper and pencil. Thus, after an introduction to abstract group theory and the realization of groups and some traditional examples involving the manipulation of 3×3 matrices, we will learn to do group theory calculations on a computer – to do them *exactly*, unhindered by the size of the matrices involved.

Exercises

- 1.1 Write down and solve the equations of motion for the system of masses and springs shown in Figure 1.5. Assume both masses to be equal and all springs to have the same force constant. Show that the eigenvalues for the energy are given by $\omega^2 m = k, 3k$, from which the eigenvectors can be found to be in agreement with the results obtained purely by symmetry arguments. Must all three force constants be equal for this result to be obtained? Can you decide based on symmetry arguments alone?
- 1.2 Write the equations of motion for Exercise 1.1 in the form $M\mathbf{u} = -\omega^2 m\mathbf{u}$, where M is a matrix. Use the two eigenvectors found in the text,

$$\mathbf{u}_1 = \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad \text{and} \quad \mathbf{u}_2 = \begin{pmatrix} 1 \\ -1 \end{pmatrix},$$

to construct the matrix

$$S = \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix},$$

where the first column of the matrix is given by $\mathbf{u}_1$ and the second column, by $\mathbf{u}_2$. Find S^{-1} and then diagonalize M according to

$$S^{-1}MS = \lambda I,$$

where I is the unit matrix, to find the eigenvalues λ .

- 1.3 Find the function generated by C_4 acting on the function $xf(r)$.
- 1.4 Show that the operation $S_n^{n/2} = I$ for $n/2$ odd. Show that for even n , S_n implies the existence of $C_{n/2}$.

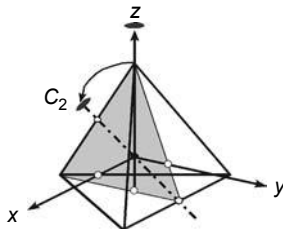


Fig. 1.15. A C_2 rotation about an axis bisecting opposite edges of a tetrahedron.

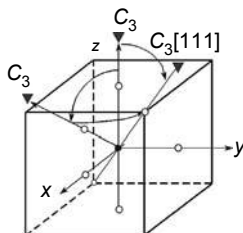


Fig. 1.16. A C_3 rotation about a $[111]$ body-diagonal axis of a cube.

- 1.5 Consider the case of an n -fold principal axis. Show that the introduction of a two-fold symmetry axis perpendicular to it implies the coexistence of n equivalent axes for n odd, and the coexistence of $n/2$ equivalent axes for n even.
- 1.6 Introduce diagonal reflection planes, σ_d , in the previous problem and show, using the three-dimensional defining matrices for a σ_d plane and a neighboring two-fold axis C'_2 , that the product $C'_2\sigma_d = S_{2n}$.
- 1.7 Show that the determinant of an improper rotation is -1 .
- 1.8 Obtain the three-dimensional rotation matrix for the C_2 axis joining two opposite edges of a tetrahedron, shown in Figure 1.15. Note that the origin of the coordinate system is the centroid of the tetrahedron. (Hint: Start with a two-fold rotation about the z -axis, then use a counterclockwise rotation about the x -axis to transform the axis to its final position, as shown in the figure.)
- 1.9 Using the results of the previous problem, find the new function generated by the function operator $\hat{C}_2$ acting on $zf(r)$.
- 1.10 Obtain the three-dimensional rotation matrix for the operation $C_3[111]$ shown in Figure 1.16. (Hint: Start with a three-fold rotation axis along the z -direction, followed by rotating the axis counterclockwise, by the same angle as in Exercise 1.8, but this time about the y -axis. Finally, rotate the axis counterclockwise by 45° about the z -axis.)

2

Symmetry and group theory

2.1 Groups and their realizations

Abstract group theory defines relationships among a set of abstract elements in terms of binary operations among the elements of the group. The operations are known as *group multiplication*.

Formally, a group consists of a set of elements with the following properties:

- (i) The *product* of any two elements in the set is a member of the set. Thus the set is closed under all group multiplication operations.
- (ii) If A , B , and C are elements of the group, then $A(BC) = (AB)C$. The associative law of multiplication holds; the commutative law of multiplication need not hold.
- (iii) There is a unit element, an *identity* element, E such that $EA = AE = A$.
- (iv) Each element A has a *unique* inverse A^{-1} such that $AA^{-1} = A^{-1}A = E$.

A typical abstract group multiplication table is given in Table 2.1, for the group we denote by G_6 , which consists of six elements.

The convention for such tables is that the ij th element in the table is the product of the i th element labeling the rows and the j th element labeling the columns. From the table we see that $AB = D$, which means that the operation B followed by the operation A is equivalent to the single operation D . Note that $AB = D$, but $BA = F$; thus $AB \neq BA$ in this case.

Abelian groups If $XY = YX$ for all elements of the group, the group is called *Abelian*. It is clear from the asymmetry about the diagonal of Table 2.1 that the group G_6 is not Abelian.

Table 2.1. *Multiplication table for the abstract group G_6 .*

	E	A	B	C	D	F
E	E	A	B	C	D	F
A	A	E	D	F	B	C
B	B	F	E	D	C	A
C	C	D	F	E	A	B
D	D	C	A	B	F	E
F	F	B	C	A	E	D

Group order The number of elements in a group is called the *order of the group* and is designated by g . When g is finite the group is designated a *finite group*. Here $g = 6$.

Cyclic groups There is one other abstract group of order 6: $E, A, A^2, A^3, A^4, A^5, A^6$. Groups comprising of $E, A, \dots, A^i, \dots, A^{n-1}$ are cyclic groups of order n .

Group rearrangement theorem Every column and every row of the multiplication table contains each element of the group once and only once. Multiplication of every element in a row or column by some element of the group other than the identity element simply rearranges the elements. This is known as the *group rearrangement theorem*.

If an element of a finite group is repeatedly multiplied by itself, it will eventually yield the identity. Thus, for example, from Table 2.1 we see that $D^3 = D(D^2) = DF = E$. The *order of an element* X is the smallest positive integer n such that $X^n = E$. The order of D is 3.

A physical example of an abstract group is called a *realization*. Distinct matrices representing distinct geometric transformations whose operations satisfy the group multiplication table are examples of realizations. Groups of numbers could also constitute a realization, but we will consider a realization of an abstract group to mean the elements of the group have a physical meaning. In order to *realize* a group, one has to:

- (i) Choose a relevant object or set of objects.
- (ii) Choose a characteristic of these objects. Coordinates, spin, or color are possibilities.
- (iii) Assign a physical meaning to the elements (the operations). Rotations, reflections, translations, and permutations are typical examples.

The NH_3 molecule is an instructive example of a physical object whose symmetry operations have a physical meaning and provide a realization of the group G_6 . The three H atoms form an equilateral triangle. The N atom lies on the symmetry axis that passes through the center of the triangle and which is perpendicular to the plane of the triangle. The symmetry operations consist of the identity, rotations of $\pm 120^\circ$ about the symmetry axis passing through the N atom, and reflections through planes defined by the symmetry axis and one of the H atoms. Thus the symmetry operations of the NH_3 molecule are the covering operations of the equilateral triangle for the case in which the triangle is restricted to remain in its original plane.

By operating on the objects and observing the resulting changes, one can induce a possible *realization* of the group if there is a one-to-one correspondence between distinct operations and distinct outcomes. We induce a realization of the abstract group G_6 using the covering operations of the NH_3 molecule, Figure 2.1. These are the set of symmetry operations that send a figure into itself.

The presence of mirror symmetry planes and a symmetry axis in the NH_3 molecule must be reflected in the electronic structure and vibrational properties of NH_3 , for these properties must be described by a Hamiltonian that is invariant under every symmetry coordinate transformation that leaves the molecule unchanged. Thus the *covering* operations of the equilateral triangle provide one of the simplest nontrivial examples of the connection between group theory and the symmetry properties of physical systems.

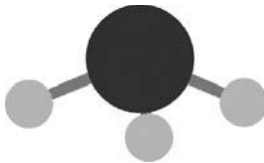
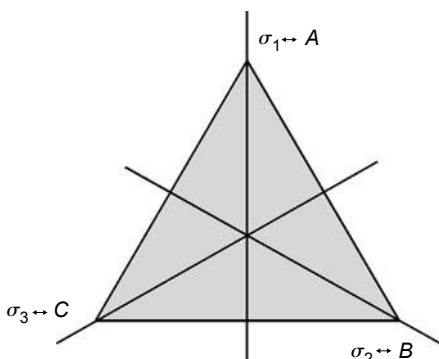
Fig. 2.1. The NH_3 molecule.

Fig. 2.2. The symmetry planes (axes) of an equilateral triangle. The axes are considered fixed in space, not attached to the triangle.

The symbol C_{3v} denotes the point-group to which both the NH_3 molecule and the equilateral triangle belong. The subscript 3 denotes a three-fold axis of symmetry perpendicular to the plane of the triangle and the subscript v denotes reflection-symmetry planes through the axis of symmetry and perpendicular to the plane of the triangle. To examine the point-group C_{3v} , we must first identify and enumerate all possible symmetry operations that leave the triangle unchanged, or *invariant*. These operations may be identified with the help of Figure 2.2. They may be classified as

- (i) E , the identity element, which leaves the triangle unchanged,
- (ii) Two *three-fold* rotations: $C_3 \equiv (2\pi/3)$ and $C_3^2 \equiv (4\pi/3)$, are *clockwise* rotations about an axis normal to the plane of the triangle and passing through its center, in a conventional (right-hand screw) coordinate system.
- (iii) Three *reflections* through planes formed by the rotation axis and the perpendicular bisectors of the triangle: σ_1 , σ_2 , σ_3 .

We now define group multiplication of two elements as the outcome of the *sequential application of the two operators*. We find that both $C_3 \equiv (2\pi/3)$ and $C_3^2 \equiv (4\pi/3)$ are mutual inverses under this multiplication law, since when they are applied sequentially they are equivalent to E . Thus, the set of operations $C_3 \equiv (2\pi/3)$, $C_3^2 \equiv (4\pi/3)$ and E satisfy all the group specifications listed above. They satisfy the right-hand group multiplication table in Table 2.2.

Similarly, we pair the identity element E with each of the σ_i s, to form three groups of order 2, each satisfying the left-hand table in Table 2.2. Moreover, we find the group

Table 2.2. *Multiplication table for the groups C_3 and C_3 .*

	E	C_3	C_3^2		E	σ_i
E	E	C_3	C_3^2	E	E	σ_i
C_3	C_3	C_3^2	E	σ_i	σ_i	E
C_3^2	C_3^2	E	C_3			

Table 2.3. *Multiplication table for the group C_{3v} .*

	E	σ_1	σ_2	σ_3	C_3	C_3^2
E	E	σ_1	σ_2	σ_3	C_3	C_3^2
σ_1	σ_1	E	C_3	C_3^2	σ_2	σ_3
σ_2	σ_2	C_3^2	E	C_3	σ_3	σ_1
σ_3	σ_3	C_3	C_3^2	E	σ_1	σ_2
C_3	C_3	σ_3	σ_1	σ_2	C_3^2	E
C_3^2	C_3^2	σ_2	σ_3	σ_1	E	C_3

criteria are fulfilled by the entire set of six elements. Thus, the group of six symmetry elements for the equilateral triangle is composed of the union of four smaller groups known as *subgroups*.

The binary multiplications of the symmetry operations of the equilateral triangle, *defined by the successive application of pairs of these operations to the triangle*, are given in Table 2.3 for the group C_{3v} . We can now make a one-to-one correspondence between the symmetry elements of C_{3v} and the abstract group elements of Table 2.1 as follows:

- (i) The notation for the identity E is the same for both G_6 and C_{3v} .
- (ii) The operations A , B , and C are in one-to-one correspondence with the set of reflections through the symmetry planes shown in Figure 2.2 and denoted by $(\sigma_1, \sigma_2, \sigma_3)$.
- (iii) The operations D and F are in one-to-one correspondence with rotations of the triangle clockwise through 120° and 240° , respectively. The standard notation is C_3 and C_3^2 .

If we compare Tables 2.1 and 2.3, we find they are identical, they differ only in the labeling of the group elements, but Table 2.3 represents a physical realization of the group. The one-to-one correspondence between elements in the two tables defines an *isomorphic* relationship.

In C_{3v} we have found a tangible *realization* of the abstract group G_6 . One can label the vertices of a cardboard cutout of an equilateral triangle to experiment with the operations of the group, although with a bit of imagination the actual cutout is not needed. It is easy to verify the multiplication table.

However, the group C_{3v} is not the only realization of G_6 . Another realization can be obtained by replacing the reflections σ by two-fold rotations, $C_2^{(1)}$, $C_2^{(2)}$, and $C_2^{(3)}$, about

the three perpendicular bisectors of the equilateral triangle. This is the *dihedral* group $\mathcal{D}_3$ associated with a two-faced equilateral triangle.

2.2 The symmetric group

Still another realization of this group is defined by a set of permutations among three objects, as illustrated in Figure 2.3 and expressed in (2.1). These operations satisfy the same multiplication table as G_6 and C_{3v} when we define multiplication as the successive application of the permutations of the three objects. We may choose the three objects to be the three vertices of a triangle. Then, for example, we may identify the operation that takes vertex 1 into vertex 2, vertex 2 into vertex 3, and vertex 3 into vertex 1 to be equivalent to C_3 of C_{3v} , as shown in Figure 2.3.

This group realization is called the *symmetric group* of order 3 and is denoted by $\mathcal{S}_3$. There are $3!$ such permutations and we can identify their correspondences with the operations of C_{3v} as follows:

$$\begin{aligned} E &\Leftrightarrow \begin{pmatrix} 1 & 2 & 3 \\ 1 & 2 & 3 \end{pmatrix}, & \sigma_1 &\Leftrightarrow \begin{pmatrix} 1 & 2 & 3 \\ 1 & 3 & 2 \end{pmatrix}, \\ \sigma_2 &\Leftrightarrow \begin{pmatrix} 1 & 2 & 3 \\ 3 & 2 & 1 \end{pmatrix}, & \sigma_3 &\Leftrightarrow \begin{pmatrix} 1 & 2 & 3 \\ 2 & 1 & 3 \end{pmatrix}, \\ C_3 &\Leftrightarrow \begin{pmatrix} 1 & 2 & 3 \\ 2 & 3 & 1 \end{pmatrix}, & C_3^2 &\Leftrightarrow \begin{pmatrix} 1 & 2 & 3 \\ 3 & 1 & 2 \end{pmatrix}. \end{aligned} \quad (2.1)$$

The one-to-one correspondence between the two sets of operations belonging to the symmetric group $\mathcal{S}_3$ and the point-group C_{3v} defines an *isomorphic* mapping between them. The set of permutation operations obeys the group multiplication table given in Table 2.3 for the group C_{3v} .

One can think of objects (the vertices of the triangle in this case) as being allocated to boxes; with exactly one object per box. Then a permutation is just a rearrangement of the objects among the boxes. The notation of the permutation operations, given in (2.1), is such that we view the top row as labels of the three objects according to their initial locations in three boxes, thus, box 1 contains object 1, etc. The bottom row then denotes

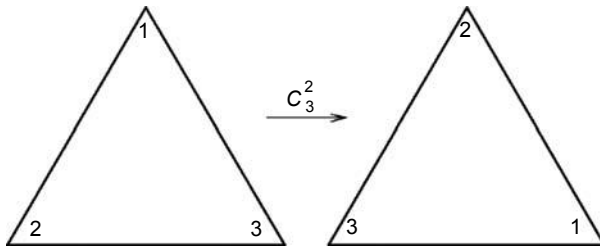


Fig. 2.3. The configuration space operator C_3^2 rotates a triangle 120° clockwise.

the box destination of these objects as defined by the permutation operation. Then a permutation matrix describes the operation of taking the object in the top box of a column to the position (the box) just below it. We define the product of two permutations, say $\sigma_1\sigma_2$, as the permutation given by σ_2 followed by the permutation given by σ_1 .

Example 2.1

From Table 2.3 we see that $\sigma_1\sigma_2 = C_3$. If we represent these operations by the permutations of (2.1), we get

$$\begin{pmatrix} 1 & 2 & 3 \\ 1 & 3 & 2 \end{pmatrix} \begin{pmatrix} 1 & 2 & 3 \\ 3 & 2 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 2 & 3 \\ 2 & 3 & 1 \end{pmatrix}.$$

A very simple procedure can be used to obtain such a permutation:

$$\begin{pmatrix} 1 & 2 & 3 \\ 1 & 3 & 2 \end{pmatrix} \begin{pmatrix} 1 & 2 & 3 \\ 3 & 2 & 1 \end{pmatrix} \Rightarrow \begin{pmatrix} 3 & 2 & 1 \\ 1 & 3 & 2 \end{pmatrix} \Rightarrow \begin{pmatrix} 1 & 2 & 3 \\ 2 & 3 & 1 \end{pmatrix};$$

we replaced the top row of the left matrix by the lower row of the right matrix, then rearranged the resulting intermediate matrix such that the top row is again cast in ascending order.

After experimenting with such operations and checking with the multiplication table to ensure agreement, one soon recognizes the pattern for writing down the final result in standard form.

Let us demonstrate that the associative law holds for these permutation operations. We ask, “Is $\sigma_1(\sigma_2 C_3) = (\sigma_1\sigma_2)C_3$?” Representing these operations by permutations, we have

$$\begin{aligned} & \begin{pmatrix} 1 & 2 & 3 \\ 1 & 3 & 2 \end{pmatrix} \left[\begin{pmatrix} 1 & 2 & 3 \\ 3 & 2 & 1 \end{pmatrix} \begin{pmatrix} 1 & 2 & 3 \\ 2 & 3 & 1 \end{pmatrix} \right] \\ &= \begin{pmatrix} 1 & 2 & 3 \\ 1 & 3 & 2 \end{pmatrix} \begin{pmatrix} 1 & 2 & 3 \\ 2 & 1 & 3 \end{pmatrix} = \begin{pmatrix} 1 & 2 & 3 \\ 3 & 1 & 2 \end{pmatrix}. \end{aligned}$$

Similarly,

$$\begin{aligned} & \left[\begin{pmatrix} 1 & 2 & 3 \\ 1 & 3 & 2 \end{pmatrix} \begin{pmatrix} 1 & 2 & 3 \\ 3 & 2 & 1 \end{pmatrix} \right] \begin{pmatrix} 1 & 2 & 3 \\ 2 & 3 & 1 \end{pmatrix} \\ &= \begin{pmatrix} 1 & 2 & 3 \\ 2 & 3 & 1 \end{pmatrix} \begin{pmatrix} 1 & 2 & 3 \\ 2 & 3 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 2 & 3 \\ 3 & 1 & 2 \end{pmatrix}. \end{aligned}$$

Cycle structure The notation for the permutation operations can be abbreviated if we notice that the operations can be decomposed into cycles. For example, the permutation corresponding to C_3 is composed of only the cycle (123). That is, vertex 1 maps into vertex 2 which in turn goes into vertex 3. Vertex 3 maps into vertex 1 which completes the cycle

denoted by (123). The permutation corresponding to σ_2 contains the two cycles (13) and (2). Thus, we could represent σ_2 by the composition of its cycles (13)(2) or by just the single cycle (13), since a cycle of an object into itself is just an identity operation and can be dropped.

The cycle structure becomes more apparent when we consider larger permutations, as illustrated with a few examples from the *symmetric group* of order 4, S_4 :

$$\begin{aligned} \begin{pmatrix} 1 & 2 & 3 & 4 \\ 1 & 4 & 3 & 2 \end{pmatrix} &= (1)(24)(3) \equiv (24), & \begin{pmatrix} 1 & 2 & 3 & 4 \\ 4 & 1 & 3 & 2 \end{pmatrix} &= (142)(3) \equiv (142), \\ \begin{pmatrix} 1 & 2 & 3 & 4 \\ 3 & 4 & 2 & 1 \end{pmatrix} &= (1324), & \begin{pmatrix} 1 & 2 & 3 & 4 \\ 4 & 3 & 2 & 1 \end{pmatrix} &= (14)(23). \end{aligned} \quad (2.2)$$

Parity of a permutation A *parity* can be assigned to a permutation according to the length of its cycles. A cycle of odd length is assigned a parity of +1 and a cycle of even length is assigned a parity of -1. The parity of the permutation is the product of the parities of its cycles. Although assigning the parity in this way may at first be confusing, it is quite logical. A cycle of length one, for example, means the object is permuted into itself. There is no change and so the parity is +1.

This definition of parity is equivalent to saying that the parity of an operation on a determinant is ± 1 depending on whether the number of columns (or rows) interchanged is even or odd.

Mathematica and combinatorics *Mathematica* provides a special package that handles permutations and other discrete mathematical functions. The permutation package can be loaded from *Mathematica* by the command

```
<< DiscreteMath 'Combinatorica'
```

The following *Mathematica* functions are useful:

- `Permute[ l, p ]` permutes list l according to permutation p .
- `InversePermutation[ p ]` yields the multiplicative inverse of permutation p .
- `PermutationGroupQ[ l ]` returns `True` if the list of permutations l forms a permutation group.
- `MultiplicationTable[ l, f ]` constructs the complete multiplication table defined by the binary relation function f on the elements of the list l . For example f could be a permutation and the command becomes `MultiplicationTable[l, Permute]`.

Mathematica provides the following function for cycle decomposition:

`ToCycle[p]`, where `p` is a permutation.

Significance of permutations in computational algorithms The essential ingredients of computational group theory are that a permutation realization of a group is *isomorphic* to some other realization of the group (meaning they are *equivalent*, with a one-to-one relationship between group elements of the two realizations) and permutation groups are easy to manipulate computationally (meaning easy to manipulate on a computer).

We now take a closer look at permutation operations, because of their central importance to computational group theory. The permutations of n objects form a permutation group known as the *symmetric* group, $\mathcal{S}_n$. Since there are $n!$ permutations of n objects, $n!$ is the order of the group $\mathcal{S}_n$. An example of a symmetric group is given by (2.1) for $\mathcal{S}_3$, which is isomorphic to the group $\mathcal{C}_{3v}$.

2.2.1 The permutation group

It is possible to describe every element of a finite group in terms of a permutation, as we have already seen. Thus, we can establish an isomorphism between the elements of a finite group $\mathcal{G}$ and a group of permutation, the latter satisfies the same multiplication table. This is just saying that we can always construct a permutation realization of any finite group. Such a group is not necessarily isomorphic with a symmetric group. We describe this permutation realization as a *permutation group*.

One possible procedure for constructing a permutation group isomorphic to a finite group $\mathcal{G}$ is to make use of the rearrangement theorem. We learned that the operation of a group element $X \in \mathcal{G}$, $X \neq E$, on the top row of the multiplication table simply rearranges the ordering of the elements in the row labeled by X . It permutes the elements. Thus, each element $X \in \mathcal{G}$ can be represented by the permutation defined by its row in the multiplication table.

Example 2.2

For the group $\mathcal{C}_{3v}$, we can use Table 2.1 to define permutation elements as follows:

$$\begin{aligned} E &= \begin{pmatrix} e & a & b & c & d & f \\ e & a & b & c & d & f \end{pmatrix} = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 1 & 2 & 3 & 4 & 5 & 6 \end{pmatrix}, \\ A &= \begin{pmatrix} e & a & b & c & d & f \\ a & e & d & f & b & c \end{pmatrix} = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 2 & 1 & 5 & 6 & 3 & 4 \end{pmatrix}, \\ B &= \begin{pmatrix} e & a & b & c & d & f \\ b & f & e & d & c & a \end{pmatrix} = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 3 & 6 & 1 & 5 & 4 & 2 \end{pmatrix}, \end{aligned}$$

$$\begin{aligned}
C &= \begin{pmatrix} e & a & b & c & d & f \\ c & d & f & e & a & b \end{pmatrix} = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 4 & 5 & 6 & 1 & 2 & 3 \end{pmatrix}, \\
D &= \begin{pmatrix} e & a & b & c & d & f \\ d & c & a & b & f & e \end{pmatrix} = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 5 & 4 & 2 & 3 & 6 & 1 \end{pmatrix}, \\
F &= \begin{pmatrix} e & a & b & c & d & f \\ f & b & c & a & e & d \end{pmatrix} = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 6 & 3 & 4 & 2 & 1 & 5 \end{pmatrix}.
\end{aligned}$$

In this case, there are six permutations, corresponding to the six elements of the group C_{3v} . However, in the case of the symmetric group S_6 , we would have $6!$, or 720 permutation elements. Thus, the permutation group above is a subgroup of the symmetric group S_6 . It is isomorphic to S_3 .

Since a group is defined by its multiplication table, the first goal in our computational program is to construct it. Thus, rather than using the multiplication table to construct a permutation realization, we use the group elements, in permutation form, to construct the multiplication table. We begin by stating Cayley's theorem, which ensures that there always exists a unique permutation group realization, but first we need to introduce the concept of subgroups.

Subgroups Given a group $\mathcal{G}$, it is often possible to select a subset of the elements of the group such that the subset $\mathcal{H}$ also constitutes a group under the same rules of binary composition, i.e. multiplication, as in $\mathcal{G}$. $\mathcal{H}$ is called a *subgroup* of $\mathcal{G}$, $\mathcal{H} \subset \mathcal{G}$.

Of course, a group always has at least two subgroups, namely the group itself and the subgroup consisting of the identity alone. These trivial subgroups are called *improper* subgroups, all others being *proper* subgroups.

Example 2.3

For the group C_{3v} , the elements C_3 , $C_3C_3 = C_3^2$, and $C_3C_3^2 = C_3^3 = E$ form a cyclic subgroup, and C_3 is of order 3. In terms of operations on the equilateral triangle, three successive applications of the operation C_3 return the triangle to its original position. The set $\{E, C_3, C_3^2\}$ forms a proper subgroup.

We are interested here in a group $\mathcal{G}$ that is a subgroup of a larger symmetric group S_n . The importance of the existence of such symmetric groups, S_n , is that we can assign a unique permutation of n objects to each element of $\mathcal{G}$, a one-to-one mapping of all elements of $\mathcal{G}$ onto a subgroup of S_n . The result is known as Cayley's theorem.

Cayley's theorem *Every group $\mathcal{G}$ of order n is isomorphic to a subgroup of the symmetric group S_n .*

This theorem asserts that there exists a finite number of distinct finite groups of order n , namely those found as subgroups of S_n .

It is clear from the above examples that the concept of a group and its binary multiplication relations transcends the particular physical realization. Thus an abstract group can be defined and identified according to the number of its elements and their multiplication relations.

Corollary *Two groups with an equal number of elements but different multiplication relations are distinctly different, otherwise they are isomorphic.*

2.3 Computational aspects

2.3.1 Generation of the Cayley (multiplication) table

Specification of a group: group generators and defining relations

The binary operations defined on the set of group elements can be expressed in terms of a series of equations of the form

$$A_i A_j = A_k, \quad A_i, A_j, A_k \in \mathcal{G}, \quad (2.3)$$

which in turn can be arranged in the form of a multiplication table (sometimes called a *Cayley table*) similar to the one displayed for the group $\mathcal{C}_{3v}$ in Table 2.3.

It is generally possible to also specify a group by using a smaller number of equations that imply the multiplication table. Such a set is called the *defining relations* for the group. The elements used in the defining relations are called the *group generators*.

Rank, basis and presentation of a group

The minimum set of group generators that can reproduce the multiplication table is called the *group basis*, which may not be unique. The number of generators present in the basis is called the *rank* of the group. The combination of defining relations and group generators is called a *presentation* of the group.

Example 2.4

For the group $\mathcal{C}_{3v}$, the group generators may be taken as σ_i and C_3 , i.e. one of the σ_i . Then, the defining relations would be $\sigma_i^2 = C_3^3 = E$, $C_3^2 \sigma_i = \sigma_i C_3$, and the rank of $\mathcal{C}_{3v}$ is 2. We could just as well have chosen C_3^2 instead of C_3 .

Given a set of generators, the full group is obtained by operating on the generators with the aid of the defining relations.

We should stress here that the generators of the isomorphic permutation group have the defining relations built in them.

Thus, by taking powers of generators, products of generators, and products among newly generated elements, we obtain all the permutation group elements. The multiplication table is subsequently obtained.

2.3.2 Computer generation of group elements

Let us consider the C_{3v} group, as an example. We take C_3 and σ_1 to be the group generators.

In principle, it is desirable to use a group basis, i.e. a minimal set of generators, as input. In practice, a minimum set might not be immediately obvious, and one might choose to use an arbitrary set of group elements. The important thing is to generate the group.

In general, one should know the order of the group and use it as input to the computer program. This will set the program to terminate element generation once the total number reaches the group order.

First, we redefine the permutations of (2.1) in terms of a two-dimensional computer array $NG(i, j)$: i is an index of the group elements, and we retain the index 1 for E , $E \equiv \mathbf{1}$. We follow that by setting the generator indices: $C_3 \equiv \mathbf{2}$, $\sigma_1 \equiv \mathbf{3}$, and so on. The index j assigns numbers to the objects to be permuted, three in the present case.

The initial definition of the array $NG(i, j)$ is as follows:

$$E \equiv \begin{cases} NG(1, 1) = 1 \\ NG(1, 2) = 2 \\ NG(1, 3) = 3 \end{cases} \quad C_3 \equiv \begin{cases} NG(2, 1) = 2 \\ NG(2, 2) = 3 \\ NG(2, 3) = 1 \end{cases} \quad \sigma_1 \equiv \begin{cases} NG(3, 1) = 1 \\ NG(3, 2) = 3 \\ NG(3, 3) = 2 \end{cases} \quad (2.4)$$

which follows from (2.1). Next we use these elements to generate the remaining three, with the help of the binary operation

$$NG(m, j) = NG(i, j) \times NG(k, j) = NG(i, NG(k, j)), \quad (2.5)$$

where $NG(m) = NG(i) \times NG(k)$.

Example 2.5

Let us find a fourth element of the group C_{3v} by taking the group product $C_3\sigma_1$ and denoting the result by $NG(4)$ with array elements

$$NG(4, 1), \quad NG(4, 2), \quad NG(4, 3).$$

We will use (2.5), but first we illustrate it with an example. With a permutation realization for C_3 and σ_1 we have

$$C_3\sigma_1 = \begin{pmatrix} 1 & 2 & 3 \\ 2 & 3 & 1 \end{pmatrix} \begin{pmatrix} 1 & 2 & 3 \\ 1 & 3 & 2 \end{pmatrix} = \begin{pmatrix} 1 & 2 & 3 \\ 2 & 1 & 3 \end{pmatrix} = \sigma_3.$$

We get this result by noting, for example, that 1 from the top box in the first column of σ_1 goes into 1, which in turn goes into 2 from the first column of C_3 , so the net result is 1 goes into 2 in the first column. In terms of (2.5) this is given by

$$NG(4, 1) = NG(2, 1) \times NG(3, 1) = NG(2, NG(3, 1)) = NG(2, 1) = 2.$$

Continuing in this fashion, we find

$$\begin{aligned}
 NG(4, 2) &= NG(2, 2) \times NG(3, 2) \\
 &= NG(2, NG(3, 2)) = NG(2, 3) = 1, \\
 NG(4, 3) &= NG(2, 3) \times NG(3, 3) \\
 &= NG(2, NG(3, 3)) = NG(2, 2) = 3,
 \end{aligned} \tag{2.6}$$

which corresponds to the permutations associated with σ_3 in (2.1). The generation of the remaining elements is done in a similar fashion.

Given the group generators in *array* form, the number of *permuted objects*, and the *number of elements* g in the group, a computer program can generate all other elements by successive multiplications of group elements till g distinct elements are generated.

The following is a simple *Mathematica* program for group generation; instead of the array $NG(i, j)$ it uses a list L , together with built-in functions we introduced above.

```

<<DiscreteMath`Combinatorica`

(* GENERATE THE GROUP ELEMENTS IN PERMUTATION FORM *)
Print["GROUP C3v"]
g=6
Print["group order: = ",g]
i=1
lgen=3
Print["NUMBER OF GENERATORS = ",lgen]
L={Range[3],{2,3,1},{2,1,3}}
Print["GROUP GENERATORS: ",L]
(* L is the list of group elements in permutation form. *)
f:=Permute[L[[i]],L[[j]]]
While[TrueQ[Length[L]<g],
  For[i=1,i<g,i++,
    For[j=1,j<(Length[L]+1),j++,
      Switch[FreeQ[L,f],True,AppendTo[L,f]]
    ]
  ]
]
Print["GROUP ELEMENTS: ",L]

```

This program can be expanded to include the construction of the Cayley table using the following *Mathematica* function:

```
Print["MULTIPLICATION TABLE"]
m=TableForm[MultiplicationTable[L,Permute]]
(* m is the multiplication table array. *)
```

For Fortran or C users, binary products of the elements of $NG(i, j)$ should be carried out and the results stored in a two-dimensional array, say

$$MULTAB(i, j) = k, \quad (2.7)$$

where i, j , and k are the three group elements related by the binary operation.

The generation of the Cayley table completes the usefulness of the permutation form of the elements. All subsequent derivations of group properties should be based on the generated Cayley table.

Example 2.6

In Example 2.5 we showed how to generate group elements from the generators of the group expressed as permutations. In this scheme the elements of the group are themselves expressed as numbers in an array. We found that with $E \equiv NG(1) = 1$, $C_3 \equiv NG(2) = 2$ and $\sigma_1 \equiv NG(3) = 3$ we generated a fourth element $\sigma_3 \equiv NG(4)$. If we had continued in this fashion, we would have found $NG(5) = NG(2) \times NG(4)$ and $NG(6) = NG(2) \times NG(2)$, which would have been represented in a Cayley table as

	1	2	3	4	5	6
1	1	2	3	4	5	6
2	2	6	4	5	3	1
3	3	5	1	6	2	4
4	4	3	2	1	6	5
5	5	4	6	2	1	3
6	6	1	5	3	4	2

At this point, we would want to collect elements into sets of elements “similar” in nature, called classes. Classes play a central role in both abstract group theory and computational group theory. We will shortly show that C_3 and C_3^2 which are three-fold rotations, belong to the same class; they are labeled 2 and 6 in the above Cayley table, preferably, they should be relabeled 2 and 3. Consequently, we would prefer that the whole table be rearranged and that some elements be relabeled.

2.4 Classes

The concepts of *classes* and class algebra are fundamental to both group theory and computational group theory. Classes consist of sets of group elements whose realizations are similar in nature. The symmetry operations $\sigma_1, \sigma_2, \sigma_3 \in \mathcal{C}_{3v}$ are all “similar” and belong to the same class. They all represent the same kind of operation. However, a rigorous definition is required because some elements that appear “similar in nature” can actually be different in a subtle way.

- (i) **Conjugate elements** Two elements A and B belonging to a group $\mathcal{G}$ are called mutually conjugate if

$$B = X A X^{-1} \quad \text{for some } X \in \mathcal{G}. \quad (2.8)$$

The operation on the r.h.s. is called *conjugation*.

- (ii) **Classes** A class is a set of *all* distinct mutually conjugate elements.

Since the identity element commutes with all other group elements, we have

$$XEX^{-1} = XX^{-1} = E, \quad \forall X.$$

Thus E is in a class by itself, which we denote by $\mathcal{C}_1$.

Geometric interpretation

There is a simple physical interpretation of conjugate elements when working with geometric realizations of a group. One can go from one element of the class to another with a similarity transformation (a conjugation!). To conform with the above definition of a class, the transformation, a matrix, must correspond to some element of the group. In a geometrical sense, say, it may rotate the coordinate system, so that the transformed operator maintains its original nature.

Consider the geometric realization of $\mathcal{C}_{3v}$ as the operations that leave the equilateral triangle unchanged. Then, for example, $\sigma_3 = C_3^{-1}\sigma_1C_3$ has the following physical interpretation: A reflection σ_3 through the C -axis of Figure 2.2 is equivalent to a 120° rotation by means of the group operation C_3 , followed by a reflection through the *fixed* A -axis, and finally followed by a 240° clockwise rotation (120° counterclockwise) by means of the operation $C_3^2 = C_3^{-1}$, which returns the triangle to its original position. This means that two elements of a group are mutually conjugate if, in the geometric realization, they can be identified with equivalent physical or geometric operations (rotations through the same angle, for instance). We should stress, however, that the conjugation connecting the two operations has to be effected by another operation in the geometric realization of the group. If such a connecting operation is absent, the conjugacy of the two elements is also absent, despite their similar natures.

In the above case, the equivalence of the elements C_3 and C_3^2 is clear. However, if we consider the symmetry operations of the square, shown in Figure 2.4, with point-group $\mathcal{C}_{4v}$, we find that not all of the $n\pi/2$ rotations fall into one class. A C_2 rotation is not connected by any of the elements of the group $\mathcal{C}_{4v}$ to the C_4 or C_4^2 rotations. In the same manner, the reflections σ_v and σ_d belong to different classes for the same reason, they are not connected by any group element.

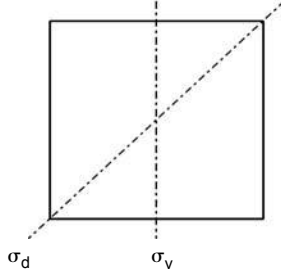


Fig. 2.4. The square mesh with C_{4v} symmetry. Two *inequivalent* types of reflection planes are shown.

Theorem A group $\mathcal{G}$ splits into “conjugacy classes” $\mathcal{C}_1, \mathcal{C}_2, \dots, \mathcal{C}_{n_c}$ such that the following properties hold:

- (i) Every element of $\mathcal{G}$ is in some class, and no element of $\mathcal{G}$ is in more than one class, so that

$$\mathcal{G} = \mathcal{C}_1 \cup \mathcal{C}_2 \cup \dots \cup \mathcal{C}_{n_c}. \quad (2.9)$$

Sometimes this relationship is written with $+$ signs rather than $\cup$ signs, but the relationship is a *union* of classes, not a *sum* of classes.

- (ii) All the elements in a given class are mutually conjugate and consequently have the same order s .
- (iii) An element that commutes with all elements of the group is in a class by itself and is called a *self-conjugate* element. The set of all self-conjugate elements of a group is called the *center* of the group.

Because all the elements of an Abelian group mutually commute, each element is self-conjugate, i.e. in a class by itself.

- (iv) The number of elements r_i in the class $\mathcal{C}_i$ is a divisor of the order of the group. Furthermore, the order of the elements of the class, s_i , is a divisor of g/r_i .
- (v) Every product of two classes can be decomposed into a sum of classes:

$$\mathcal{C}_i \mathcal{C}_j = \sum_k h_{ijk} \mathcal{C}_k, \quad (2.10)$$

where the sum is an addition, as in ordinary arithmetic, not a union. This relationship is crucial for the development of computational group theory.

In Section 2.4.2 we will elaborate on its significance in computational aspects of *representation theory*.

- (vi) The elements R of a class are rearranged by the conjugacy relation $X^{-1}RX$, just as the elements of a row or column of the multiplication table are rearranged by operating on every element by some member of the group other than the identity element. This is known as the *class rearrangement theorem*.

2.4.1 Computer generation of classes and class arrays

In this section we introduce the definition of several Mathematica[®] based functions that will be useful to subsequent programs. Using the definition of a conjugacy class as the distinct set of elements $B = XAX^{-1}$, $\forall X \in \mathcal{G}$, we next generate

- (i) A one-dimensional array of inverse elements $Inv(i) = j$.

In *Mathematica* this is implemented by the following code:

```
LInv=Map[InversePermutation,L]
(* where LInv is a list of the inverses of the list L
   of group elements, given in the same order, and in
   permutation form. *)
Print["INVERSE ELEMENTS IN PERMUTATION FORM: ",LInv]
(* A compact form of the inverse elements is generated
   as follows: *)
LInv={1}
For[i=2,i<g+1,i++,
  For[j=1,j<g+1,j++,
    Switch[TrueQ[m[[1,i,j]]==1],True,
      AppendTo[LInv,j] ]
  ]
]
Print["INVERSE ELEMENTS IN PERMUTATION FORM: ",LInv]
```

- (ii) A two-dimensional integer array $Class(i,j) = k$ identifying element k as the j th element in class i :

```
Class={{1}}
i=1
nc=1
f:=m[[1,m[[1,j,i]],LInv[[j]]]]
Block[{p=Range[g],C1={}},p[[1]]=0;
  While[Apply[Plus,p]≠0,i=i+1;
    Switch[TrueQ[p[[i]]≠0],True,C1={i};p[[i]]=0;
    For[j=2,j<g+1,j++,
      Switch[FreeQ[C1,f],True,
        AppendTo[C1,f];p[[f]]=0
      ]
    ];
  ];
```

```

AppendTo[Class,C1];nc=nc+1;C1={}
]
]
]
Print["NUMBER OF CLASSES = ",nc]
Print["CLASSES: ",Class]

```

(iii) A one-dimensional array $NCL(i)$, the number of elements in class i .

In *Mathematica* the number of elements in class i is given by

```
Length[Class[[i]]]
```

(iv) the number of classes NC , given above as nc .

(v) A one-dimensional array $Ind\ Class(i)$, identifying the class to which element i belongs.

In *Mathematica* this is generated as follows:

```

Do[j=1;
  While[j<nc,
    Switch[MemberQ[Class[[j]],i],
      True,IndClass[i]=j;j=nc+1,
      False,j=j+1]
    ],{i,1,g}
]

```

(vi) A one-dimensional array $InvClass(i)$, identifying the class containing the inverse element of class i . In *Mathematica* we write:

```
Do[InvClass[i]=IndClass[LInv[[i]]],{i,1,g}]
```

(vii) A two-dimensional array $IndPow(i,j)$, identifying the class to which i^j belongs:

```

Do[
  IndPow[i,1]=1;el=Class[[i,1]];IndPow[i,2]=i;
  Do[
    Switch[i==1,True,IndPow[i,j]=1,
      False,el=m[[1,el,Class[[i,1]]]];k=1;
      While[FreeQ[Class[[k]],el],k=k+1];
      IndPow[i,j]=k
    ],{j,1,nn}
  ],{i,1,nc}
]

```

- (viii) A one-dimensional array $ClassExp(i)$ defining the order (or class exponent) of class i :

```

ClassExp={1}
Do[
  t=Class[[i,1]];ncc=1;
  While[t≠1,t=m[[1,Class[[i,1]],t]];ncc=ncc+1;
  AppendTo[ClassExp,ncc],{i,1,nc}
]
Print["CLASS EXPONENTS: ",ClassExp]

```

2.4.2 Class multiplication

We have asserted in (2.10) above that the product of two classes can be decomposed into a sum of classes

$$\mathcal{C}_i \mathcal{C}_j = \sum_k h_{ijk} \mathcal{C}_k,$$

where classes may appear any number of times or not at all. This implies that we have to keep track of the number of times a class element appears.

Class rearrangement theorem

In order to prove this very important relation we will make use of the rearrangement theorem, which specifies that

A conjugation operation simply rearranges the list of distinct elements of a class.

Since a conjugacy operation may be considered in view of the associative property of group multiplication, $(XA)X^{-1}$, its outcome is unique as asserted by the group rearrangement theorem. Thus, given an arbitrary element $X \in \mathcal{G}$, and two distinct elements $A, B \in \mathcal{C}$; $\mathcal{C} \subset \mathcal{G}$, we assert that

$$XAX^{-1} \neq XBX^{-1},$$

and hence

$$X\mathcal{C}X^{-1} = \mathcal{C}, \quad \forall X \in \mathcal{G}. \quad (2.11)$$

It is also true that any set of elements, $\mathcal{S} \subset \mathcal{G}$, satisfying

$$X\mathcal{S}X^{-1} = \mathcal{S}, \quad (2.12)$$

is composed of complete classes.

Class algebra

To clarify what we mean by the product of classes, we begin by defining a sum over the elements of a class as

$$\bar{\mathcal{C}}_i = \sum_{A \in \mathcal{C}_i} A, \quad (2.13)$$

where $\bar{\mathcal{C}}_i$ is called the *class sum*, and each element in the class appears only once in the summation. Consequently we can rewrite (2.9) as

$$\bar{\mathcal{G}} = \sum_{i=1}^{n_c} \bar{\mathcal{C}}_i, \quad (2.14)$$

where each class sum appears once and only once, and so each group element appears once and only once.

However, our new introduction of the operation of addition of group elements allows to count frequent occurrences of an element, for example we write

$$A + A = 2A !$$

This is more akin to traditional arithmetic and the ordinary meaning of summation. By introducing this extra binary operation, to go along with the binary composition of multiplication of group elements, we have defined *an algebra on the group*, the *Frobenius algebra*.

We can use (2.11) to prove (2.10)

$$\begin{aligned} \bar{\mathcal{C}}_i \bar{\mathcal{C}}_j &= X \bar{\mathcal{C}}_i X^{-1} X \bar{\mathcal{C}}_j X^{-1} \\ &= X \bar{\mathcal{C}}_i \bar{\mathcal{C}}_j X^{-1}, \end{aligned}$$

where we also used (2.12) with $\mathcal{S} = \bar{\mathcal{C}}_i \bar{\mathcal{C}}_j$, which demonstrates that $\bar{\mathcal{C}}_i \bar{\mathcal{C}}_j$ is composed of complete classes, and that a given class may appear more than once.

Thus, every product of two class sums $\bar{\mathcal{C}}_i \bar{\mathcal{C}}_j$ can be decomposed into a sum of classes,

$$\bar{\mathcal{C}}_i \bar{\mathcal{C}}_j = \sum_{k=1}^{n_c} h_{ijk} \bar{\mathcal{C}}_k, \quad (2.15)$$

where the coefficients h_{ijk} are called the *class multiplication coefficients*, and are positive integers or zero. This equation is frequently written without the bar over the class symbols and is described simply as a product of classes rather than a product of class *sums*.

Example 2.7

For the group $\mathcal{C}_{3v}$ we can define the class sums

$$\bar{\mathcal{C}}_1 = E, \quad \bar{\mathcal{C}}_2 = C_3 + C_3^2; \quad \bar{\mathcal{C}}_3 = \sigma_1 + \sigma_2 + \sigma_3.$$

The class multiplications are then: $\bar{\mathcal{C}}_1 \bar{\mathcal{C}}_i = \bar{\mathcal{C}}_i \bar{\mathcal{C}}_1 = \bar{\mathcal{C}}_i$, $\bar{\mathcal{C}}_2^2 = 2\bar{\mathcal{C}}_1 + \bar{\mathcal{C}}_2$, $\bar{\mathcal{C}}_2 \bar{\mathcal{C}}_3 = 2\bar{\mathcal{C}}_3 = \bar{\mathcal{C}}_3 \bar{\mathcal{C}}_2$, $\bar{\mathcal{C}}_3^2 = 3(\bar{\mathcal{C}}_1 + \bar{\mathcal{C}}_2)$.

Theorem A class sum of a group $\mathcal{G}$ commutes with all the elements of $\mathcal{G}$.

Proof For $A \in \mathcal{G}$ we define a conjugacy class of A as

$$\bar{\mathcal{C}}(A) = \sum_{R \in \mathcal{G}} RAR^{-1}. \quad (2.16)$$

Then, for any element $X \in \mathcal{G}$, we find

$$\begin{aligned} X\bar{\mathcal{C}}(A) &= \sum_{R \in \mathcal{G}} XRAR^{-1}X^{-1}X \\ &= \sum_{R \in \mathcal{G}} (XR)A(XR)^{-1}X \\ &= \bar{\mathcal{C}}(A)X. \end{aligned} \quad (2.17)$$

Since a class sum commutes with all elements of the group, it must commute with all other classes. Thus $\mathcal{C}_i\mathcal{C}_j = \mathcal{C}_j\mathcal{C}_i$, and so from (2.11) we must have

$$h_{ijk} = h_{jik}. \quad (2.18)$$

2.4.3 Computer generation of class multiplication matrices

The class multiplication coefficients h_{ijk} are defined as a three-dimensional array $H(i, j, k)$. It is generated by enumerating the frequency of occurrence of a representative element of class k when all elements of class i are multiplied by all elements of class j .

Example 2.8

Using Example 2.7 we have

$$\bar{\mathcal{C}}_2\bar{\mathcal{C}}_3 = (C_3 + C_3^2)(\sigma_1 + \sigma_2 + \sigma_3) = 2(\sigma_1 + \sigma_2 + \sigma_3).$$

We see that we need only enumerate the occurrence of, say, σ_1 from the class $\bar{\mathcal{C}}_3$ in order to determine $h_{233} = 2$.

In *Mathematica* we generate the class multiplication matrices with the aid of the following code:

```
Print["CLASS MULTIPLICATION MATRICES"]
Do[ H[i,j,k]=0,{i,1,nc},{j,1,nc},{k,1,nc}]
Do[H[1,i,i]=1;H[i,1,i]=1,{i,1,nc}];
s:=m[[1,Class[[i,1]],Class[[j,k]]]];
Do[
For[l=1,l<Length[Class[[i]]]+1,l++,
```

```

For[k=1,k<Length[Class[[j]]]+1,k++,
  For[m1=1,m1<nc+1,m1++,
    Switch[MemberQ[Class[[m1]],s],True,
      H[i,j,m1]+=1]
    ]
  ]
]
Do[
  H[i,j,m1] = H[i,j,m1]/Length[Class[[m1]]],
  {m1,1,nc}
],{i,2,nc},{j,2,nc}
];
Print["CLASS MULTIPLICATION MATRICES: ",
  MatrixForm[H1=Array[H,{nc,nc,nc}]]]

```

2.5 Homomorphism, isomorphism, and automorphism

Given two groups $\mathcal{G}$ and $\mathcal{G}'$, a mapping θ of $\mathcal{G}$ onto $\mathcal{G}'$ that preserves multiplication is called a *homomorphism*. For a homomorphism θ ,

$$(\theta A_i)(\theta A_j) = \theta(A_i A_j) \quad \text{for all } A_i, A_j \in \mathcal{G}. \quad (2.19)$$

The smaller group is called the *homomorph* of the larger. The subset of elements of $\mathcal{G}$ that map onto the identity of the smaller group $\mathcal{G}'$ is called the *kernel* of the homomorphism.

- If θ is a one-to-one mapping, it is called an *isomorphism* and the groups $\mathcal{G}$ and $\mathcal{G}'$ are said to be *isomorphic*.
- If θ is an isomorphism and $\mathcal{G} = \mathcal{G}'$, then θ is called an *automorphism*.
- If θ is an automorphism and the mapping from $\mathcal{G}$ onto itself is such that

$$\theta \mathcal{G} = X \mathcal{G} X^{-1}; \text{ for } X \in \mathcal{G},$$

that is, such that the automorphism is produced by conjugation, it is called an *inner automorphism*, all others being called *outer automorphisms*.

Examples

- (i) If $\mathcal{G} = G_6$ and $\mathcal{G}' = G_2 \equiv \{E, A'\}$, then the mapping

$$\theta(E) = \theta(D) = \theta(F) = E$$

$$\theta(A) = \theta(B) = \theta(C) = A'$$

is a homomorphism of G_6 onto G_2 .

- (ii) The groups $\mathcal{C}_{3v}$, $\mathcal{D}_3$ and $\mathcal{S}_3$ are isomorphic: They have the same order and share the same multiplication table.
- (iii) If $\theta(E) = E$, $\theta(A) = B$, $\theta(B) = C$, $\theta(C) = A$, $\theta(D) = F$, and $\theta(F) = D$, the mapping is an automorphism of G_6 onto itself.

2.6 Direct- or outer-product groups

Given two groups $\mathcal{G}$ and $\mathcal{H}$ of order g and h , such that all the elements of $\mathcal{G}$ commute with all the elements of $\mathcal{H}$,

$$G_i H_j = H_j G_i \quad \forall G_i \in \mathcal{G} \text{ and } H_i \in \mathcal{H}, \quad (2.20)$$

Table 2.4. *Schoenflies (Sch.) and Hermann–Mauguin (H-M) notation for point-groups.*

Group notation			Group order	Group generators
Sch.	H-M			
$\mathcal{C}_n$	n		n	C_n
$\mathcal{C}_{nv}$	nmm	$(n \text{ even})$	nmm	C_n, σ_v, σ_d
	nm	$(n \text{ odd})$	nm	C_n, σ_v
$\mathcal{S}_{2n}$	$\bar{n}$		$2n$	S_{2n}
$\mathcal{C}_{nh}$	$\frac{n}{m}$	$(n \text{ even})$	$\frac{n}{m}$	C_n, σ_h
	$\bar{n}$	$(n \text{ odd})$	$\bar{n}$	C_n, I
$\mathcal{D}_n$	$n22$	$(n \text{ even})$	$n22$	C_n, C_2, C_2'
	$n2$	$(n \text{ odd})$	$n2$	C_n, C_2
$\mathcal{D}_{nh}$	$\frac{n}{m} \frac{2}{m} \frac{2}{m}$	$(n \text{ even})$	$\frac{n}{mmm}$	C_n, C_2, C_2', σ_h
$\mathcal{D}_{nd}$	$\bar{n}m$	$(n \text{ odd})$	$\bar{n}m$	C_n, C_2, I
$\mathcal{T}$	23		23	C_3, C_2
$\mathcal{T}_h$	$\frac{2}{m} \bar{3}$		$m\bar{3}$	C_3, C_2, I
$\mathcal{T}_d$	$\bar{4}3m$		$\bar{4}3m$	C_3, C_2, σ_v
$\mathcal{O}$	432		432	C_4, C_3, C_2
$\mathcal{O}_h$	$\frac{4}{m} \bar{3} \frac{2}{m}$		$m\bar{3}m$	C_4, C_3, C_2

Column 2 gives the full H-M notation, while column 4 gives the abbreviated one.

and the only element in common is the identity, then the set of all combinations $G_i H_j$ forms a group of order gh , called a *direct-* or *outer-product* group.

Product groups, including the direct-product, are the subject of Chapter 8. Here we simply note that the importance of direct-product groups often arises when the two sets of operators (those from group $\mathcal{G}$ and those from group $\mathcal{H}$) operate on independent sets of functions or coordinates. Examples are given in Exercises 2.17–2.19.

The meaning of (2.20) is illustrated as follows. Given a group G_A with i elements $(E, A_2, A_3, \dots, A_i)$ and another group G_B with j elements $(E, B_2, B_3, \dots, B_j)$, the direct-product group is

$$\begin{aligned} & (E, A_2, A_3, \dots, A_i) \otimes (E, B_2, B_3, \dots, B_j) \\ &= (E, A_2, A_3, \dots, A_i, A_2, A_2 B_2, \dots, A_i B_2, \dots, A_i B_j), \end{aligned} \quad (2.21)$$

which forms a group containing ij elements.

Exercises

Note on the exercises: Exercises 2.1 through 2.17 range from those which help in developing an understanding of the *theory* of groups to those which are in the nature of finger exercises and help in developing familiarity with group theory and some dexterity in performing the mathematical manipulations of group theory. Exercises 2.17 and 2.18 are crucial. The solution to Exercise 2.18 provides the basis for the remaining computational methods that follow in later chapters. Exercise 2.19 provides a check on the program developed in Exercise 2.18. Exercises 2.20 through 2.25 provide an introduction to crystallographic point-groups. They should all be read and thought about, and at least a few of them carried to completion. Geometric figures are provided to elucidate the properties of these point-groups. The vertices of the figures are numbered sequentially, to facilitate the construction of permutation operations associated with the groups. In addition to the particular questions posed in each problem, apply the program developed in Exercise 2.18 to each of Exercise 2.20 through 2.25.

2.1 Convert the following permutation from bracket notation to cycle notation:

$$\begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 \\ 6 & 5 & 2 & 3 & 4 & 1 & 7 \end{pmatrix}$$

2.2 Convert (163275) to bracket notation.

2.3 Given permutation operators p and q defined by

$$p = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 \\ 1 & 7 & 4 & 5 & 3 & 2 & 6 \end{pmatrix} \quad q = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 \\ 5 & 1 & 2 & 4 & 3 & 7 & 6 \end{pmatrix},$$

(a) find the product pq in bracket notation;

(b) use the `Permute` function defined in *Mathematica*, or any other computer language code you develop, to carry out the permutation product.

2.4 Repeat Exercise 2.3 for the following pairs of permutation operators:

(a) $p = (567)$, $q = (2673)$;

(b) $p = (246)(37)$, $q = (143)(56)$.

Write the products pq in cycle notation. Try to do this by sight without writing out the implicit cycles in p or q .

- 2.5 Find the inverse and degree of each of the following permutation operations, by long-hand, using the *Mathematica* function `InversePermutation`, or developing your own code in C or FORTRAN:

$$p = \begin{pmatrix} 1 & 2 & 3 \\ 1 & 3 & 2 \end{pmatrix} \quad q = \begin{pmatrix} 1 & 2 & 3 \\ 3 & 2 & 1 \end{pmatrix} \quad r = \begin{pmatrix} 1 & 2 & 3 & 4 \\ 4 & 3 & 1 & 2 \end{pmatrix}$$

$$s = \begin{pmatrix} 1 & 2 & 3 & 4 \\ 2 & 1 & 4 & 3 \end{pmatrix} \quad t = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 \\ 5 & 4 & 1 & 2 & 3 \end{pmatrix}$$

$$u = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 \\ 1 & 4 & 7 & 6 & 3 & 2 & 5 \end{pmatrix} \quad v = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 \\ 6 & 5 & 2 & 3 & 4 & 7 & 1 \end{pmatrix}$$

$$w = (12)(34657)$$

- 2.6 Show that the permutations of n objects which form the symmetric group $\mathcal{S}_n$ is of order $n!$.
- 2.7 Show for the symmetric group $\mathcal{S}_3$ that elements with the same form of decomposition into cycles belong to the same class. When generating the group classes with a *Mathematica* program, use the function `ToCycle[p]` to generate the cycle structure of the elements.
- 2.8 Determine the classes of the symmetric group $\mathcal{S}_4$.
- 2.9 Show that the number of elements $\text{nc}(i)$ of a class $\mathcal{C}_i$ of a finite group $\mathcal{G}$ divides its order, i.e. $g/\text{nc}(i)$ is an integer.
- 2.10 Show that the set composed of all inverses of the elements of a class $\mathcal{C}_i$ of a group $\mathcal{G}$ is also a class of $\mathcal{G}$, which we may denote by $\mathcal{C}_j = \mathcal{C}_i^{-1}$. Such classes are called *mutually reciprocal classes*. If a class contains its own inverse elements it is called a *self-inverse class*.
- 2.11 Consider the isomorphic realizations $\mathcal{C}_{4v}$ and $\mathcal{D}_4$ of the square. These realization groups contain 8 elements:

$$E, C_4, C_4^{-1}, C_2, \sigma_1(C_2'^1), \sigma_2(C_2''^2), \sigma_1'(C_2''^2), \sigma_2'(C_2''^2).$$

In addition to the identity operation, we find in each realization four-fold rotations and reflections (or two-fold rotations). However, if we examine the class structure of these realization groups, we find: $\mathcal{C}_1 = \{E\}$, $\mathcal{C}_2 = \{C_4, C_4^{-1}\}$, $\mathcal{C}_3 = C_2$, $\mathcal{C}_4 = \{\sigma_1(C_2'^1), \sigma_2(C_2''^2)\}$, $\mathcal{C}_5 = \{\sigma_1'(C_2''^2), \sigma_2'(C_2''^2)\}$. How do you justify this class structure when each of the set of reflections or the set of two-fold rotations are similar in nature?

- 2.12 Prove that if class $\mathcal{C}_j$ contains the inverse of element R in class $\mathcal{C}_i$, then $\mathcal{C}_j$ must be composed of all the inverse elements of $\mathcal{C}_i$, and $\text{nc}(j) = \text{nc}(i)$, where $\text{nc}(i)$ is the number of elements in class $\mathcal{C}_i$. An *ambivalent* class is a class that is its own inverse.
- 2.13 Find the class multiplication coefficients h_{ijk} for the groups $\mathcal{C}_{3v}$ and $\mathcal{C}_{4v}$.
- 2.14 Show that the following general relations are satisfied by the class multiplication coefficients.

- (i) $h_{ijk} = h_{jik}$ (This is equivalent to proving that $\mathcal{C}_i X = X \mathcal{C}_i$ for all elements X . Let X range over all elements in $\mathcal{C}_j$.)
- (ii) $\sum_{k=1}^{\text{nc}l} h_{ijk} h_{klm} = \sum_{k=1}^{\text{nc}l} h_{jlk} h_{ikm}$
- (iii) $\text{nc}(i) \text{nc}(j) = \sum_{k=1}^{\text{nc}l} h_{ijk} \text{nc}(k)$.
- (iv) $h_{ijk} = h_{i\bar{j}\bar{k}}$
- (v) $\text{nc}(k) h_{ijk} = \text{nc}(i) h_{k\bar{j}i} = \text{nc}(i) h_{j\bar{k}i} = \text{nc}(j) h_{i\bar{k}\bar{j}}$
- (vi) $h_{ij1} = \text{nc}(i) \delta_{i\bar{j}}$ where $\text{nc}(i)$ is the number of elements in class $\mathcal{C}_i$ and where bars denote the inverse class. That is, $\mathcal{C}_{\bar{i}}$ is a class that contains the inverses of the elements of class $\mathcal{C}_i$. Note that the third subscript on h is the number 1, not the letter l.
- (vii) Show that a mapping of one group onto another can be completely specified by the action of the mapping on the generators of the larger group.

2.15 Prove the group rearrangement theorem.

2.16 Prove the class rearrangement theorem.

2.17 Prove that the set of integers $1, 2, 3, \dots, (k-1)$ form a group of order $(k-1)$ under ordinary multiplication modulo k . (Note: Two integers m and n are equal, modulo k , if $m = n + jk$, where j is an integer.)

Multiplication, modulo a prime number, plays an important role in Dixon's method for determining the characters of irreducible representations.

2.18 Write a general computer program, guided by the outlines in the text, which makes use of the minimal set of group generators to

- (i) generate the group elements in permutation form,
- (ii) construct the corresponding Cayley tables,
- (iii) generate the inverse elements,
- (iv) generate the classes and class arrays, specified in Section 2.3.1,
- (v) generate the class multiplication matrices.

2.19 Use the program from the previous problem to obtain the group multiplication tables for the point-groups $\mathcal{C}_{3v}$, $\mathcal{C}_{4v}$, $\mathcal{C}_{5v}$. The surface nets of Figure 2.5 can be modified by replacing the reflection planes σ_v with two-fold rotation axes C_2 that are perpendicular to the principal C_n axis, and by replacing the reflection planes σ_d with two-fold C'_2 axes, giving rise to the dihedral symmetry groups $\mathcal{D}_n$ shown in Figure 2.6, which are isomorphic to the $\mathcal{C}_{nv}$ groups.

2.20 Figure 2.5 shows the primitive meshes corresponding to allowed two-dimensional surface lattices (nets). The vertices are sequentially numbered, clockwise. Also shown are the allowed types of reflection planes, designated by σ_v and σ_d .

(a) Find all the physically realizable point-symmetry operations for the four meshes of Figure 2.5. Write out these symmetry operations as permutations of the vertex numbering, in cycle notation. (Note: there are 4, 8, 6, and 12 operations for these meshes, respectively; and the identity operation and the rotations maintain the clockwise ordering of the labeling. The mirror reflections change the labeling to counter-clockwise.)

(b) Why aren't the remaining permutations, like (1324) for $\mathcal{C}_{4v}$ symmetry operations?

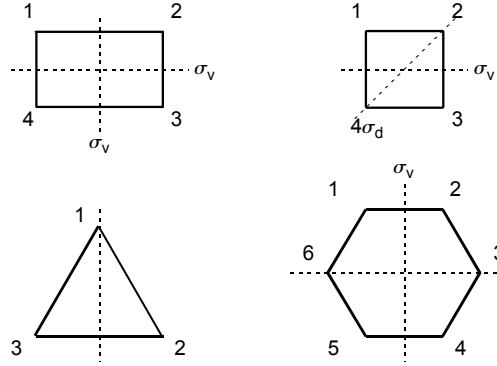


Fig. 2.5. Clockwise from top left: symmetries of the point-groups C_{2v} , C_{4v} , C_{6v} , and C_{3v} , respectively.

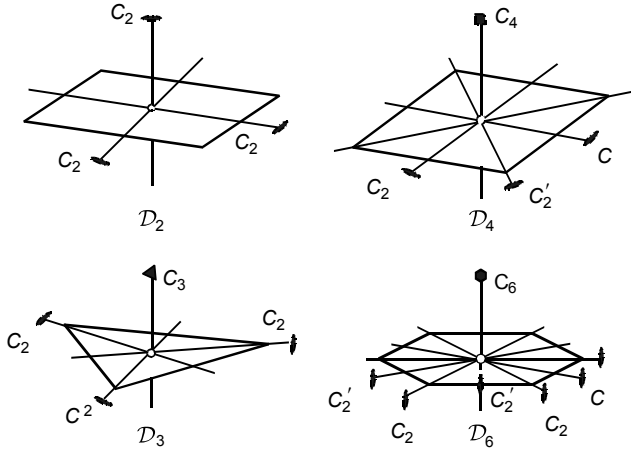


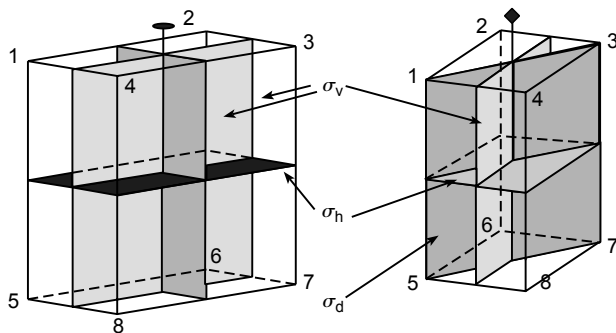
Fig. 2.6. Symmetries of the dihedral groups D_2 , D_4 , D_3 , and D_6 .

2.21 Figure 2.7 shows the primitive (Wigner–Seitz) cells for lattices with symmetry involving a *major* axis of rotation and a horizontal reflection plane σ_h , that is, a reflection plane perpendicular to the major axis. These *improper* point-symmetry groups are designated C_{nh} , where $n = 2, 3, 4, 6$.

Show that these groups have the following properties:

- (i) Since groups with even n include the two-fold rotation $C_2 = C_n^{n/2}$, by taking the major axis along the z -direction, and defining the C_2 and σ_h by the three-dimensional rotation matrices, show that

$$C_2\sigma_h = \sigma_h C_2 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} = I,$$

Fig. 2.7. Primitive cells with C_{nh} symmetries.

which is just the matrix that defines the inversion symmetry operation $\mathbf{r} \rightarrow -\mathbf{r}$. Thus, C_{nh} symmetries with even n contain the inversion operation, i.e. the corresponding primitive cells have a center of inversion. Groups with odd n do not contain the inversion.

- (ii) For $n = 1$, the group C_{1h} is composed of the identity E and σ , and is usually denoted by C_s . Thus, show that we can express the C_{nh} groups as the outer-products

$$C_{nh} = C_n \otimes C_s,$$

containing $2n$ elements.

- (iii) Each has $2n$ classes.

2.22 When the dihedral groups $\mathcal{D}_n$ are augmented by a σ_h reflection plane, perpendicular to the major axis, as shown in Figure 2.8, we obtain the improper point-groups $\mathcal{D}_{nh}$. Again, I is an element of the group, only if n is even. Show that the $\mathcal{D}_n$ point-groups have the following properties:

- (i) The group order is $4n$.
- (ii) They contain $n\sigma_v$ reflection planes, in addition to the $n C_2$ rotations.
- (iii) σ_h commutes with all the elements of the group. Hence we can express these groups as

$$\mathcal{D}_{nh} = \mathcal{D}_n \otimes C_s.$$

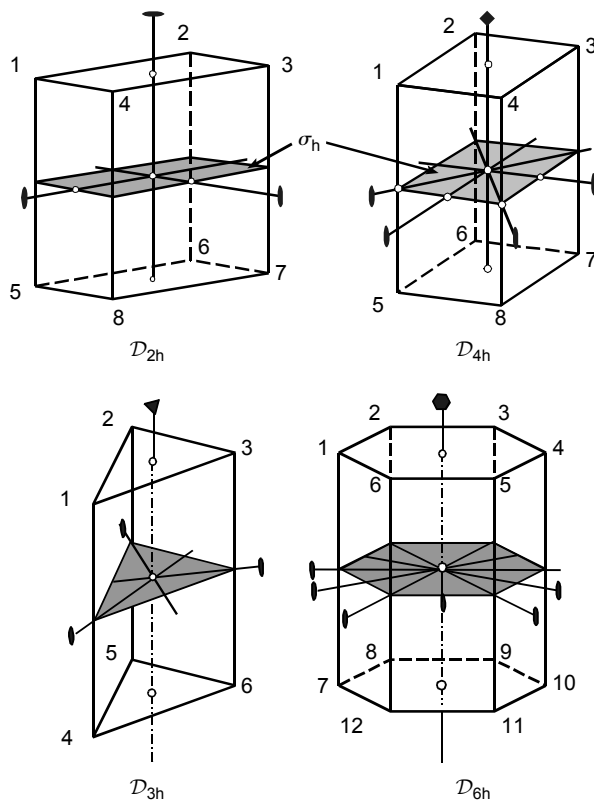
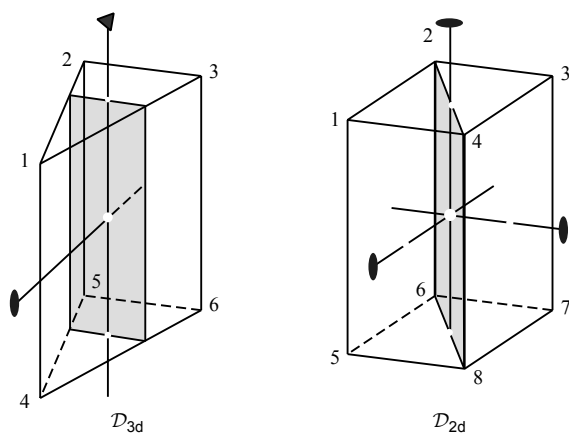
2.23 In Figure 2.9, we show the case of augmenting $\mathcal{D}_n$ by a vertical σ_d reflection plane that bisects the angle between two neighboring C_2 axes. The ensuing groups are designated $\mathcal{D}_{nd}$.

Show that

- (i) the operation

$$C_2\sigma_d = S_{2n},$$

where C_2 is one of the neighboring two-fold axes;

Fig. 2.8. Primitive cells with D_{nh} symmetries.Fig. 2.9. Primitive cells with D_{nd} symmetries.

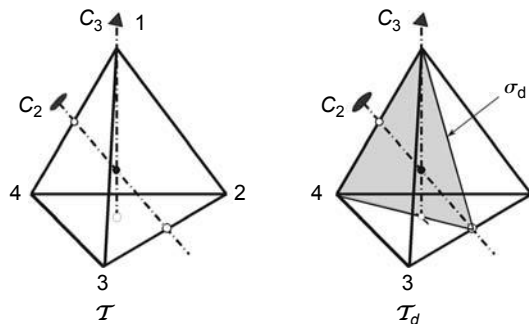


Fig. 2.10. Primitive cells with tetrahedral symmetries $\mathcal{T}$ and $\mathcal{T}_d$.

(ii) for n odd, there is one σ_d plane perpendicular to one of the two-fold axes, and that, in this case, the group can be expressed as

$$\mathcal{D}_{nd} = \mathcal{D}_n \otimes \mathcal{C}_i.$$

2.24 Figure 2.10 shows two regular tetrahedra with symmetries $\mathcal{T}$ and $\mathcal{T}_d$.

(a) For the tetrahedron shown with point-group symmetry $\mathcal{T}$, write out the symmetry operations in cycle notation for the various rotations about the axes that pass through an apex of the tetrahedron and the center of the opposite face. These consist of rotations denoted by C_3 and C_3^2 . Do the same for symmetry operations that consist of rotations about a two-fold axis that passes through the midpoint of one edge, the center of the tetrahedron, and the midpoint of the opposite edge. Show that these 11 operations together with the identity form a group, the $\mathcal{T}$ group.

(b) In addition to the operation of part (a), the tetrahedron with point-group symmetry $\mathcal{T}_d$ shows reflection planes that pass through one edge of the tetrahedron and bisect the opposite edge. Each of these reflection planes contains one 2-fold and two 3-fold axes, and bisects the angle between the remaining two 2-fold axes, thus designated σ_d . Show that each σ_d plane converts the 2-fold axis it contains into a 4-fold rotary reflection axis S_4 .

Write out the symmetry operations corresponding to the reflections σ_d in cycle form. Expand the group of part (a) by including these symmetry operations in the group. Note that this *requires* the inclusion of other symmetry operations to complete the group, an example being $(1234) = (14)(123)$, which corresponds to a rotation followed by a reflection. This group is designated $\mathcal{T}_d$.

(c) Figure 2.11 shows the primitive cell with $\mathcal{T}_h$ symmetry. In this figure the three-fold axes are rotated to coincide with the body diagonals of a cube. One of the two-fold axes is now along the z -axis. The σ_h reflection planes are perpendicular to the two-fold axes and bisect the angles between the three-fold axes. Carry out all the steps stated in parts (a) and (b).

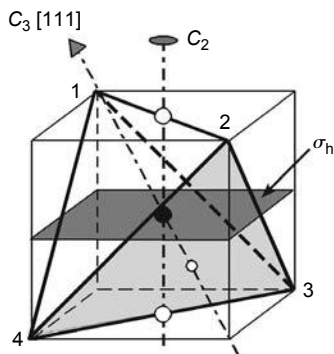


Fig. 2.11. Primitive cell with T_h tetrahedral symmetries.

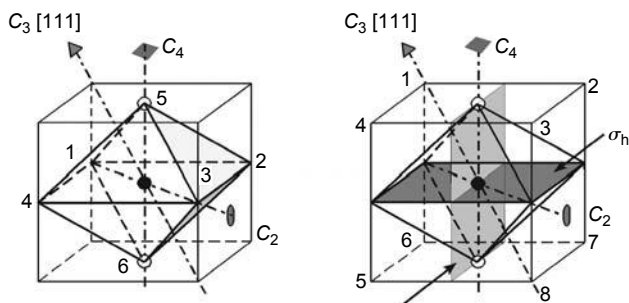


Fig. 2.12. The octahedral primitive cell with O and O_h symmetries.

2.25 Figure 2.12 shows the primitive cell with O and O_h symmetry. O is composed of allowed rotation and reflection operations except σ_h , it has 24 operations. Obviously, O_h contains σ_h . Carry out all the steps stated in parts (a) and (c) of the previous problem for these two octahedral groups.

3

Group representations: concepts

In Chapter 1 we presented configuration-space translation operators, t_A , and function-space counterparts, $\hat{t}_A$. The latter transforms functions such that the value of the new transformed function at the new transformed coordinates equals the value of the original function at the original coordinates. Generalizing these operators to include rotations and other transformations, we write the defining relation between configuration-space operators R and function-space operators $\hat{R}$ as

$$\hat{R}f(\mathbf{r}) = f(R^{-1}\mathbf{r}). \quad (3.1)$$

Note carefully here that we refer to two different spaces. We have *configuration space*, in which the operator R is defined, and *function-space* in which the function operator $\hat{R}$ is defined. The latter effects transformations among functions in Hilbert (function) space.

A key point A coordinate transformation in configuration space *induces* a transformation of a function defined on the space. Equation (3.1) defines the way in which we determine the function-space operator.

In Chapter 2 we discussed configuration-space operators that provide a geometric *realization* of a group. We used permutation matrices to describe mathematically the effect of configuration-space operators on objects placed in that space. These permutations obey the group multiplication table and are also a realization of the group. We employed them to generate the multiplication table of the group. Generally, however, we find it more useful to use configuration-space matrices that operate on vectors. Such matrices are the natural choice for describing symmetry properties related to geometry, such as translations, rotations, and reflections. This set of matrices also obeys the group multiplication table and is also called a realization of the group.

We now introduce the concept of a *representation of a group*.

A tentative definition A *representation* of a group is a mapping of the elements of a group onto a set of matrices that obey the group multiplication table.

The reader will note that a few sentences earlier we stated that the set of configuration-space matrices that obey the group multiplication table is a *realization* of the group. Here, we should remind the reader that the realization is required to be isomorphic, i.e. we have to establish a one-to-one correspondence between distinct group elements and distinct matrices, and ensure that this mapping satisfies the multiplication table.

Thus, we identify a matrix realization of a group as a representation, but we should be careful and state that not all representations can be accepted as realizations. For example, we may map all group operators onto the identity matrix. This satisfies the multiplication table, but cannot be a realization. Thus, we mean much more by group representations than just geometrical transformations in configuration space.

Having introduced the more general concept of a *representation* of a group, we are now set to explore how function operators $\hat{R}$ may *induce* a *representation* of a group $\mathcal{G}$ in function-space, i.e. how to construct matrices that effect transformations induced by the $\hat{R}$ s on a set of functions. To find the *effect* of a function operator acting on a function, we must employ (3.1). This is both important and nontrivial. It is often the source of much confusion.

What we mean by a representation will become clear after some further development of the idea, helped along by examples. If physical applications of group theory were simply a matter of rotating triangles and the like, the subject would be trivial. It is the application to functions that makes all the difference between triviality and substance.

Representations are central to the basic theory, and so it is important to develop a clear understanding of the main concepts, particularly what a representation *is* and how it may differ from a realization.

3.1 Representations and realizations

As a prelude to matrix representations, and as a way of developing a connection between permutation matrices and matrix descriptions of coordinate transformations, we now consider permutations of three balls of different colors: red, blue, and green. Following our prescription for realizing a group, we have:

- (i) objects: three balls;
- (ii) characteristic: color (red, blue, and green);
- (iii) operations: permutations of the balls.

Using the permutations defined in (2.1), with 1, 2, and 3 replaced by red, blue, and green, we can construct the realization given in Figure 3.1. Figure 3.1 is simply a pictorial way of describing the permutations of the colored balls; it can be transformed into a matrix format as shown in Figure 3.2, which is a kind of half-way house between the description provided by (2.1) and the matrix realization that results from replacing all dots by ones and placing zeroes elsewhere.

Now suppose the balls were all the same color. There would be no distinguishable configurations, thus all permutations could be realized by the identity matrix or by just the number 1. We will see, in following chapters, that this is an important representation of the group even though it is trivial here.

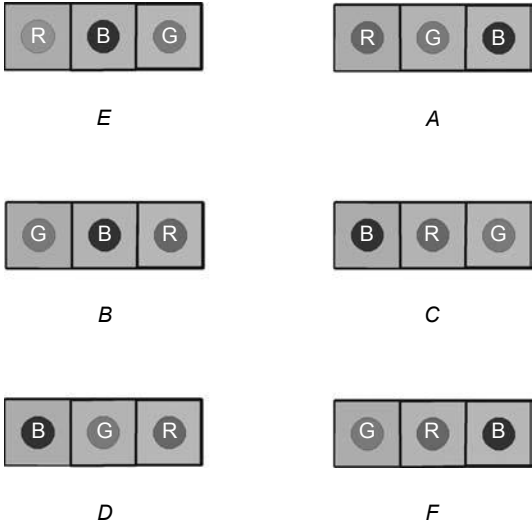


Fig. 3.1. A colorful representation of the permutations of (2.1).

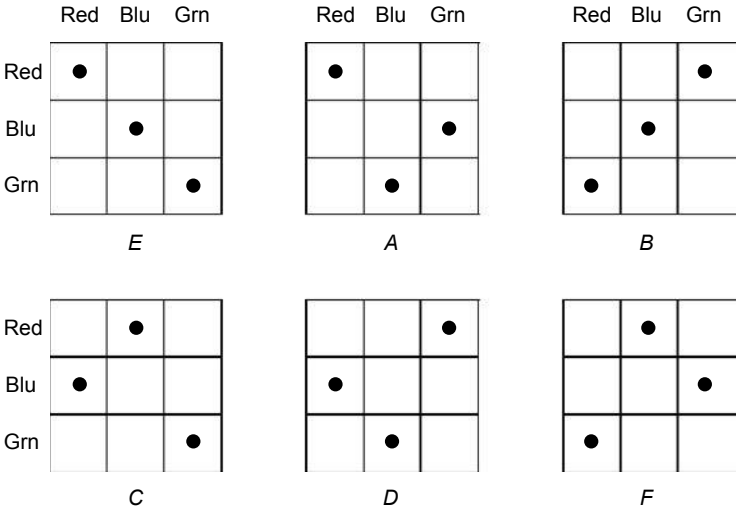


Fig. 3.2. A permutation-matrix representation of G_6 .

The representation for the permutations of colored balls displayed in Figure 3.1 could also serve as a realization for the set of operations that leave an equilateral triangle unchanged. This could be done simply by letting the colors of the balls represent the vertices of the triangle. On the other hand, if the object were a sphere and the operations

were those that leave the sphere unchanged, the result would be the same as for the case with all balls the same color.

3.1.1 Transformation of coordinates

We have seen that the symmetry operations of the equilateral triangle obey the group multiplication rules of Table 2.2. It is physically easy to perform these operations with a cardboard cutout of an equilateral triangle or even simply to imagine them. Rotating or inverting the triangle is quite natural. One *knows* that it can be done. The question is, “How does one *describe* these operations mathematically?”

To start with, we need a reference frame. For permutation groups, the frame of reference is the *boxes* among which we permute objects. For rotation groups it is a set of *coordinate axes*.

Suppose we consider the clockwise rotation of the equilateral triangle as depicted in Figure 2.3. We use a right-handed coordinate system with fixed axes (x, y, z) . The z -axis points out from the plane of the triangle. The element C_3 rotates the triangle clockwise by 120° as viewed from above the plane of the triangle. Vertex 1, which originally lay on the positive y -axis, now lies below the x -axis.

To describe this rotation of the triangle mathematically, we do just as we did in Chapter 1 for a traveling wave: we refer to the inverse problem. We recognize that rotating the triangle clockwise in a fixed coordinate system is *mathematically* equivalent to keeping the triangle fixed in space and rotating the coordinate system counterclockwise, as illustrated in Figure 3.3. Then, under the *passive* operation C_3 , denoted by $C_3(p)$ in Figure 3.3, the new coordinates (x', y') in the new (x', y') coordinate axes are given in terms of the original coordinates (x, y) by

$$\begin{bmatrix} x' \\ y' \end{bmatrix} = \begin{bmatrix} \cos\left(\frac{2\pi}{3}\right) & \sin\left(\frac{2\pi}{3}\right) \\ -\sin\left(\frac{2\pi}{3}\right) & \cos\left(\frac{2\pi}{3}\right) \end{bmatrix} = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix}. \quad (3.2)$$

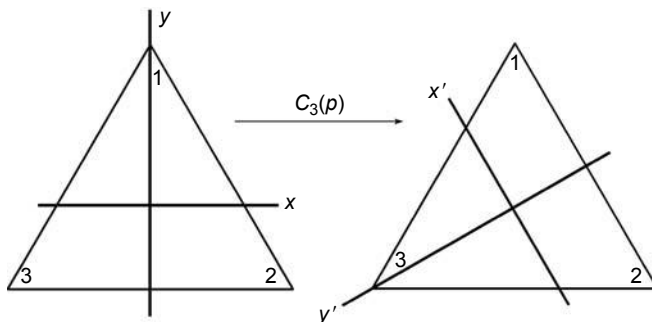


Fig. 3.3. A 120° counterclockwise rotation of the coordinate system by the passive operator $C_3(p)$ to a new (x', y', z') coordinate system.

Thus the operation C_3 can be described *mathematically* by the matrix

$$C_3 = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}, \quad (3.3)$$

but in the *active view* we *interpret* C_3 to describe the clockwise rotation of the triangle by 120° about the origin of a *fixed* coordinate system, as was done in Chapter 2, Figure 2.3.

Examining all operations of the group C_{3v} in this manner, we find the following set of matrices to describe the operations.

$$\begin{aligned} E &= \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} & \sigma_1 &= \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} & \sigma_2 &= \begin{bmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \\ \sigma_3 &= \begin{bmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} & C_3 &= \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} & C_3^2 &= \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \end{aligned} \quad (3.4)$$

We enclose the matrices in brackets $[\dots]$ to indicate that they correspond to transformations of coordinates in the physical space in which symmetry operations on the real objects take place. These sets of matrices are mathematical realizations of the group. We refer to the transformations as taking place in *configuration space*.

We reserve brackets $(\dots)$ to enclose matrices that *represent* operations in *function-space*.

Equations (3.4) provide a matrix *realization* of the group G_6 . They are often called a matrix *representation* of C_{3v} , but they are not *the* representation, nor are they a representation in the sense of representing operations on functions. We generally reserve the term *representation* for those sets of matrices that represent groups of *function* operators, a subtlety we will deal with in more detail.

The group of physical symmetry operations that transform an object into an equivalent position, in a fixed coordinate system, is useful for generating a group multiplication table. That is how we generated Table 2.2, which represents a physical realization of the group. These symmetry transformations are directly related to the physical symmetry of the system; but they may not include *all* the symmetry transformations of its Hamiltonian, exchange of electrons being an example of a symmetry not included.

3.1.2 Transformation of functions

Our primary interest is the group of symmetry transformations of the Hamiltonian and operations on functions that are eigenfunctions of the Hamiltonian. For these purposes, we treat the mathematical description of coordinate transformations (configuration-space operators) as a means of generating representations. Matrix realizations such as (3.4) are also a representation in some sense but not in the sense of representing operations on functions. The distinction between realizations and representations is important if one is not to miss the whole point of generating representations. Our goal is to make this clear and thus avoid a common misperception.

Both group operators in configuration space and group operators in function-space obey the group multiplication table. The two groups are isomorphic, subject to a degree of subtlety to be described further on in this section; but the group of function operators

is closer to our real interests, which, for example, may be eigenvalues and eigenfunctions. Transformations in configuration space provide a means for *inducing* transformations in function-space, as we illustrate in this section.

Function operators, or **F-operators**, are represented by the symbol $\hat{R}$, in contrast to their configuration counterparts, which are given simply the symbol R . The relationship between the two sets of group operators is formally defined by the equation

$$\hat{R}f(R\mathbf{r}) = f(\mathbf{r}) \quad (3.5)$$

or its equivalent, but generally more useful, form

$$\hat{R}f(\mathbf{r}) = f(R^{-1}\mathbf{r}), \quad (3.6)$$

which shows that $\hat{R}f$ is itself a function. Thus the value of the function f at the point $\mathbf{r}$ equals the value of the new (transformed) function $\hat{R}f$ at the transformed point $\mathbf{r}' = R\mathbf{r}$.

We interpret $\hat{R}f(\mathbf{r})$ as a new function, $f'(\mathbf{r})$, defined in the same coordinate system as $f(\mathbf{r})$, and obtained by operating on $f(\mathbf{r})$ with an F -operator $\hat{R}$. That is,

$$f'(\mathbf{r}) = \hat{R}f(\mathbf{r}) = f(R^{-1}\mathbf{r}). \quad (3.7)$$

Equation (3.7) provides a simple but complete prescription for determining the new function $\hat{R}f(\mathbf{r})$, given $f(\mathbf{r})$.

A prescription To generate a new function from a given function $f(\mathbf{r})$, replace the *components* of $\mathbf{r}$ in $f(\mathbf{r})$ by the corresponding *components* of $R^{-1}\mathbf{r}$.

It is through this prescription we will find matrix representations of function operators that satisfy the group multiplication table.

We denote operations in configuration space as before, with symbols that indicate the kind of symmetry operation, such as C_3 for a clockwise rotation by $2\pi/3$ about a three-fold symmetry axis; but, for the corresponding operations in function-space we include a caret over the operator to indicate that it operates on functions, in conformity with (3.6). For example, we use $\hat{C}_3$ to denote a function operator corresponding to the configuration-space operator C_3 .

The relationship between operators C_3 and $\hat{C}_3$, corresponding to (3.6) is

$$\hat{C}_3 f(\mathbf{r}) = f((C_3)^{-1}\mathbf{r}) = f(\tilde{C}_3\mathbf{r}), \quad (3.8)$$

where the second equality holds because $(C_3)^{-1}$ is a real orthogonal matrix and thus equals the *transpose* matrix $\tilde{C}_3$. Generally, we deal only with real orthogonal matrices, these being the kind of matrices that describe the transformations between orthogonal coordinate systems, or with unitary matrices.

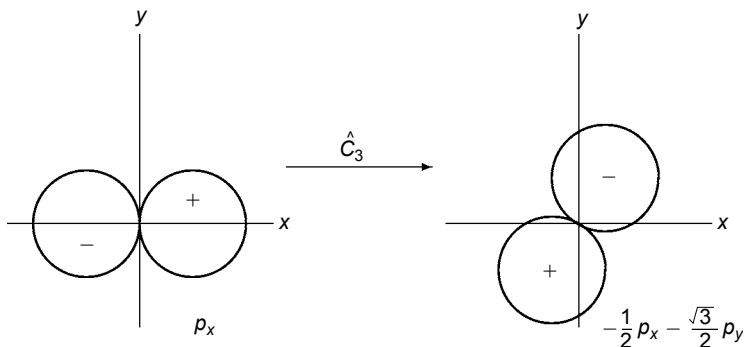


Fig. 3.4. $\hat{C}_3$ acting on p_x produces $-\frac{1}{2}p_x - \frac{\sqrt{3}}{2}p_y$.

In the active picture, which we have chosen, C_3 is a configuration-space operator that carries a point clockwise by 120° (Figure 2.3) and induces the function operator $\hat{C}_3$, which “carries” a function clockwise by 120° , as illustrated in Figure 3.4. The action of $\hat{C}_3$ on the function is determined by (3.8) and it is *represented* by the matrix for C_3 , as we will soon see.

Now, for a simple but important illustration, let the functions of interest be atomic p-states

$$p_x = xe^{-r}, \quad p_y = ye^{-r}, \quad p_z = ze^{-r}. \quad (3.9)$$

We can ignore the exponential factor, when convenient to do so, since all the directional dependence in these functions is contained in the prefactor. Considering p_z , it is clear that none of the operations in the group C_{3v} change the z -dependence. Thus we must have, for example,

$$\hat{C}_3 p_z = ze^{-r} = 1 \times p_z. \quad (3.10)$$

Since all operators of the group C_{3v} leave p_z unchanged, we have generated a *representation* of the group in which *all the elements are mapped onto unity*. This is a *homomorphic* mapping, that is, a many-to-one mapping which satisfies the group criteria as well as the multiplication table for C_{3v} . It is a representation because it describes the effect of group operators on *functions*, the p-orbitals. We could do the same thing with a vector or a dipole along the z -axis and obtain the same result. In general, whether we are dealing with a vector, a dipole or a p-orbital, the representation will be the same. The representation transcends the physical system and is characteristic only of the symmetry properties.

We have just encountered an important difference between realizations and representations. The set of configuration operators constitute a realization of a group. In this case the operators $\{E, C_3, \dots\}$ are a realization of the group C_{3v} , and they satisfy the multiplication table for the group. The set of F-operators $\{\hat{E}, \hat{C}_3, \dots\}$ also satisfy the multiplication table for the group C_{3v} , and this set of operators is isomorphic to the configuration-space operators, as we proved in Section 1.3. However, and this is the important difference, the

set of matrices that describe operations in configuration space are all distinct. There is a unique matrix for each configuration operator and, in some sense, one could say the matrices *are* the operators; but there is no such restriction for the matrices that represent function-space operators. We have just encountered a case in which the entire set of function-space operators are “represented” by 1×1 matrices, all of which are equal to unity.

Now let us consider the effect of group operations on p_x and p_y . From (3.8), substituting p_x for f , we have

$$\hat{C}_3 p_x(\mathbf{r}) = p_x(C_3^{-1} \mathbf{r}), \quad (3.11)$$

and, similarly,

$$\hat{C}_3 p_y(\mathbf{r}) = p_y(C_3^{-1} \mathbf{r}). \quad (3.12)$$

Using the inverse of C_3 , which is the transpose of C_3 , we find

$$C_3^{-1} \mathbf{r} = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix} = \begin{bmatrix} -\frac{1}{2}x & -\frac{\sqrt{3}}{2}y \\ \frac{\sqrt{3}}{2}x & -\frac{1}{2}y \end{bmatrix}. \quad (3.13)$$

Note that in (3.13) we have used brackets $[\dots]$, because these are operations in configuration space.

Since in (3.11) and (3.12) the operator $\hat{C}_3$ operating on a p-orbital just replaces $\mathbf{r}$ by $C_3^{-1} \mathbf{r}$, we see from (3.13) that x is replaced by

$$-\frac{1}{2}x - \frac{\sqrt{3}}{2}y$$

and y is replaced by

$$\frac{\sqrt{3}}{2}x - \frac{1}{2}y.$$

Thus,

$$\hat{C}_3 p_x = -\frac{1}{2}p_x - \frac{\sqrt{3}}{2}p_y, \quad (3.14)$$

$$\hat{C}_3 p_y = \frac{\sqrt{3}}{2}p_x - \frac{1}{2}p_y. \quad (3.15)$$

Since in both cases we obtain linear combinations of p_x and p_y , we can treat these two functions as partners under the transformation $\hat{C}_3$ and describe the operation of $\hat{C}_3$ on these functions by the equation

$$\hat{C}_3 \begin{bmatrix} p_x \\ p_y \end{bmatrix} = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \begin{bmatrix} p_x \\ p_y \end{bmatrix}. \quad (3.16)$$

Now (3.16) is mathematically correct, and it is possible to write similar equations for the remaining function operators of the group, but they are *not* a good choice. The problem

with this choice of matrices is that they do *not* satisfy the group multiplication table. (See Exercise 3.3) That is why we have used brackets $[\dots]$. The set of 2×2 matrices determined as was done for (3.16) is not a *representation* of the group. The proper way to express the relationship of (3.16) is

$$\hat{C}_3 \begin{pmatrix} p_x & p_y \end{pmatrix} = \begin{pmatrix} p_x & p_y \end{pmatrix} \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}, \quad (3.17)$$

where the 2×2 matrix *represents* the action of the function operator $\hat{C}_3$. That is, in order to use the coordinate transformation matrix as a representation, we must treat p_x and p_y as components of a row matrix and operate, from the left, on the *transpose* of the 2×2 matrix of (3.16). With this choice we obtain (3.17). We also have consistency, since then the matrices used for realizations conform with those for representations.

We can write (3.17) in more general form as

$$\hat{R} \Psi_i = \sum_j \Psi_j \Gamma_{ji}(\hat{R}), \quad (3.18)$$

where Γ_{ji} are the elements of a matrix representation. We will *prove* the correctness of this more general form in Chapter 4.

Comparison of C_3 and $\hat{C}_3$ The operator C_3 rotates the object clockwise. $\hat{C}_3$ creates a new function that “looks” like the original function but has a different functional form. Put differently, C_3 rotates the triangle, or NH_3 molecule, carrying with it the original numerical value of p_x but expressed after rotation in a new functional form as given by $\hat{C}_3 p_x$. See Figures 2.3 and 3.3 for comparison.

We could continue in this fashion for all the function-space operators for the group C_{3v} and determine the set of matrices that constitute a matrix representation for C_{3v} . The result is another representation as given by (3.19).

$$\begin{aligned} E &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} & \sigma_1 &= \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \\ \sigma_2 &= \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} & \sigma_3 &= \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \\ C_3 &= \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} & C_3^2 &= \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \end{aligned} \quad (3.19)$$

We notice, perhaps not surprisingly, that the representation is just the set of matrices describing the rotation of a vector in two dimensions by the group C_{3v} , and that the set of matrices given by (3.19) satisfies a group multiplication table for the group C_{3v} that is isomorphic to Table 2.2. This is, as stated, perhaps not surprising, but it can also be the source of confusion. One source of confusion is the common practice of illustrating function operators by using p-orbitals for the functions, just as we have done. The potential source of confusion is the vector nature of p-orbitals. How does one distinguish a vector from a function? It appears as if we have gained nothing. We have, however, learned that representations need not be a set of unique matrices; later we will

deal with functions of higher order, which should clarify further the nature of function operators.

For now, we have found two representations for C_{3v} based on operators in function-space. One of these is a set of operators all of which are equal to unity. The other is the set of 2×2 matrices given by (3.19). We can incorporate both of these representations into a single 3×3 matrix representation for which all the matrices are of block-diagonal form, as given in (3.20).

$$\begin{aligned}
 E &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & \sigma_1 &= \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \\
 \sigma_2 &= \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} & \sigma_3 &= \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \\
 C_3 &= \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} & C_3^2 &= \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}.
 \end{aligned} \tag{3.20}$$

This is a *reducible* representation, an important topic to which we will soon return.

We have thus far found two irreducible representations for the group C_{3v} . There is a third! We will later prove that there are only three irreducible representations for C_{3v} .

The third representation can be determined by considering Figure 3.5. The directed circles located at each corner of the triangle denote a current flow that produces a magnetic dipole. There is a function that describes a magnetic dipole, but here we examine it pictorially. We ask, “What is the effect of acting on the magnetic dipole with the function operators of C_{3v} ?”

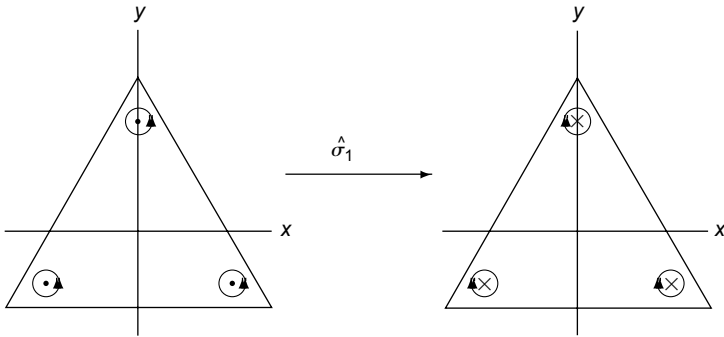


Fig. 3.5. The operator $\hat{\sigma}_1$ reverses the direction of the magnetic dipole vector. The directed circles indicate current loops associated with the magnetic dipoles. The reversal of the current direction leads to reversing the dipole direction.

The magnetic dipole is a vector quantity, usually represented by an arrow, but the vector is an *axial* vector (properly named an *antisymmetric tensor of rank 2*), not a *polar* vector. Typically in this case, each axial vector denoting a magnetic dipole would be pictured by an arrow (an *icon*) normal to the plane of the triangle and pointing out of the page for the left-hand side of Figure 3.5. Here, each outward axial vector on the left-hand side is denoted by a dot in the center of each directed circle. The arrows are aimed toward the reader!

Now, if each magnetic dipole were *truly* represented by the icon of an arrow, the mirror reflection operation σ_1 would leave the arrows unchanged, and the matrix representation for the mirror reflections would simply be the one-dimensional matrices $[1]$. This is the danger in putting all one's faith in the use of icons to represent the actual physics. If one looks at the current flow, it is clear that the mirror reflections reverse the current flow. Thus the arrow (the icon) now points into the page and is denoted by a cross in the center of each directed circle on the right-hand side of Figure 3.5. The arrow is aimed away from the reader.

Mathematically, the same result would have been obtained by considering the angular momentum operator $m\mathbf{r} \times d\mathbf{r}/dt$.

We now have a third irreducible representation generated by function operators in which the group operations are represented by the one-dimensional matrices $[1]$ for the identity $\hat{E}$ and the two three-fold function rotation operators $\hat{C}_3$, $\hat{C}_3^2$, and by the one-dimensional matrices $[-1]$ for the function reflection operators $\hat{\sigma}_1$, $\hat{\sigma}_2$, $\hat{\sigma}_3$.

A discussion of realization versus representations The difference between operations in *configuration space* and *function-space* is of such importance that it is timely to discuss once more the idea of these operations. We use the equilateral triangle and the permutation of three objects, from Chapter 2, as examples.

We may consider the triangle as a “function” and thus the symmetry operators are then function operators. However, (3.7) allows us to execute the symmetry operations in configuration space, and thus define the corresponding realization of the group operators as in (3.20).

In a similar manner, we may consider the three objects to be in function-space, while the boxes among which the objects are permuted are thought of as being in configuration space. In this case, we can think of operations in configuration space as permuting the boxes instead of the objects. We refer to the group of configuration-space operators as a *realization* of an abstract group. It is a realization in the sense that it is *always* an isomorphism of the original group.

In contrast, we use the term *representation* in the conventional sense, namely, to describe realizations of group operators in function-space. These representations are *homomorphic* realizations. We have seen this difference in (3.10) for the operation of $\hat{C}_3$ on p_z orbitals.

Now let us consider the effect of the 3×3 matrix representation for the group $\mathcal{D}_3$ based on function operators. With the group $\mathcal{D}_3$, the triangle is allowed to rotate about the axes denoted by A , B , C in Figure 2.1. The group elements E , C_3 , and C_3^2 remain the same, but the reflection elements σ_1 , σ_2 , and σ_3 from $\mathcal{C}_{3v}$ are replaced by two-fold rotation axes perpendicular to the main three-fold axis (henceforth we denote such axes by the

symbol U) U_1 , U_2 , and U_3 for the group $\mathcal{D}_3$. Each of the three 2-fold rotations transform z into $-z$. Thus, the 3×3 function-space matrix representation for $\mathcal{D}_3$ is

$$\begin{aligned} E &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & U_1 &= \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \\ U_2 &= \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & -1 \end{pmatrix} & U_3 &= \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & -1 \end{pmatrix} \\ C_3 &= \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} & C_3^2 &= \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \end{aligned} \quad (3.21)$$

which is a reducible representation consisting of one irreducible representation identical to that of (3.19) and a second representation that consists of $+1$ for each of the function operators $\hat{E}$, $\hat{C}_3$, and $\hat{C}_3^2$ and -1 for each of the three 2-fold function-rotation operators. Of course, $\mathcal{D}_3$ also has the one-dimensional identity representation consisting of all ones. Thus the point-groups $\mathcal{C}_{3v}$ and $\mathcal{D}_3$ are each represented by the same three irreducible representations, but with some slight differences in terms of basis functions for the one-dimensional representation consisting of three positive unit matrices and three negative unit matrices.

An important invariant of a matrix representation of a group is the *character* of the group elements. The character of a matrix is its trace, that is, the sum of the diagonal elements of the matrix. It is invariant under any similarity transformation. Many applications of group theory in quantum mechanical problems, such as selection rules for electronic and vibrational transitions, can be determined from the use of characters alone. Two representations related by a similarity transformation are called *equivalent representations* of a group $\mathcal{G}$, namely,

$$\Gamma(\hat{R}) \sim \Gamma'(\hat{R}), \quad (3.22)$$

if,

$$\Gamma(\hat{R}) = \mathbf{S} \Gamma'(\hat{R}) \mathbf{S}^{-1}, \quad \forall R \in \mathcal{G}. \quad (3.23)$$

Equivalent representations have the same set of characters, since the trace of a matrix is invariant under a similarity transformation.

3.2 Generation of representations on a set of basis functions

Thus far, we have considered in detail only functions that describe atomic p-orbitals. Since the radial parts of these functions are spherically symmetric, only the x , y , or z components are important. This can lead to some confusion between the effects of symmetry operations on coordinates $\{x, y, z\}$ and operations on functions $\{x, y, z\}$ that are of the same form as the coordinates.

We now examine operations on higher-order functions to reveal more generally the process of determining the action of a function operator on a function. Before doing so, we first recapitulate what we now know about operations in function-space and their representations.

A recapitulation We denote a general function-space operator by $\hat{R}$, but we represent it with respect to a set of basis vectors by a matrix $\Gamma(\hat{R})$. There are generally at least two or three nonequivalent irreducible representations (Irreps). Thus here we introduce an index μ to label the different Irreps.

Each set of matrices ${}^{(\mu)}\Gamma(\hat{R})$, $\hat{R} \in \mathcal{G}$, for each representation, satisfies the group multiplication table.

To determine the effect of $\hat{R}$ operating on a function, we must use (3.6):

$$\hat{R}f(\mathbf{r}) = f(R^{-1}\mathbf{r}).$$

Once a matrix representation is known, the effect of $\hat{R}$ operating on a basis function can be expressed as

$$\hat{R}f_i = \sum_j f_j {}^{(\mu)}\Gamma_{ji}(\hat{R}).$$

Now consider the pair of functions $\{x^2, y^2\}$ and ask, “What happens when we operate on these functions with the function operators of $\mathcal{C}_{3v}$?”

Suppose we wish to find $\hat{C}_3$. Rewriting (3.8), we have for this case

$$\hat{C}_3 F(\mathbf{r}) = F(C_3^{-1}\mathbf{r}), \quad (3.24)$$

where

$$F(\mathbf{r}) = \begin{pmatrix} f_1(\mathbf{r}) = x^2 \\ f_2(\mathbf{r}) = y^2 \end{pmatrix} \quad (3.25)$$

and $\hat{C}_3 F(\mathbf{r})$ is the new function we wish to determine.

The prescription To generate $\hat{C}_3 F(\mathbf{r})$ from $F(\mathbf{r})$, replace the *components* of $\mathbf{r}$ in $F(\mathbf{r})$ by the corresponding *components* of $C_3^{-1}\mathbf{r}$.

We have to generalize our notion of components a bit, as we will see, but for the moment let us proceed as before, finding the coordinates

$$\mathbf{r}' = \begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = C_3^{-1}\mathbf{r} = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}, \quad (3.26)$$

and, this time, the squares of the coordinates

$$\begin{aligned} x'^2 &= \frac{1}{4}x^2 + \frac{3}{4}y^2 + \frac{\sqrt{3}}{2}xy, \\ y'^2 &= \frac{3}{4}x^2 + \frac{1}{4}y^2 - \frac{\sqrt{3}}{2}xy. \end{aligned} \quad (3.27)$$

It is clear that the two functions $\{x^2, y^2\}$ do not span the entire linear function-space of the C_{3v} operators. That is, the new functions generally cannot be expressed just as linear combinations of the original functions x^2 and y^2 . The appearance of a term in xy in the equations for x'^2 and y'^2 makes it clear that in order to span the entire space *it is necessary to include xy as a partner basis function*. Thus the complete set of basis functions is $\{x^2, y^2, xy\}$.

We can incorporate this set of basis functions into a function $\mathcal{F}(\mathbf{r})$ defined as

$$\mathcal{F}(\mathbf{r}) = \begin{pmatrix} f_1(\mathbf{r}) = x^2 \\ f_2(\mathbf{r}) = y^2 \\ f_3(\mathbf{r}) = xy \end{pmatrix} = \begin{bmatrix} x^2 \\ y^2 \\ xy \end{bmatrix}. \quad (3.28)$$

The operation of $\hat{C}_3$ on $\mathcal{F}(\mathbf{r})$ will produce a new function. From (3.27) we know the relationship between $\{x'^2, y'^2\}$ and $\{x^2, y^2\}$. The other relationship we need is obtained from (3.26):

$$\begin{aligned} x'y' &= \left(-\frac{1}{2}x - \frac{\sqrt{3}}{2}y\right)\left(\frac{\sqrt{3}}{2}x - \frac{1}{2}y\right) \\ &= -\frac{\sqrt{3}}{4}x^2 + \frac{\sqrt{3}}{4}y^2 - \frac{1}{2}xy. \end{aligned} \quad (3.29)$$

We now generalize our understanding of “The prescription” to interpret the components of $\mathbf{r}$ to include the *basis functions* of $\mathcal{F}(\mathbf{r})$.

A generalized prescription To use the operator $\hat{R}$ to generate a new set of basis functions from an old set of basis functions, replace the variables $\{x, y, z\}$ in the old set of basis functions by the corresponding new variables as given by the components of $R^{-1}\mathbf{r}$.

Thus the basis functions of $\mathcal{F}(\mathbf{r})$ are replaced by the basis functions of (3.27) and (3.29), and the new basis functions expressed in terms of the old are given by

$$\begin{aligned} \hat{C}_3 \mathcal{F}(\mathbf{r}) &= \begin{bmatrix} x'^2 \\ y'^2 \\ x'y' \end{bmatrix} \\ &= \begin{bmatrix} \frac{1}{4} & \frac{3}{4} & \frac{\sqrt{3}}{2} \\ \frac{3}{4} & \frac{1}{4} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{4} & \frac{\sqrt{3}}{4} & -\frac{1}{2} \end{bmatrix} \begin{bmatrix} x^2 \\ y^2 \\ xy \end{bmatrix}. \end{aligned} \quad (3.30)$$

This determines the effect of the operation of $\hat{C}_3$ on the basis set $\{x^2, y^2, xy\}$. However, the *representative* of the function operator $\hat{C}_3$ is the *inverse* of the 3×3 matrix of (3.30). We must use the inverse matrix, not the transpose, because the matrices here are not unitary matrices.

Repeating this procedure with the remaining elements of the group we obtain the set of three-dimensional matrices of C_{3v} that represent the function operators relative to the basis set $\{x^2, y^2, xy\}$. In carrying through this procedure we note that reflection operator

representatives are their own inverses and that $\widehat{C}_3$ is the *inverse* of $\widehat{C}_3^2$. Thus,

$$\begin{aligned}
 {}^{(\text{red})}\Gamma(\widehat{E}) &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & {}^{(\text{red})}\Gamma(\widehat{C}_3^2) &= \begin{pmatrix} 1/4 & 3/4 & \sqrt{3}/2 \\ 3/4 & 1/4 & -\sqrt{3}/2 \\ -\sqrt{3}/4 & \sqrt{3}/4 & -1/2 \end{pmatrix} \\
 {}^{(\text{red})}\Gamma(\widehat{C}_3) &= \begin{pmatrix} 1/4 & 3/4 & -\sqrt{3}/2 \\ 3/4 & 1/4 & \sqrt{3}/2 \\ \sqrt{3}/4 & -\sqrt{3}/4 & -1/2 \end{pmatrix} & {}^{(\text{red})}\Gamma(\widehat{\sigma}_1) &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \\
 {}^{(\text{red})}\Gamma(\widehat{\sigma}_2) &= \begin{pmatrix} 1/4 & 3/4 & -\sqrt{3}/2 \\ 3/4 & 1/4 & \sqrt{3}/2 \\ -\sqrt{3}/4 & \sqrt{3}/4 & 1/2 \end{pmatrix} \\
 {}^{(\text{red})}\Gamma(\widehat{\sigma}_3) &= \begin{pmatrix} 1/4 & 3/4 & \sqrt{3}/2 \\ 3/4 & 1/4 & -\sqrt{3}/2 \\ \sqrt{3}/4 & -\sqrt{3}/4 & 1/2 \end{pmatrix}
 \end{aligned} \tag{3.31}$$

This set of matrices deals with the problem of properly representing the group, as discussed previously with regard to (3.16)–(3.18). However, it is not a group of unitary matrices, i.e. a *unitary representation*.

Let us ask if it is possible to find a unitary representation. This question is raised by the thought that a different set of basis functions might lead to a unitary matrix representation. The answer is, yes, we can choose linear combinations $\{x^2 + y^2, x^2 - y^2, 2xy\}$ as basis functions, leading to the function

$$\mathbf{F}(\mathbf{r}) = \begin{pmatrix} f_1(\mathbf{r}) = x^2 + y^2 \\ f_2(\mathbf{r}) = x^2 - y^2 \\ f_3(\mathbf{r}) = 2xy \end{pmatrix} = \begin{bmatrix} x^2 + y^2 \\ x^2 - y^2 \\ 2xy \end{bmatrix}. \tag{3.32}$$

It is necessary to choose $2xy$ as a basis function, rather than xy , to obtain a unitary representation. (See Exercise 3.5.)

Now we know from (3.27) and (3.29) that

$$\begin{aligned}
 x'^2 + y'^2 &= x^2 + y^2, \\
 x'^2 - y'^2 &= -\frac{1}{2}(x^2 - y^2) + \frac{\sqrt{3}}{2}(2xy), \\
 2x'y' &= -\frac{\sqrt{3}}{2}(x^2 - y^2) - \frac{1}{2}(2xy).
 \end{aligned} \tag{3.33}$$

Thus,

$$\begin{bmatrix} x'^2 + y'^2 \\ x'^2 - y'^2 \\ 2x'y' \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1/2 & \sqrt{3}/2 \\ 0 & -\sqrt{3}/2 & -1/2 \end{bmatrix} \begin{bmatrix} x^2 + y^2 \\ x^2 - y^2 \\ 2xy \end{bmatrix}. \tag{3.34}$$

and the matrix representative of $\widehat{C}_3$ relative to the basis functions $\{x^2 + y^2, x^2 - y^2, 2xy\}$ is the *transpose* of the 3×3 matrix of (3.32), when written to conform with (3.18).

Note that the matrix representative is now in block-diagonal form. Indeed, this new set of basis functions leads to *all* the matrix representatives of C_{3v} being of the same block-diagonal form. Thus, a set of matrices that satisfies the group multiplication table for C_{3v} , as given in Table 2.3, constitutes a matrix representation of this group *relative to the basis set* $\{x^2 + y^2, x^2 - y^2, 2xy\}$, a set of d-orbital functions, given by:

$$\begin{aligned}
 {}^{(\text{red})}\Gamma(\hat{E}) &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & {}^{(\text{red})}\Gamma(\hat{\sigma}_1) &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \\
 {}^{(\text{red})}\Gamma(\hat{\sigma}_2) &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1/2 & -\sqrt{3}/2 \\ 0 & -\sqrt{3}/2 & 1/2 \end{pmatrix} & {}^{(\text{red})}\Gamma(\hat{\sigma}_3) &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1/2 & \sqrt{3}/2 \\ 0 & \sqrt{3}/2 & 1/2 \end{pmatrix} \\
 {}^{(\text{red})}\Gamma(\hat{C}_3) &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1/2 & -\sqrt{3}/2 \\ 0 & \sqrt{3}/2 & -1/2 \end{pmatrix} & {}^{(\text{red})}\Gamma(\hat{C}_3^2) &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1/2 & \sqrt{3}/2 \\ 0 & -\sqrt{3}/2 & -1/2 \end{pmatrix}.
 \end{aligned} \tag{3.35}$$

where we used the notation ${}^{(\text{red})}\Gamma$ to describe a reducible representation, as will be discussed below.

We notice some similarity between (3.35) and (3.20), but why are they different at all? It is simply a result of the order in which we chose the set of basis functions. If we had chosen them in reverse order, i.e. if we had chosen $\{2xy, x^2 - y^2, x^2 + y^2\}$ we would have obtained (3.20) rather than (3.33).

Just as in (3.17), we represent the action of $\hat{C}_3$ on a set of basis functions by a row vector operating on the representative matrix. For example,

$$\begin{aligned}
 &\hat{C}_3 \begin{pmatrix} x^2 + y^2, & x^2 - y^2, & 2xy \end{pmatrix} \\
 &= (x^2 + y^2, x^2 - y^2, 2xy) \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1/2 & -\frac{\sqrt{3}}{2} \\ 0 & \frac{\sqrt{3}}{2} & -1/2 \end{pmatrix}.
 \end{aligned} \tag{3.36}$$

Such matrices can all be decomposed into two smaller matrices, or, conversely, the 3×3 matrix can be considered as the augmentation into block-diagonal form of the two smaller matrices. For example, the matrix representing $\hat{C}_3$ is decomposed into

$$(1) \quad \text{and} \quad \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix}.$$

We write such a relation as

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1/2 & -\sqrt{3}/2 \\ 0 & \sqrt{3}/2 & -1/2 \end{pmatrix} = (1) \oplus \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix}, \tag{3.37}$$

which reads that the l.h.s. matrix is the *direct sum* of the two r.h.s. matrices, namely a 1×1 and a 2×2 matrix. This process, denoted by the encircled plus sign, shows that a matrix representation (Rep) of the group function operator $\hat{C}_3$ can be constructed from

two smaller matrix Reps. We say the l.h.s. matrix Rep is *induced* from the two r.h.s matrix Reps.

Several questions can be raised at this point:

- When will the process of decomposition or reduction cease to be possible? In other words, when do the matrix Reps obtained become irreducible?
- How do we systematically find *irreducible representations* (Irreps)?
- Is there a finite number of these Irreps?

In the present example we were able to reduce the three-dimensional Rep into one 1D and one 2D Reps. Attempts to reduce the two-dimensional Rep will fail. These two Reps, together with the one 1D Rep generated by D_3 on p_z are the three Irreps of C_{3v} and its isomorphs. There are no others!

A very remarkable result emerges from the above presentation; namely, that functions distinguishable under isotropic symmetry become indistinguishable when the symmetry is reduced to that of the triangle. We find that s -, p_z - and d_{z^2} -states have the same transformation properties. They transform according to the irreducible representation with all symmetry elements represented by unity! Furthermore, we find that the pairs $\{p_x, p_y\}$ and $\{d_{x^2-y^2}, d_{xy}\}$ transform like the vector

$$\begin{bmatrix} x & y \end{bmatrix}.$$

The functions are thus classified according to a set of well-defined categories of symmetries: the Irreps. Any general function can be decomposed into components that belong to well-defined symmetry classes.

In some of what we have done thus far in this chapter, we have used prior knowledge of the theory of representations. This was particularly true in the development leading up to (3.35), where we chose appropriate functions to illustrate some important points. Next, we need to further explore and clarify the fundamental principles and concepts of the theory of group representations, and outline the computational techniques that will simplify their construction. This will be done in the next chapter.

Exercises

- 3.1 Replace the dots in Figure 3.2 with ones, and fill the blank squares with zeroes; show that the resultant matrices satisfy the group multiplication rules of Table 2.1.
- 3.2 Consider an equilateral triangle with sides of unit length. The triangle is in the xy -plane with its center of gravity at the origin and the coordinates of its apices being

$$(0, \sqrt{3}/3), (1/2, -\sqrt{3}/6), (-1/2, -\sqrt{3}/6).$$

Show that the first apex is taken into the second apex by a clockwise rotation of 120° . Let C_3 be the operator that rotates the triangle clockwise by 120° . Show that the *transpose* of C_3 is the operator $\hat{C}_3$ that, operating on the *function* represented by the vector directed from the origin to the second apex, generates a new function represented by the vector from the origin to the first apex.

- 3.3 Show that the set of matrices analogous to the one in (3.16) do not satisfy the group multiplication table give in Table 2.3.
- 3.4 Show that the set of function-operator matrices as illustrated by (3.16) for $\widehat{C}_3$ do not satisfy the group multiplication table.
- 3.5 Consider $x^2 - y^2$ and xy as two possible basis functions for the group C_{3v} . Writing $x = r \cos \phi$, $y = r \sin \phi$, show that one must use $2xy$ rather than xy as a basis function in order that $x^2 - y^2$ and $2xy$ have the same normalization and thus lead to a unitary matrix representation of C_{3v} .
- 3.6 The ammonia molecule, NH_3 , belongs to the point-group C_{3v} . Consider three functions $\{f_A, f_B, f_C\}$ that describe the three valence bonds connecting the N atom with the three H atoms. The operation of $\widehat{C}_3$ on the valence bond functions can be described by

$$\widehat{C}_3(f_A \ f_B \ f_C) = (f_A \ f_B \ f_C) \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}.$$

Find the remaining matrices that provide a matrix representation based on the three valence bond functions. Check that the matrices actually obey the group multiplication table.

We assume the original basis set to be normalized as well as being orthogonal. Now consider three new (orthonormal) basis functions (vectors) that are linear combinations of the original set:

$$\begin{aligned} \phi_1 &= \frac{1}{\sqrt{3}}(f_A + f_B + f_C) \\ \phi_2 &= \frac{1}{\sqrt{6}}(f_A + f_B - 2f_C) \\ \phi_3 &= \frac{1}{\sqrt{2}}(f_A - f_B) \end{aligned}$$

Construct a matrix S whose columns (corresponding to $\{\phi_1, \phi_2, \phi_3\}$) are the coefficients of the original basis functions $\{f_A, f_B, f_C\}$. Perform the similarity transformation $S^{-1}\widehat{M}S$ for each matrix representative of C_{3v} based on the original basis set to find the new transformed representation relative to the transformed basis set. What can be said about the new-found representation?

4

Group representations: formalism and methodology

In Chapter 3, we presented the ideas of *partner basis functions*, on which the action of group elements engender a matrix representation. In this chapter we develop the machinery necessary for the *generation of a matrix representation given knowledge of the operation of a function operator on a basis function*.

We note that when we operate on a set of basis functions that spans the linear space of the symmetry operators, i.e. a complete set, we generate a matrix Rep of the symmetry group, which we now write as

$$\hat{R}\Psi_i = \sum_j \Psi_j \Gamma_{ji}(\hat{R}), \quad (4.1)$$

as given in (3.18). $\Gamma(\hat{R})$ is the matrix representative of the operator $\hat{R}$ with respect to the basis functions $\{\Psi_j\}$. This result is implied by the steps leading up to (3.17), where we saw the need to write the operation of a function operator acting on a set of basis functions as the product of a row matrix operating from the left on the matrix Rep of the operation. We now wish to prove that (3.18) and (4.1) are correct. Following that we will develop the theory of group Reps more fully.

4.1 Matrix representations

We associate a matrix $\Gamma(R)$ with each element R of a group, and the assigned matrices obey the group multiplication law. If each matrix is different, the Rep is said to be *true*, or *faithful*.

We identified the trivial but important nonfaithful case where all group elements are mapped onto unity as the identity or invariant Irrep.

Writing (4.1) as

$$\hat{S}\Psi_i = \sum_j \Psi_j \Gamma_{ji}(\hat{S}), \quad (4.2)$$

and operating on it with $\widehat{R}$, we get

$$\begin{aligned}\widehat{R} \widehat{S} \Psi_i &= \sum_j (\widehat{R} \Psi_j) \Gamma_{ji}(\widehat{S}) \\ &= \sum_{j,k} \Psi_k \Gamma_{kj}(\widehat{R}) \Gamma_{ji}(\widehat{S}) \\ &= \sum_k \Psi_k \Gamma_{ki}(\widehat{R} \widehat{S}).\end{aligned}\tag{4.3}$$

Then, using the completeness of the set $\{\Psi_i\}$ over the linear space spanned by the group elements, we can write

$$\Gamma_{ki}(\widehat{R} \widehat{S}) = \sum_j \Gamma_{kj}(\widehat{R}) \Gamma_{ji}(\widehat{S}),\tag{4.4}$$

thus simultaneously demonstrating,

- (i) that (4.3) (and hence (4.1)) is the proper way to describe the action of a function operator on a function and,
- (ii) that the matrix Reps generated obey the group multiplication table.

We now state several important properties of group representations.

- **Equivalent representations** Any Rep of a group can be transformed into an *equivalent representation* by a similarity transformation, as we demonstrated in Section 3.2:

$$\Gamma'(\widehat{R}) = U \Gamma(\widehat{R}) U^{-1}, \quad \forall \widehat{R} \in \mathcal{G},$$

where U is a unitary square matrix of the same dimension as $\text{Rep } \Gamma(\widehat{R})$. We can, therefore find an infinite number of Reps equivalent to a given Rep.

- **Unitary representations** We confine our attention to unitary Reps which are guaranteed by the following theorem:
- **Theorem** *Any Rep of a finite group is equivalent to a unitary Rep.*

These Reps, however, may be reducible, as we demonstrated in the examples of Chapter 3. A very important test of whether a Rep is reducible or not is provided by Schur's lemmas.

Schur's first lemma *Given two inequivalent Irreps μ and ν , the only matrix M that satisfies the relation*

$$^{(\mu)}\Gamma(\widehat{R}) M = M ^{(\nu)}\Gamma(\widehat{R})$$

is a null matrix.

Schur's second lemma *A matrix that commutes with every member of a set of matrices belonging to an Irrep must be a constant, that is, a number times the unit matrix.*

A simple way of demonstrating Schur's second lemma is through the following theorem:

Theorem *If an operator $\mathcal{O}$ commutes with all the elements of a group G , then the eigenspace of $\mathcal{O}$ is composed entirely of irreducible spaces of G .*

Proof Given

$$[\mathcal{O}, R] = 0, \quad \forall R \in G, \quad (4.5)$$

and

$$\mathcal{O} \Psi_\lambda = \lambda \Psi_\lambda, \quad (4.6)$$

where Ψ_λ is an eigenfunction of $\mathcal{O}$ with eigenvalue λ , the set $\{\Psi_\lambda\}$ forms a complete basis set of the eigenspace of $\mathcal{O}$. From (4.5) and (4.6) we obtain

$$\mathcal{O} R \Psi_\lambda = R \mathcal{O} \Psi_\lambda = \lambda R \Psi_\lambda, \quad (4.7)$$

and $R \Psi_\lambda$ is still an eigenvector of $\mathcal{O}$ with eigenvalue λ . Thus, for a degenerate, or an invariant, subspace $\{\Psi_{\lambda,i}\}$ of $\mathcal{O}$, we generate the Rep

$$\hat{R} \begin{bmatrix} \Psi_{\lambda,1} \\ \Psi_{\lambda,2} \\ \vdots \\ \Psi_{\lambda,d_\lambda} \end{bmatrix} = [\Psi_{\lambda,1} \quad \Psi_{\lambda,2} \quad \dots \quad \Psi_{\lambda,d_\lambda}]^{(\lambda)} \Gamma(\hat{R}), \quad (4.8)$$

where d_λ is the dimension of the invariant space, while

$$\mathcal{O} \begin{bmatrix} \Psi_1^{(\lambda)} \\ \Psi_2^{(\lambda)} \\ \vdots \\ \Psi_{d_\lambda}^{(\lambda)} \end{bmatrix} = \lambda \begin{bmatrix} \Psi_1^{(\lambda)} \\ \Psi_2^{(\lambda)} \\ \vdots \\ \Psi_{d_\lambda}^{(\lambda)} \end{bmatrix}, \quad (4.9)$$

which is true for every invariant eigen-subspace of $\mathcal{O}$. $\square$

Put differently, Schur's lemma states that, apart from a constant numerical factor, *only* the unit matrix commutes with *all* matrices of an Irrep. Although the statement of this lemma might seem to suggest that we determine an Irrep by the exhaustive demonstration of the noncommutativity of its matrices with the set of all matrices of the same dimension, its real significance lies in just the opposite.

A key point If we know that a particular operator or observable commutes with all the symmetry group operators, then its matrix representative must commute with any matrix Rep of the group operators, including the Irreps. Consequently, Schur's lemma then asserts that such quantities have to be represented by a scalar times a unit matrix!

To demonstrate the power of this approach let us explore further the properties of matrix Reps.

4.1.1 Diagonal matrix representatives

There is an infinite number of equivalent Reps of a finite group. Any matrix M can be transformed into an equivalent matrix M' by a similarity transformation

$$M' = U^{-1} M U.$$

The new set of matrices obtained by applying the same similarity transformation to each group element also obeys the group multiplication table.

A particularly interesting transformation is the one that diagonalizes one or more of a set of matrix representatives. It is always possible to diagonalize a real orthogonal matrix, the result generally being a unitary matrix.

Let us consider the matrix representative

$$\Gamma(C_3) = \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix}. \quad (4.10)$$

We can diagonalize the matrix as follows. First we must find the eigenvalues λ that satisfy the secular equation, which for a general 2×2 matrix can be written

$$\begin{vmatrix} M_{11} - \lambda & M_{12} \\ M_{21} & M_{22} - \lambda \end{vmatrix} = 0. \quad (4.11)$$

The value of the determinant of the secular equation can be expressed by the quadratic equation

$$\lambda^2 - (M_{11} + M_{22})\lambda + (M_{11}M_{22} - M_{12}M_{21}) = 0, \quad (4.12)$$

which has solutions

$$\lambda = \frac{(M_{11} + M_{22})}{2} \pm \sqrt{\frac{(M_{11} + M_{22})^2}{4} - (M_{11}M_{22} - M_{12}M_{21})}. \quad (4.13)$$

For the particular case of the group element C_3 the solutions are

$$\lambda = -\frac{1}{2} \pm i\frac{\sqrt{3}}{2} = e^{\pm i2\pi/3},$$

and the matrix representative is

$$\Gamma(\hat{C}_3) = \begin{pmatrix} -1/2 + i\sqrt{3}/2 & 0 \\ 0 & -1/2 - i\sqrt{3}/2 \end{pmatrix}. \quad (4.14)$$

The matrix elements in (4.14) are complex roots of unity. Indeed, *all* orthogonal-matrix Reps can be transformed to unitary diagonal matrices whose diagonal elements are complex roots of unity. In the computer method that we shall describe in Chapter 5, and which is based on Dixon's method, all the matrices *will* be diagonalized to yield diagonal elements that are complex *primitive* roots of unity, for the purpose of determining the *characters*. Thus the diagonal elements will be of the form $e^{\pm i(2\pi/n)}$. In the particular case of the group element C_3 , the matrix is then

$$\Gamma(\hat{C}_3) = \begin{pmatrix} e^{i(2\pi/3)} & 0 \\ 0 & e^{-i(2\pi/3)} \end{pmatrix}. \quad (4.15)$$

4.1.2 Reducible representations

Suppose we have a set of matrices $\Gamma(E), \Gamma(A), \dots, \Gamma(F)$ that satisfy the multiplication table for our example group G_6 as given by Table 2.1. That is,

$$\Gamma(A)\Gamma(B) = \Gamma(D), \quad \Rightarrow \quad AB = D.$$

Now transform each matrix in the Rep by a similarity transformation. Then, if $\Gamma'(A) = S^{-1}\Gamma(A)S$, we have

$$\begin{aligned}\Gamma'(A)\Gamma'(B) &= [S^{-1}\Gamma(A)S][S^{-1}\Gamma(B)S] \\ &= S^{-1}\Gamma(A)\Gamma(B)S \\ &= S^{-1}\Gamma(AB)S \\ &= \Gamma'(AB).\end{aligned}\tag{4.16}$$

Thus, the transformed matrices $\Gamma'(E), \Gamma'(A), \dots, \Gamma'(F)$ also form a Rep. This new Rep is *equivalent* to the original Rep given by the set of matrices $\Gamma(E), \Gamma(A), \dots, \Gamma(F)$. The two Reps differ only in that they are stated with respect to different sets of coordinate axes or different sets of basis functions.

Suppose it is possible to find a similarity transformation that, at once, transforms *all* the matrices $\Gamma(E), \Gamma(A), \Gamma(B), \dots$ into the block-diagonalized form

$$\Gamma'(A) = S^{-1}\Gamma(A)S = \begin{pmatrix} \Gamma'_1(A) & 0 & 0 \\ 0 & \Gamma'_2(A) & 0 \\ 0 & 0 & \Gamma'_3(A) \end{pmatrix}, \tag{4.17}$$

where $\Gamma'_1(A)$ is a square matrix with the same dimension as $\Gamma'_1(B), \dots, \Gamma'_1(F)$. Then, for example, since $AB = D$ in our six-element example group, G_6 , we would have

$$\begin{aligned}\Gamma'_1(A)\Gamma'_1(B) &= \Gamma'_1(D), \\ \Gamma'_2(A)\Gamma'_2(B) &= \Gamma'_2(D), \\ \Gamma'_3(A)\Gamma'_3(B) &= \Gamma'_3(D).\end{aligned}$$

That is, the matrix Rep $\Gamma(E), \Gamma(A), \dots, \Gamma(F)$, is said to be *reducible* and to have been reduced by the similarity transformation matrix S . In this case, the Rep has been reduced to three different Reps. If there is no similarity transformation that will further reduce all the matrices of a given Rep, the Rep is said to be *irreducible*, i.e. an Irrep.

In many applications, each Irrep has the same transformation properties as a set of degenerate eigenfunctions. We will see examples of this in later sections.

There is a particularly interesting set of matrices that forms a reducible Rep of a group, a set that can be block-diagonalized to give *all* its Irreps. It is known as the *regular* representation.

4.1.3 The regular representation

The *regular representation* is a useful but artificial construct that is generated on a basis set defined by a faithful mapping of the group elements themselves, i.e. for every group operator $\hat{R}$ there corresponds a basis vector R .

It can be defined most easily with the help of the group multiplication table. First, construct the multiplication table such that the diagonal elements are just the identity, hence: the first row is labeled by the inverse of the element labeling the first column, the second row is labeled by the inverse of the element labeling the second column, and so forth, as illustrated in Table 4.1 for the group $\mathcal{C}_{3v}$.

The regular Rep is probably the most interesting and useful of the reducible Reps, as will become apparent to some extent in this chapter but especially in Chapters 6 and 7, where it is incorporated into a systematic method for constructing the Irreps. The matrices of the regular Rep are constructed with the aid of the following relation:

$${}^{(\text{reg})}\Gamma_{jk}(\widehat{R}_i) = \begin{cases} 1, & \text{if } \widehat{R}_j \widehat{R}_k^{-1} = \widehat{R}_i; \\ 0, & \text{otherwise.} \end{cases} \quad (4.18)$$

Example 4.1

The group $\mathcal{C}_{3v}$

Using the *regularized* multiplication table, Table 4.1, it is straightforward to construct the regular Rep for $\mathcal{C}_{3v}$, using the prescription described by (4.18). To find the regular Rep for $\widehat{\sigma}_1$, for example, we simply substitute a 1 for $\widehat{\sigma}_1$ wherever $\widehat{\sigma}_1$ appears in Table 4.1. Otherwise the matrix element is 0. This recipe gives the following *regular* Rep for $\mathcal{C}_{3v}$,

Table 4.1. *The “regular” multiplication table for $\mathcal{C}_{3v}$.*

	$\widehat{E}$	$\widehat{\sigma}_1$	$\widehat{\sigma}_2$	$\widehat{\sigma}_3$	$\widehat{C}_3^2$	$\widehat{C}_3$
$\widehat{E}$	$\widehat{E}$	$\widehat{\sigma}_1$	$\widehat{\sigma}_2$	$\widehat{\sigma}_3$	$\widehat{C}_3^2$	$\widehat{C}_3$
$\widehat{\sigma}_1$	$\widehat{\sigma}_1$	$\widehat{E}$	$\widehat{C}_3$	$\widehat{C}_3^2$	$\widehat{\sigma}_3$	$\widehat{\sigma}_2$
$\widehat{\sigma}_2$	$\widehat{\sigma}_2$	$\widehat{C}_3^2$	$\widehat{E}$	$\widehat{C}_3$	$\widehat{\sigma}_1$	$\widehat{\sigma}_3$
$\widehat{\sigma}_3$	$\widehat{\sigma}_3$	$\widehat{C}_3$	$\widehat{C}_3^2$	$\widehat{E}$	$\widehat{\sigma}_2$	$\widehat{\sigma}_1$
$\widehat{C}_3$	$\widehat{C}_3$	$\widehat{\sigma}_3$	$\widehat{\sigma}_1$	$\widehat{\sigma}_2$	$\widehat{E}$	$\widehat{C}_3^2$
$\widehat{C}_3^2$	$\widehat{C}_3^2$	$\widehat{\sigma}_2$	$\widehat{\sigma}_3$	$\widehat{\sigma}_1$	$\widehat{C}_3$	$\widehat{E}$

$${}^{(\text{reg})}\Gamma(\widehat{E}) = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \quad {}^{(\text{reg})}\Gamma(\widehat{\sigma}_1) = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \end{pmatrix}$$

$${}^{(\text{reg})}\Gamma(\widehat{\sigma}_2) = \begin{pmatrix} 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \end{pmatrix} \quad {}^{(\text{reg})}\Gamma(\widehat{\sigma}_3) = \begin{pmatrix} 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \end{pmatrix}$$

$${}^{(\text{reg})}\Gamma(\widehat{C}_3) = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{pmatrix} \quad {}^{(\text{reg})}\Gamma(\widehat{C}_3^2) = \begin{pmatrix} 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

Generating the regular representation with Mathematica

We represent the matrices of the regular Rep as

$${}^{(\text{reg})}\Gamma_{jk}(\widehat{R}_i) \equiv R[i, j, k],$$

and recast the condition in (3.18) as $R_j = R_i R_k$. We can then write the program for generating the regular Rep as:

```
Do[R[i, j, k] = 0, {i, 1, g}, {j, 1, g}, {k, 1, g}]
Do[
  Do[
    Switch[j == m[[i, k]], True, R[i, j, k] = 1,
      {j, 1, g}, {k, 1, g}
    ], {i, 1, g}
  ]
  Regrep = Array[R, {g, g, g}]
  Do[Print[MatrixForm[Regrep[[i]]]], {i, 1, g}].
```

The array `m[[j, k]]` is the multiplication table generated in Chapter 2.

4.1.4 The great orthogonality theorem

The great orthogonality theorem is central to the quantitative development of a group theoretical treatment of physical systems.

The theorem asserts that Irreps of a group $\mathcal{G}$ satisfy the following orthogonality relation:

$$\sum_{\widehat{R} \in \mathcal{G}} {}^{(\alpha)}\Gamma_{ij}(\widehat{R}) [{}^{(\alpha')} \Gamma(\widehat{R})]_{j' i'}^{-1} = \frac{g}{d_\alpha} \delta_{\alpha\alpha'} \delta_{ii'} \delta_{jj'}, \quad (4.19)$$

where d_α is the dimension of $\text{Irrep}^{(\alpha)}\Gamma$. The standard proof of the orthogonality theorem can be found in many books on group theory, such as [1], or in Wigner's classic book [2].

A more intuitive argument begins with the simple requirement of a group that every element has an inverse:

$$\hat{R} \hat{R}^{-1} = \hat{E}.$$

Summing over all g elements of the group gives

$$\sum_{\hat{R}} \hat{R} \hat{R}^{-1} = g \hat{E}. \quad (4.20)$$

The corresponding equation for the matrix representatives is

$$\sum_{\hat{R}} [\Gamma(\hat{R})] [\Gamma(\hat{R}^{-1})] = \sum_{\hat{R}} [\Gamma(\hat{R})] [\Gamma(\hat{R})]^{-1} = g \Gamma(\hat{E}), \quad (4.21)$$

where the second step relies on the relationship

$$[\Gamma(\hat{R}^{-1})] = [\Gamma(\hat{R})]^{-1},$$

which follows directly from a comparison of the two equations:

$$[\Gamma(\hat{R})][\Gamma(\hat{R}^{-1})] = \Gamma(E),$$

$$[\Gamma(\hat{R})][\Gamma(\hat{R})]^{-1} = \Gamma(E).$$

Equation (4.21) is a sum rule! Though trivial, it serves as a starting point for the great orthogonality theorem.

A convenient device for obtaining orthogonality relations is to insert a unit matrix into (4.21). We can use the identity matrix representative for convenience. It has the correct dimension. Thus

$$\sum_{\hat{R}} \Gamma(\hat{R}) \Gamma(\hat{E}) \Gamma(\hat{R}^{-1}) = g \Gamma(\hat{E}). \quad (4.22)$$

In terms of a summation over matrix elements, (4.22) becomes

$$\sum_{jj'} \sum_{\hat{R}} \Gamma_{ij}(\hat{R}) \Gamma_{jj'}(\hat{E}) \Gamma_{j'i'}(\hat{R}^{-1}) = g \Gamma_{ii'}(\hat{E}). \quad (4.23)$$

Now, expressing the identity representative as a Kronecker delta, we have

$$\sum_{jj'} \sum_{\hat{R}} \Gamma_{ij}(\hat{R}) \delta_{jj'} \Gamma_{j'i'}(\hat{R}^{-1}) = g \delta_{ii'}. \quad (4.24)$$

The summation on the left-hand side is zero unless $j = j'$. Thus,

$$\begin{aligned} \sum_j \sum_{\hat{R}} {}^{(\alpha)}\Gamma_{ij}(\hat{R}) {}^{(\alpha)}\Gamma_{j'i'}(\hat{R}^{-1}) &= d_\alpha \sum_{\hat{R}} {}^{(\alpha)}\Gamma_{ij}(\hat{R}) {}^{(\alpha)}\Gamma_{j'i'}(\hat{R}^{-1}) \\ &= g \delta_{ii'} \delta_{jj'}, \end{aligned} \quad (4.25)$$

where now we specify that this applies to each Irrep $^{(\alpha)}\Gamma_{ij}(\hat{R})$ of dimension d_α . Thus, the sum rule for matrix elements leads to the orthogonality relationship

$$\sum_{\hat{R}} ^{(\alpha)}\Gamma_{ij}(\hat{R}) ^{(\alpha)}\Gamma_{j'i'}(\hat{R}^{-1}) = \frac{g}{d_\alpha} \delta_{ii'} \delta_{jj'}. \quad (4.26)$$

Equation (4.26) is a subset of the orthogonality conditions described by (4.22). It also contains a normalization factor $1/d_\alpha$ to account for the dimensionality of the Irrep, which arises from the sum over matrix elements in (4.25).

It is important to recognize that the second term of (4.25) is a matrix element of the inverse group operator, which may not belong to the same class as the first operator. This will be important when we later use modular arithmetic to determine group characters and Reps.

For a unitary group Rep,

$$\sum_{\hat{R}} ^{(\alpha)}\Gamma_{ij}(\hat{R}) ^{(\alpha')} \Gamma_{i'j'}(\hat{R})^* = \frac{g}{d_\alpha} \delta_{\alpha\alpha'} \delta_{ii'} \delta_{jj'}. \quad (4.27)$$

This rather imposing relationship is conveniently interpreted as describing the orthonormality of vectors in a g -dimensional space whose axes are labeled by the g elements of the group, and for which the components of a vector are given by a set of matrix elements, all belonging to the same row and column in the matrix Rep. Using our example group G_6 , which is of order $g = 6$, this means that the six matrix elements $^{(\alpha)}\Gamma_{ij}(E), ^{(\alpha)}\Gamma_{ij}(A), \dots, ^{(\alpha)}\Gamma_{ij}(F)$, corresponding to the same row and column of each matrix, can be regarded as the six components of a six-dimensional vector $\mathbf{v}_{ij}^\alpha$, which is orthogonal to any of the other vectors obtained by a different choice of subscripts, i' or j' , corresponding to a different row or column in the irreducible matrix Rep. The vector $\mathbf{v}_{ij}^\alpha$ is also orthogonal to *any* vector designated by a different superscript, α' , thus belonging to a *different* Irrep.

How many orthogonal vectors are there? Within a given Irrep $^{(\alpha)}\Gamma$ of dimension d_α , there are d_α^2 matrix elements for each operation of the group. Summing over all nonequivalent irreps, there are $\sum_\alpha d_\alpha^2$ vectors; but, in a g -dimensional space there can be only g orthogonal vectors. Thus, we get Burnside's theorem:

$$\sum_\alpha d_\alpha^2 = g. \quad (4.28)$$

A rigorous proof of (4.28), Burnside's theorem, together with a particularly useful interpretation, is given in Section 4.3.

In the case of our six-element example group, we have three irreps, thus we must have

$$\sum_\alpha d_\alpha^2 = 1^2 + 1^2 + 2^2 = 6$$

as the only possibility. These irreps were discussed extensively in Chapter 3.

4.2 Character of a matrix representation

The *character* of a matrix Rep of a group $\mathcal{G}$ is a set of g numbers $\chi(E), \chi(A), \chi(B), \dots$, one for each group element, given by

$$\chi(R) = \text{Tr}[\Gamma(R)] = \sum_{i=1}^d \Gamma_{ii}(R), \quad (4.29)$$

where Tr is called the *trace*, and d is the dimension of Γ .

Since a unitary transformation maps a matrix Rep into an equivalent Rep, it preserves the traces of the constituent matrices. Alternatively, we may say that equivalent Reps have identical characters for the matrices representing the same operator. We can use this criterion to differentiate between distinct or equivalent Reps. We also recognize that since class elements are related by conjugacy operations, which in a matrix Rep become similarity transformations, *group elements belonging to the same class have identical characters*.

The identity matrix has only ones along the diagonal, so the trace, or the character, is just the dimension of the Rep. Thus

$$\chi(\hat{E}) = d, \quad (4.30)$$

where d is the dimension of the Rep. Because the diagonal elements of a diagonalized unitary matrix Rep are roots of unity, d is an upper bound on the character.

In the following sections, we will develop some orthogonality relations and equalities that can be used to determine Irrep characters.

4.2.1 Character orthogonality relations

We can derive an orthonormality condition for the characters of Irreps by making use of the great orthogonality theorem. When we set $j = i, j' = i'$ in (4.19) and sum over i, i' we obtain, using (4.29),

$$\begin{aligned} \sum_{i,i'} \sum_R {}^{(\alpha)}\Gamma_{ii}(R) {}^{(\alpha')} \Gamma(R^{-1})_{i'i'} &= \sum_R \sum_{i,i'} {}^{(\alpha)}\Gamma_{ii}(R) {}^{(\alpha')} \Gamma(R^{-1})_{i'i'} \\ &= \sum_R {}^{(\alpha)}\chi(R) {}^{(\alpha')} \chi(R^{-1}) \\ &= \frac{g}{d_\alpha} \sum_{i,i'} \delta_{ii'} \\ &= g \delta_{\alpha\alpha'}. \end{aligned} \quad (4.31)$$

Equating the third and fifth terms of these equations gives

$$\sum_R {}^{(\alpha)}\chi(R) {}^{(\alpha')} \chi(R^{-1}) = g \delta_{\alpha\alpha'}. \quad (4.32)$$

Thus, the characters are also the components of an orthogonal set of vectors in the g -dimensional group-element space.

If we now collect the group elements according to classes, within which the characters are identical, we can change the last equation to a sum over classes, yielding

$$\sum_{\mathcal{C}_i} \text{nc}(i) {}^{(\alpha)}\chi(\mathcal{C}_i) {}^{(\alpha')} \chi(\mathcal{C}_i^{-1}) = g \delta_{\alpha\alpha'}, \quad (4.33)$$

where $\chi(\mathcal{C}_i)$ is the character of class $\mathcal{C}_i$, and $\chi(\mathcal{C}_i^{-1})$ is that of its inverse class, and $\text{nc}(i)$ is the number of elements in $\mathcal{C}_i$. The summation is over all classes in the group. This orthogonality relationship can be interpreted as follows: The characters of the various Irreps form an orthogonal set of vectors in a vector space where axes are labeled by the classes $\mathcal{C}_i$ rather than the group elements $\hat{R}$. A second character orthogonality relation is given by

$$\sum_{\alpha} {}^{(\alpha)}\chi(\mathcal{C}_i) {}^{(\alpha)}\chi(\mathcal{C}_j^{-1}) = \frac{g}{\text{nc}(i)} \delta_{ij}. \quad (4.34)$$

The proof is left as Exercise 4.3.

Suppose there are l classes in the group. Then the space in which axes are labeled by classes is an l -dimensional space. Since there can be l orthogonal vectors in an l -dimensional space, and the orthogonality is between characters from different Irreps, there can be a maximum of l Irreps. Thus l , the number of classes, is an upper bound on the number of Irreps. Thus we have the important equality:

$$\text{Number of Irreps} = \text{Number of classes}. \quad (4.35)$$

We are now in a position to determine the class characters for the group $\mathcal{C}_{3v}$. Of course, we already know the matrix Irreps for the group $\mathcal{C}_{3v}$ and so we could calculate the characters directly by summing the diagonal elements of the representative matrices. However,

we want to show that it is possible to determine the characters without explicit knowledge of the matrix Irreps.

Example 4.2

The group $\mathcal{C}_{3v}$ consists of three classes. Thus, from (4.35) we know there must be three Irreps. Then, from (3.28) and the discussion thereafter we know that these Irreps must be of dimensions 1, 1, and 2. We have denoted them earlier by $^{(1)}\Gamma$, $^{(2)}\Gamma$, and $^{(3)}\Gamma$, respectively. One of these Irreps must be the one-dimensional *invariant* Irrep, which we take to be $^{(1)}\Gamma$. Thus, the first row of the character table, corresponding to $^{(1)}\Gamma$, consists of all ones. The first column of the table, corresponding to class $\mathcal{C}_1 = E$ must be equal to the dimension of the Irrep, as we know from (4.25). Thus we can immediately write down a partial character table, as follows.

Table 4.2. *Partial character table for the point-group $\mathcal{C}_{3v}$.*

	$\chi(\mathcal{C}_1)$ $\chi(\mathcal{C}_1^{-1})$	$\chi(\mathcal{C}_2)$ $\chi(\mathcal{C}_2^{-1})$	$\chi(\mathcal{C}_3)$ $\chi(\mathcal{C}_3^{-1})$
Γ_1	1	1	1
Γ_2	1		
Γ_3	2		

Notice that the classes of $\mathcal{C}_{3v}$ are such that

$$\mathcal{C}_i^{-1} = \mathcal{C}_i.$$

We can fill in the other values of the table by trial and error, making use of (4.33), which is an orthogonality relationship between rows of the character table. If we take class $\mathcal{C}_2$ to be the class consisting of the two elements $\{\mathcal{C}_3, \mathcal{C}_3^2\}$, and $\mathcal{C}_3$ to consist of $\{\sigma_1, \sigma_2, \sigma_3\}$, then the orthogonality relationship for characters is satisfied only by Table 4.3. Columns of the table are orthogonal, as expected from (4.34).

Table 4.3. *Character table for the point-group $\mathcal{C}_{3v}$.*

	$\chi(\mathcal{C}_1)$ $\chi(\mathcal{C}_1^{-1})$	$\chi(\mathcal{C}_2)$ $\chi(\mathcal{C}_2^{-1})$	$\chi(\mathcal{C}_3)$ $\chi(\mathcal{C}_3^{-1})$
Γ_1	1	1	1
Γ_2	1	1	-1
Γ_3	2	-1	0

The example we have just gone through typifies what is generally done to determine character tables, but it presents difficulties in practice for large tables. There is

a systematic way of determining characters, known as Burnside's method; we present it in Section 4.3.

4.2.2 Character decomposition

If ${}^{(\text{red})}\chi(\widehat{R})$ is the character of a reducible Rep of element $\widehat{R} \in \mathcal{G}$, then it is possible to decompose it into Irrep characters according to

$${}^{(\text{red})}\chi(\widehat{R}) = \sum_{\alpha} \langle \text{red} | \alpha \rangle {}^{(\alpha)}\chi(\widehat{R}), \quad (4.36)$$

where $\langle \text{red} | \alpha \rangle$ is the number of times the α th Irrep appears in the reducible Rep ${}^{(\text{red})}\Gamma$; it is called the *multiplicity* or the *decomposition frequency* of Irrep α in the reducible Rep. We can therefore write ${}^{(\text{red})}\Gamma$ in the form of a direct sum over Irreps as

$${}^{(\text{red})}\Gamma = \bigoplus_{\alpha} \langle \text{red} | \alpha \rangle {}^{(\alpha)}\Gamma. \quad (4.37)$$

we determine $\langle \text{red} | \alpha \rangle$ from the following relation:

$$\langle \text{red} | \alpha \rangle = \frac{1}{g} \sum_R {}^{(\alpha)}\chi(R^{-1}) {}^{(\text{red})}\chi(R), \quad (4.38)$$

or,

$$\langle \text{red} | \alpha \rangle = \frac{1}{g} \sum_{i=1}^{N_c} \text{nc}(i) {}^{(\alpha)}\chi(\mathcal{C}_i^{-1}) {}^{(\text{red})}\chi(\mathcal{C}_i), \quad (4.39)$$

where N_c is the number of classes and $\text{nc}(i)$ is the number of elements in class $\mathcal{C}_i$. A proof of (4.38) and (4.39) is easily obtained using (4.32) or (4.33). Equations (4.37)–(4.39) will be used extensively in subsequent chapters.

Let us now use (4.38) or (4.39) to determine the character decomposition frequencies for the *regular* Rep. We know from the definition of the regular Rep as given by (4.18), and from the example of (4.19), that the identity element only has nonzero character. Thus, we find that

$${}^{(\text{reg})}\chi(\widehat{R}_i) = \begin{cases} g, & \text{if } \widehat{R}_i = \widehat{E}; \\ 0, & \text{otherwise.} \end{cases} \quad (4.40)$$

Now, using this result in (4.39) we get

$$\begin{aligned}
 \langle \text{reg} | \alpha \rangle &= \frac{1}{g} \sum_{i=1}^{N_C} \text{nc}(i) {}^{(\alpha)}\chi(\mathcal{C}_i^{-1}) {}^{(\text{reg})}\chi(\mathcal{C}_i) \\
 &= \frac{1}{g} {}^{(\alpha)}\chi(E^{-1}) {}^{(\text{reg})}\chi(E) \\
 &= \frac{1}{g} \times d_\alpha \times g = d_\alpha,
 \end{aligned} \tag{4.41}$$

This is a very important result. It is a restatement of Burnside's theorem as given in (4.35), but now given in a way that is particularly insightful and useful. It is simply this:

Burnside's theorem *An Irrep of dimension d_α appears d_α times in the regular Rep.*

The character turns out to be the single most useful invariant of a Rep. This is because the sum of the eigenvalues is given by the sum of the diagonal elements of a matrix *in any Rep*, and it is invariant under a similarity transformation.

4.2.3 Class matrices and Dirac characters

In a given Irrep ${}^{(\alpha)}\Gamma$ we define a *class matrix* as

$$\mathbf{C}_i^{(\alpha)} = \sum_{\hat{R} \in \mathcal{C}_i} {}^{(\alpha)}\Gamma(\hat{R}). \tag{4.42}$$

The class matrices are constructed by adding corresponding matrix elements (same row and column) from each matrix for each group element in the class, as illustrated in the following examples.

Example 4.3

The class matrices for the two-dimensional Irrep ${}^{(3)}\Gamma$ of $\mathcal{C}_{3v}$ are

$$\begin{aligned}
 {}^{(3)}\mathbf{C}_1 &= {}^{(3)}\Gamma(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \\
 {}^{(3)}\mathbf{C}_2 &= {}^{(3)}\Gamma(C_3) + {}^{(3)}\Gamma(C_3^2) \\
 &= \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix} + \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix} \\
 &= \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}
 \end{aligned}$$

$$\begin{aligned}
{}^{(3)}\mathbf{C}_3 &= {}^{(3)}\Gamma(\sigma_1) + {}^{(3)}\Gamma(\sigma_2) + {}^{(3)}\Gamma(\sigma_3) \\
&= \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} 1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix} + \begin{pmatrix} 1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix} \\
&= \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}
\end{aligned}$$

The class matrix for the i th class in the regular Rep can be written as

$${}^{(\text{reg})}\mathbf{C}_i = \sum_j {}^{(\text{reg})}\Gamma(i, j), \quad (4.43)$$

where ${}^{(\text{reg})}\Gamma(i, j)$ is the regular Rep of the j th element in class $\mathcal{C}_i$. The regular class matrix for the identity class is the unit matrix of dimension g .

Example 4.4

For the regular class matrices of the group $\mathcal{C}_{3v}$, other than the identity matrix, we get

$$\begin{aligned}
{}^{(\text{reg})}\mathbf{C}_2 &= {}^{(\text{reg})}\Gamma(\widehat{C}_3) + {}^{(\text{reg})}\Gamma(\widehat{C}_3^2) \\
&= \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \\
&= \begin{pmatrix} 0 & 0 & 0 & 0 & 1 & 1 \\ 0 & 0 & 1 & 1 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 1 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 1 & 0 \end{pmatrix}
\end{aligned}$$

$$\begin{aligned}
{}^{(\text{reg})}\mathbf{C}_3 &= {}^{(\text{reg})}\Gamma(\widehat{\sigma}_1) + {}^{(\text{reg})}\Gamma(\widehat{\sigma}_2) + {}^{(\text{reg})}\Gamma(\widehat{\sigma}_3) \\
&= \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \end{pmatrix}
\end{aligned}$$

$$\begin{aligned}
& + \begin{pmatrix} 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \end{pmatrix} \\
& = \begin{pmatrix} 0 & 1 & 1 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 & 1 & 1 \\ 1 & 0 & 0 & 0 & 1 & 1 \\ 1 & 0 & 0 & 0 & 1 & 1 \\ 0 & 1 & 1 & 1 & 0 & 0 \\ 0 & 1 & 1 & 1 & 0 & 0 \end{pmatrix}
\end{aligned}$$

Class matrices also satisfy the class multiplication relations as defined in Section 2.2:

$$\mathcal{C}_i \mathcal{C}_j = \sum_{k=1}^{N_C} h_{ijk} \mathcal{C}_k, \quad (4.44)$$

namely,

$${}^{(\alpha)}\mathbf{C}_i {}^{(\alpha)}\mathbf{C}_j = \sum_{k=1}^{N_C} h_{ijk} {}^{(\alpha)}\mathbf{C}_k. \quad (4.45)$$

However, unlike the multiplication of classes in (4.44), where the coefficients are uniquely determined by the multiplication process, this is not so for (4.45). That is, the actual multiplication of two class matrices gives a *single* matrix which can be decomposed according to (4.45), but the coefficients must be known from (4.44).

Example 4.5

Consider multiplication of the class matrix ${}^{(3)}\mathbf{C}_2$ by itself:

$$\begin{aligned}
{}^{(3)}\mathbf{C}_2 {}^{(3)}\mathbf{C}_2 &= \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} \\
&= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.
\end{aligned}$$

Comparison with the results of Example 4.3 might (incorrectly) suggest the decomposition is given by

$${}^{(3)}\mathbf{C}_2 {}^{(3)}\mathbf{C}_2 = {}^{(3)}\mathbf{C}_1 \quad \text{WRONG!}$$

with $h_{221} = 1$ and all other $h_{ijk} = 0$. However, by analogy with Example 2.7, we know that

$$\mathbf{C}_2 \mathbf{C}_2 = 2\mathbf{C}_1 + \mathbf{C}_2,$$

where the superscripts (3) have been deleted to clearly emphasize that $h_{221} = 2$ and $h_{222} = 1$. The point is that one cannot *uniquely* decompose the product of two class matrices from a knowledge of the product matrix alone. It requires that the coefficients h_{ijk} be known from (4.44).

The trace of a class matrix has the form

$$\text{Tr} \left({}^{(\alpha)}\mathbf{C}_i \right) = \sum_{\hat{R} \in \mathcal{C}_i} \text{Tr} \left({}^{(\alpha)}\Gamma(\hat{R}) \right) = \text{nc}(i) \chi(\mathcal{C}_i), \quad (4.46)$$

where $\text{nc}(i)$ is the number of elements in class $\mathcal{C}_i$.

A class sum commutes with all the elements of the group (2.17), thus Schur's lemma requires that its matrix representative in ${}^{(\alpha)}\Gamma$ be of the form

$$\boxed{{}^{(\alpha)}\mathbf{C}_i = {}^{(\alpha)}\lambda_i \mathbb{I},} \quad (4.47)$$

where the scalar ${}^{(\alpha)}\lambda_i$ is a *class constant* or *Dirac character* [14], and $\mathbb{I}$ is the unit matrix of dimension d_α . Consequently,

$$\text{Tr}(\mathbf{C}_i) = {}^{(\alpha)}\lambda_i d_\alpha. \quad (4.48)$$

The Dirac character is an eigenvalue solution to an equation used to determine the group characters by Burnside's method, which we develop in the next section. Combining (4.46) and (4.48) we obtain the following relationship between the character and the Dirac character (class constant) of a class:

$$\boxed{{}^{(\alpha)}\lambda_i = \frac{\text{nc}(i)\chi_i^{(\alpha)}}{d_\alpha}.} \quad (4.49)$$

In the next section we learn how to determine the Dirac character of all the classes and all the Irreps in one fell swoop by means of Burnside's method. Equation (4.49) then allows us to convert to the character χ_i that is used in actual group theory calculations.

4.3 Burnside's method

We learned in Section 4.2 how to construct character tables for Irreps by using the simple rules of orthogonality relations for characters; sometimes this requires some guessing and checking. There are other more systematic methods that can be used, generally involving the solution of sets of equations. A particularly useful and informative method is that

of Burnside [3]. It is essentially a transformation of the problem to the solution of an eigenvalue equation.

Burnside's method for the calculation of characters of Irreps is based on the diagonalization of the class constant matrices. It is systematic and unambiguous, but it may suffer from numerical round-off errors that result from computer solutions of eigenvalue problems, especially for large groups. Dixon [4] proposed a method for obtaining the eigenvalues and eigenvectors, which we will describe in Chapter 5, that avoids the numerical errors inherent in the traditional Burnside's approach. This method employs a clever transformation of the problem to one in "prime number" space, where the solutions are integers and hence can be found *exactly* and then transformed back to the space of real numbers. Thus, for both tutorial and historical reasons, a treatment of Burnside's method provides an excellent introduction to Dixon's method.

We start with (4.45), the class multiplication relation for class sum matrices,

$${}^{(\alpha)}\mathbf{C}_i {}^{(\alpha)}\mathbf{C}_j = \sum_{k=1}^{N_C} h_{ijk} {}^{(\alpha)}\mathbf{C}_k,$$

and substitute for the $\mathbf{C}_i$ s from (4.47). We obtain the following relations among the class constants:

$${}^{(\alpha)}\lambda_i {}^{(\alpha)}\lambda_j = \sum_k h_{ijk} {}^{(\alpha)}\lambda_k. \quad (4.50)$$

The coefficients h_{ijk} are independent of the Irrep; they are properties of the group. They can be considered as the elements of a class-coefficient matrix $H^{(i)}$, with rows and columns labeled by j and k , namely

$$H^{(i)} = \begin{pmatrix} h_{i11} & h_{i12} & h_{i13} & \cdots \\ h_{i21} & h_{i22} & h_{i23} & \cdots \\ \cdot & \cdot & \cdot & \cdots \\ \cdot & \cdot & \cdot & \cdots \end{pmatrix},$$

and the class constants ${}^{(\alpha)}\lambda_i$ can be considered as components of a vector

$${}^{(\alpha)}\Lambda = \begin{pmatrix} {}^{(\alpha)}\lambda_1 \\ {}^{(\alpha)}\lambda_2 \\ \vdots \end{pmatrix}.$$

For each class i , the set of equations, given by (4.50) when j assumes all possible values, can thus be written as an eigenvalue equation, namely,

$$H^{(i)} {}^{(\alpha)}\Lambda = {}^{(\alpha)}\lambda_i {}^{(\alpha)}\Lambda. \quad (4.51)$$

Notice that the eigenvalues, which are the class constants ${}^{(\alpha)}\lambda_i$, also make up the components of the eigenvectors. Hence, *the class matrices $H^{(i)}$ share the same eigenvectors*, and

can be *simultaneously* diagonalized by a similarity transformation, V , comprising these eigenvectors

$$V^{-1} H^{(i)} V = \Delta,$$

to yield the diagonal matrix Δ , whose diagonal elements are the eigenvalues of $H^{(i)}$. This is a powerful statement. *Every* class matrix is diagonalized by the same similarity transformation! This is a wonderful byproduct of the special connection between eigenvalues and the components of eigenvectors for this particular circumstance. We demonstrate it in Example 4.6.

There are numerous methods to diagonalize a matrix. However, Mathematica[®] provides three functions for the solution of a matrix eigenvalue problem:

```
Eigensystem[H]    gives the complete set of eigenvalues and
                  corresponding eigenvectors,
Eigenvalues[H]    gives only the eigenvalues,
Eigenvectors[H]   gives only the eigenvectors.
```

The following program illustrates the use of these Mathematica[®] functions in the construction of the character table.

```
h = Array[a,{nc, nc, nc}];
Print["CLASS MULTIPLICATION MATRICES"];
Do[Print["H(", i, ") = ", MatrixForm[h[[i]]]],{i, 2, nc}
];
Do[d[mu] = 1,{mu, 1, nc}]; nv = 1; nm = 1; Λ = {};
While[nv < nc, nm++;
  Switch[nm ≤ nc,
    True,
    EN = Eigenvalues[h[[nm]]];
  Do[
    EG = EN[[iv]];
    Switch[Length[Position[EN, EG]] == 1,
      True, EV = Eigenvectors[h[[nm]]]
    ];
  ];
```

```

Switch[FreeQ[ $\Lambda$ , EV[[iv]]], True,
  AppendTo[ $\Lambda$ , EV[[iv]]];nv++
],{iv, 1, nc}
],
False,
nc1 = 1;
While[nc1 < nc - 1, nc1++; ic1 = nc1;
  While[ic1 < nc, ic1++;
    Do[bb[i, j] = a[nc1, i, j] + a[ic1, i, j],
      {i,1, nc}, {j, 1, nc}
    ];
    Array[bb,{nc, nc}];
    Do[
      EG = EN[[iv]];
      Switch[Length[Position[EN, EG]] == 1,
        True, EV = Eigenvectors[hh];
        Switch[FreeQ[ $\Lambda$ , EV[[iv]]], True,
          AppendTo[ $\Lambda$ ,EV[[iv]]];
          nv++
        ], {iv, 1, nc}
      ]
    ]
  ]
]; Print["Dirac characters : ", MatrixForm[ $\Lambda$ ]];
Do[
  din = 0;
  Do[
    din +=  $\Lambda$ [[iv, ic]]Conjugate[ $\Lambda$ [[iv, ic]]]/
    Length[LC[[ic]]], {ic, 1, nc}
  ]; d[iv] = Simplify[gq/din]; d[iv] =  $\sqrt{d[iv]}$ ;
Print["The Irrep dimensions are"]
Print["d[" , iv, "] = ", d[iv]], {iv, 1, nc}];
 $\chi$  = {};

```

```

Do[
  Do[
    chi = d[mu]  $\wedge$  [[mu,ic]]/Length[LC[[ic]]];
    AppendTo[ $\chi$ , chi], {ic,1, nc}
  ], {mu, 1, nc}
];  $\chi$  = Partition[ $\chi$ , nc];
Print["The Irrep characters are"];
Do[Print[" $\Gamma$ ", mu, " : ",  $\chi$ [[mu]]], {mu, 1, nc}]

```

Example 4.6

The group C_{3v} contains the classes $\mathcal{C}_1 = E$, $\mathcal{C}_2 = C_3, C_3^2$ and $\mathcal{C}_3 = \sigma_1, \sigma_2, \sigma_3$. We begin by using class multiplication to determine the coefficients h_{ijk} that provide the matrix elements for $H^{(i)}$. With the help of Table 2.1 for group multiplication we find, for example, that

$$\begin{aligned}
 \mathcal{C}_2 \mathcal{C}_2 &= (C_3 + C_3^2)(C_3 + C_3^2) \\
 &= C_3^2 + C_3^2 C_3 + C_3 C_3^2 + C_3^4 \\
 &= C_3^2 + E + E + C_3 \\
 &= 2\mathcal{C}_1 + \mathcal{C}_2.
 \end{aligned}$$

From this we see that $h_{221} = 2$ and $h_{222} = 1$. Continuing in this fashion for all other products of classes, we find

$$\begin{aligned}
 h_{111} &= h_{122} = h_{133} = h_{212} = h_{222} = h_{313} = 1, \\
 h_{221} &= h_{233} = h_{323} = 2, \\
 h_{331} &= h_{332} = 3.
 \end{aligned}$$

All other $h_{ijk} = 0$.

We use the coefficients h_{ijk} to construct the matrices $H^{(i)}$:

$$\begin{aligned}
 H^{(1)} &= \begin{pmatrix} h_{111} & h_{112} & h_{113} \\ h_{121} & h_{122} & h_{123} \\ h_{131} & h_{132} & h_{133} \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \\
 H^{(2)} &= \begin{pmatrix} h_{211} & h_{212} & h_{213} \\ h_{221} & h_{222} & h_{223} \\ h_{231} & h_{232} & h_{233} \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 \\ 2 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix}, \\
 H^{(3)} &= \begin{pmatrix} h_{311} & h_{312} & h_{313} \\ h_{321} & h_{322} & h_{323} \\ h_{331} & h_{332} & h_{333} \end{pmatrix} = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 2 \\ 3 & 3 & 0 \end{pmatrix}.
 \end{aligned}$$

Applying the function **Eigenvectors** to the matrix $H^{(3)}$ we obtain the set of three class constant eigenvectors:

$$^{(1)}\Lambda = \begin{pmatrix} 1 \\ 2 \\ 3 \end{pmatrix}, \quad ^{(2)}\Lambda = \begin{pmatrix} 1 \\ 2 \\ -3 \end{pmatrix}, \quad ^{(3)}\Lambda = \begin{pmatrix} 1 \\ -1 \\ 0 \end{pmatrix}.$$

We normalized the eigenvectors such that the class constants corresponding to the identity element are set to unity. This is necessary in order to satisfy the relation between the class constants and the class characters, as stated in (4.49), and ensures that the columns of the matrix V are eigenvectors *whose elements are exactly equal to the eigenvalues*. Moreover, we notice that because the matrices we wish to diagonalize are not all symmetric, the eigenvectors are not orthogonal, but the “vectors” we eventually determine (whose components are the class characters) will be orthogonal in the sense of (4.32) and (4.34).

The class constant eigenvectors then form the similarity transformation matrix

$$V = \begin{pmatrix} 1 & 1 & 1 \\ 2 & 2 & -1 \\ 3 & -3 & 0 \end{pmatrix}$$

with its inverse given by

$$V^{-1} = \begin{pmatrix} 1/6 & 1/6 & 1/6 \\ 1/6 & 1/6 & -1/6 \\ 4/6 & -2/6 & 0 \end{pmatrix}.$$

Now, as an example, we apply this transformation to diagonalize the matrix $H^{(3)}$ in order to find the class constants for the class $\mathcal{C}_3$. Of course, we actually already know them from the matrix V , but it is instructive to carry through with the matrix diagonalization to assure ourselves that everything is consistent.

$$\begin{aligned} V^{-1}H^{(3)}V &= \begin{pmatrix} 1/6 & 1/6 & 1/6 \\ 1/6 & 1/6 & -1/6 \\ 4/6 & -2/6 & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 2 \\ 3 & 3 & 0 \end{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 2 & 2 & -1 \\ 3 & -3 & 0 \end{pmatrix} \\ &= \begin{pmatrix} 3 & 0 & 0 \\ 0 & -3 & 0 \\ 0 & 0 & 0 \end{pmatrix} = \begin{pmatrix} \lambda_3^{(1)} & 0 & 0 \\ 0 & \lambda_3^{(2)} & 0 \\ 0 & 0 & \lambda_3^{(3)} \end{pmatrix}. \end{aligned}$$

Table 4.4. *Class constants for the point-group $\mathcal{C}_{3v}$.*

	$\lambda(\mathcal{C}_1)$	$\lambda(\mathcal{C}_2)$	$\lambda(\mathcal{C}_3)$
$^{(1)}\Gamma$	1	2	3
$^{(2)}\Gamma$	1	2	-3
$^{(3)}\Gamma$	1	-1	0

We have now obtained the class constants for the class $\mathcal{C}_3$ of the point-group $\mathcal{C}_{3v}$ by diagonalizing the matrix $H^{(3)}$. Each of the columns of the matrix V that yields the diagonalization provides the class constants for one of the Irreps. The columns of V become the rows of the class constant table, as in Table 4.4.

A key point The matrix V that diagonalizes the class-coefficient matrix $H^{(i)}$ is of dimension $N_C \times N_C$, where N_C is the number of classes and also equals the number of Irreps. The columns of V are eigenvectors whose components are the class constants for an Irrep. Each column is distinct and each corresponds to a single Irrep.

We have demonstrated how to determine class constants for each Irrep in an unambiguous way. We now obtain the corresponding irreducible character table with the aid of (4.49), which can be written as

$$\chi_i^{(\alpha)} = \frac{d_\alpha}{\text{nc}(i)} {}^{(\alpha)}\lambda_i, \quad (4.52)$$

where $\text{nc}(i)$ is the number of group elements in class $\mathcal{C}_i$.

To calculate the characters from the class constants we need to know the dimensions of the Irreps. We make use of the orthogonality relationship given by (4.33), which, together with (4.52), gives

$$\sum_i \text{nc}(i) {}^{(\alpha)}\chi_i {}^{(\alpha)}\chi_i^* = g.$$

From (4.33) and (4.52) we find

$$d_\alpha^2 = \frac{g}{\sum_i {}^{(\alpha)}\lambda_i {}^{(\alpha)}\lambda_i^* / \text{nc}(i)}. \quad (4.53)$$

We can now determine the class characters.

Example 4.7

Using (4.53) we find the dimension d_3 of the Irrep ${}^{(3)}\Gamma$ for the group $\mathcal{C}_{3v}$:

$$d_3^2 = \frac{6}{\frac{1}{1} + \frac{1}{2} + \frac{0}{3}} = 4.$$

Thus $d_3 = 2$. Similarly, we find d_1 and $d_2 = 1$. From Table 4.3 and (4.52), together with our knowledge of the dimensions of the Reps we find, with no trial and error, that we reproduce the character Table 4.3 for $\mathcal{C}_{3v}$.

We notice that the class matrix $H^{(3)}$ has three nondegenerate eigenvalues, and thus the corresponding eigenvectors can be unambiguously identified with the different Irreps. If we had chosen to diagonalize $H^{(2)}$ instead, we would have obtained the eigenvalues $\{2, 2, -1\}$. The eigenvectors corresponding to the two-fold degenerate eigenvalue, 2, cannot be unambiguously identified with Irreps, since any linear combination of the eigenvectors $[1, 2, 3]$ and $[1, 2, -3]$ constitutes an eigenvector of $H^{(2)}$ with eigenvalue 2. To resolve this shortcoming, when encountered, we pick only the eigenvector corresponding to the nondegenerate eigenvalue, -1 , and seek the remaining two by proceeding to diagonalize $H^{(3)}$.

A very tricky situation is encountered when attempting to use Burnside's method for the group $\mathcal{C}_{4v}$.

Example 4.8

$\mathcal{C}_{4v}$ has five classes: $\mathcal{C}_1 = E$, $\mathcal{C}_2 = \{C_4, C_4^{-1}\}$, $\mathcal{C}_3 = \{\sigma_1, \sigma_2\}$, $\mathcal{C}_4 = \{C_2\}$, $\mathcal{C}_5 = \{\sigma_{1d}, \sigma_{2d}\}$. The corresponding class matrices, apart from the identity matrix, are given by

$$\begin{aligned}
 H^{(2)} &= \begin{pmatrix} 0 & 1 & 0 & 0 & 0 \\ 2 & 0 & 0 & 2 & 0 \\ 0 & 0 & 0 & 0 & 2 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 2 & 0 & 0 \end{pmatrix} & H^{(3)} &= \begin{pmatrix} 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2 \\ 2 & 0 & 0 & 2 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 2 & 0 & 0 \end{pmatrix} \\
 H^{(4)} &= \begin{pmatrix} 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 2 & 0 & 0 \\ 0 & 2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 \\ 2 & 0 & 0 & 2 & 0 \end{pmatrix} & H^{(5)} &= \begin{pmatrix} 0 & 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}
 \end{aligned}$$

We find that $H^{(2)}$ has eigenvalues $\{-1, 1, 1, 1, 1\}$, and $H^{(3)}$, $H^{(4)}$, and $H^{(5)}$ have the same eigenvalues $\{-2, -2, 0, 2, 2\}$. The *nondegenerate* eigenvector in each case is the same, namely, $[1, 0, 0, -1, 0]$. Note that *eigenvalues* are enclosed in braces $\{\}$ and *eigenvectors* are enclosed in brackets $[]$.

In order to determine the remaining eigenvectors we use the fact that linear combinations of these matrices will have the same set of eigenvectors, but new eigenvalues. The new nondegenerate eigenvalues may reveal the sought-after eigenvectors. In fact, for the case of $\mathcal{C}_{4v}$ the remaining eigenvectors

$$[1, 2, 2, 1, 2], [1, -2, -2, 1, 2], [1, -2, 2, 1, -2], [1, 2, -2, 1, -2]$$

are obtained from pair sums of the class matrices, i.e. $H^{(i)} + H^{(j)}$.

Table 4.5. Class constants for the point-group $\mathcal{C}_{4v}$.

	$\lambda(\mathcal{C}_1)$	$\lambda(\mathcal{C}_2)$	$\lambda(\mathcal{C}_3)$	$\lambda(\mathcal{C}_4)$	$\lambda(\mathcal{C}_5)$
$^{(1)}\Gamma$	1	2	2	1	2
$^{(2)}\Gamma$	1	2	-2	1	-2
$^{(3)}\Gamma$	1	-2	2	1	-2
$^{(4)}\Gamma$	1	-2	-2	1	2
$^{(5)}\Gamma$	1	0	0	-1	0

We next use (4.53) to obtain the dimensions of the Rep. We find

$$[1, 0, 0, -1, 0] : \quad d^2 = \frac{8}{\frac{1}{1} + \frac{0}{2} + \frac{0}{2} + \frac{1}{1} + \frac{0}{2}} = 4 \rightarrow d = 2,$$

$$[1, -2, -2, 1, 2] : \quad d^2 = \frac{8}{\frac{1}{1} + \frac{4}{2} + \frac{4}{2} + \frac{1}{1} + \frac{4}{2}} = 1 \rightarrow d = 1,$$

$$[1, 2, 2, 1, 2] : \quad d^2 = \frac{8}{\frac{1}{1} + \frac{4}{2} + \frac{4}{2} + \frac{1}{1} + \frac{4}{2}} = 1 \rightarrow d = 1,$$

$$[1, -2, 2, 1, -2] : \quad d^2 = \frac{8}{\frac{1}{1} + \frac{4}{2} + \frac{4}{2} + \frac{1}{1} + \frac{4}{2}} = 1 \rightarrow d = 1,$$

$$[1, 2, -2, 1, -2] : \quad d^2 = \frac{8}{\frac{1}{1} + \frac{4}{2} + \frac{4}{2} + \frac{1}{1} + \frac{4}{2}} = 1 \rightarrow d = 1.$$

Finally, we use (4.52) to obtain the characters, starting with

$$[1, 2, 2, 1, 2] : \chi_1^{(1)} = 1, \chi_2^{(1)} = 1, \chi_3^{(1)} = -1, \chi_4^{(1)} = 1, \chi_5^{(1)} = 1,$$

$$[1, 2, -2, 1, -2] : \chi_1^{(2)} = 1, \chi_2^{(2)} = 1, \chi_3^{(2)} = 1, \chi_4^{(2)} = 1, \chi_5^{(2)} = -1,$$

$$[1, -2, 2, 1, -2] : \chi_1^{(3)} = 1, \chi_2^{(3)} = -1, \chi_3^{(3)} = 1, \chi_4^{(3)} = 1, \chi_5^{(3)} = -1,$$

$$[1, -2, -2, 1, 2] : \chi_1^{(4)} = 1, \chi_2^{(4)} = -1, \chi_3^{(4)} = -1, \chi_4^{(4)} = 1, \chi_5^{(4)} = 1,$$

$$[1, 0, 0, -1, 0] : \chi_1^{(5)} = 2, \chi_2^{(5)} = 0, \chi_3^{(5)} = 0, \chi_4^{(5)} = -2, \chi_5^{(5)} = 0,$$

Table 4.6. *Characters for the point-group C_{4v} .*

	$\chi(\mathcal{C}_1)$	$\chi(\mathcal{C}_2)$	$\chi(\mathcal{C}_3)$	$\chi(\mathcal{C}_4)$	$\chi(\mathcal{C}_5)$
$(1)\Gamma$	1	1	1	1	1
$(2)\Gamma$	1	1	-1	1	-1
$(3)\Gamma$	1	-1	1	1	-1
$(4)\Gamma$	1	-1	-1	1	1
$(5)\Gamma$	2	0	0	-2	0

which are given in Table 4.6 in a compact form.

Exercises

- 4.1 Show that a similarity transformation relating two equivalent unitary Irreps must be unitary if its determinant is 1, i.e. if it is unimodular.
- 4.2 Use Schur's lemma to demonstrate that all the Irreps of an Abelian group are one dimensional. Hence the number of Reps equals the order of the group.
- 4.3 Show that the character is invariant under a similarity transformation.
- 4.4 Prove the character orthogonality relationship,

$$\sum_{\alpha} {}^{(\alpha)}\chi(\mathcal{C}_i) {}^{(\alpha)}\chi^*(\mathcal{C}_j) = \frac{g}{\text{nc}(j)} \delta_{ij},$$

for the complete set of unitary Irreps of a group G . This is useful for checking the orthonormality of columns in a character table such as in Table 4.1. (Hint: Use the first orthogonality relation to demonstrate the unitarity of the matrix

$$U_{\alpha i} = \left(\frac{\text{nc}(i)}{g} \right)^{1/2} {}^{(\alpha)}\chi(\mathcal{C}_i), \quad UU^* = E,$$

and hence show that simple commutation of this product yields the second orthogonality relation.)

- 4.5 Show that

$$\sum_{R \in \mathcal{G}} {}^{(\mu)}\chi(R) = 0,$$

for any Irrep (μ) of $\mathcal{G}$ except the identity Irrep.

- 4.6 Since the characters form an orthogonal set of vectors, as described by (4.33) and (4.34), multiply (4.37) on both sides by ${}^{(\alpha')} \chi(\hat{R}^{-1})$, sum over group elements $\hat{R}$, collect elements into classes and obtain (4.40).
- 4.7 Use Burnside's method to determine the Irreps and characters of the point-group C_3 . Do not use a computer program, rather work it out by hand.
- 4.8 Construct the character table for the group C_{4v} following the steps of Example 4.2.
- 4.9 Construct the character table for the tetrahedral point-group T .

- 4.10 Construct the class matrices for the two-dimensional Irrep of the group $\mathcal{C}_{4v}$:

$$E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad C_4 = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}, \quad C_4^{-1} = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}, \quad C_2 = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix},$$

$$\sigma_x = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \sigma'_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma'_2 = \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}.$$

Show that they commute with all the corresponding matrix operators of the group. Hence, according to Schur's lemma they should have the form of a constant (the Dirac character) times the two-dimensional unit matrix. Diagonalize these class matrices and obtain the corresponding Dirac characters.

- 4.11 Show that a necessary and sufficient condition for the irreducibility of a Rep (α) of a finite group $\mathcal{G}$ is

$$\frac{1}{g} \sum_{R \in \mathcal{G}} \left| {}^{(\alpha)}\chi(R) \right|^2 = 1.$$

- 4.12 Transform the permutations obtained in Exercise 2.16 for the point-group $\mathcal{C}_{4v}$ into matrix form, and show that it forms a matrix Rep of $\mathcal{C}_{4v}$ of dimension 4. Show that this Rep is reducible. Determine the multiplicities of the Irreps of $\mathcal{C}_{4v}$ in this Rep.
- 4.13 Determine the multiplicities of the three Irreps of $\mathcal{C}_{3v}$ in its regular Rep.

Computational projects

- (i) Write a program to generate the regular Rep. Check that the matrix representatives for $\mathcal{C}_{3v}$ are given correctly by (3.49).
- (ii) (a) Augment the class multiplication matrices program, developed in Chapter 2, with matrix diagonalization capabilities (either by using diagonalization subroutines, or using *Mathematica* functions such as `Eigenvalues[m]`, `Eigenvectors[m]`, or `Eigensystem[m]`).
- (b) Use this new program to calculate the Dirac characters of the groups: $\mathcal{C}_{6v}$, $\mathcal{D}_{3h}$, $\mathcal{T}_d$.
- (c) Determine the dimensionality of the respective Irreps.
- (d) Use (4.47) to construct the corresponding irreducible character tables.

5

Dixon's method for computing group characters

The characters of group elements in a matrix representation are complex numbers. To determine these irreducible characters with Burnside's method we begin by diagonalizing a matrix of coefficients h_{ijk} that describe the results of class multiplication. The eigenvalues obtained in this manner are simply related to the irreducible characters, as described in Chapter 4. If only groups of small order were of interest, Burnside's method might be sufficient. However, for large groups, the introduction of numerical round-off errors can be serious. Moreover, for many purposes one wants the characters expressed in algebraic form.

In 1967, John Dixon [4] devised a powerful method by which the characters can be calculated in algebraic form without suffering from numerical errors. The essence of Dixon's method is a transformation of the Burnside method from the field of complex numbers to the field of integers modulo p . For a suitable prime number p , the modular integer characters can be easily and *exactly* determined. They can then be transformed back to the ordinary irreducible characters in the field of complex numbers.

With Dixon's method, one does not actually diagonalize the class-coefficient matrix in order to determine the eigenvalues. Rather, one assumes an eigenvalue on a trial basis and then checks to see if it is correct. This is made possible because the solutions are all integers mod p where, as we shall see, $p > 2\sqrt{g}$. Even for a group with as many as, say, 10^6 elements, we need only choose $p > 2000$. It is quite simple and quick to check all of several thousand integers to see which ones satisfy the eigenvalue equations.

In this chapter we begin by considering Burnside's eigenvalue equation transformed to the field of integers modulo p , which we assume to be rigorous. After familiarizing ourselves with its solution, we introduce Dixon's method for irreducible characters. In Appendix 1, we demonstrate the validity of Burnside's eigenvalue equation in modular form.

5.1 The eigenvalue equation modulo p

Burnside's eigenvalue equation, which was described in Chapter 4 is

$$H_i \, {}^{(\alpha)}\Lambda = {}^{(\alpha)}\lambda_i \, {}^{(\alpha)}\Lambda. \quad (5.1)$$

The equivalent equation in the field of integers modulo p is

$$H_i \, \Theta \left({}^{(\alpha)}\Lambda \right) = \Theta \left({}^{(\alpha)}\lambda_i \right) \Theta \left({}^{(\alpha)}\Lambda \right), \quad (5.2)$$

where the mapping $\Theta^{(\alpha)}(\Lambda)$ is given by

$$\Theta^{(\alpha)}(\Lambda) = \left[\Theta^{(\alpha)}\lambda_1, \Theta^{(\alpha)}\lambda_2, \dots, \Theta^{(\alpha)}\lambda_{N_C} \right]. \quad (5.3)$$

Since the eigenvalues $\Theta^{(\alpha)}\lambda_i$ must be congruent to one of the integers $0, 1, \dots, p-2, p-1$, one can find all the eigenvalues by testing these p numbers. This procedure is carried out until all the eigenvalues and eigenvectors are determined.

Let us for the moment assume the correctness of (5.2), and use it in an example by modifying Burnside's method to use modular integer arithmetic. Solving it is the first step in Dixon's method, which differs from Burnside's method at this stage only in using modular arithmetic.

Example 5.1

Solving eigenvalue equations with modular arithmetic

Consider the class $\mathbf{C}_2 = \{C_3, C_3^{-1}\}$ of the point-group $\mathcal{C}_{3v}$. From (5.2) we know that the class constants λ satisfy the eigenvalue equation

$$H^{(2)} \Theta(\Lambda) = \Theta(\lambda_2) \Theta(\Lambda),$$

where the superscripts (α) have been omitted for simplicity. We know the coefficients making up the matrix $H^{(2)}$ from Example 4.6.

Now, to solve this in the spirit of Dixon's method we would first choose a suitable prime number. There are six elements in the group $\mathcal{C}_{3v}$ so we choose $p > 2\sqrt{6}$. Let's pick $p = 7$. Now we see which integers λ satisfy the eigenvalue equations such that $0 \leq \lambda < 7$. We could try 0 and find that it does not satisfy the equations. The same would hold for 1, 3, 4, and 5. We know that 2 is an eigenvalue for the class constants and so we should find that 2 satisfies the equations. It does. But it is a doubly degenerate eigenvalue. To avoid the complications arising from degeneracy, when our intent here is simply to illustrate modular arithmetic, let us go on to try $\lambda = 6$.

A good way to check whether $\lambda = 6$ is a satisfactory solution is to use Gaussian elimination with an augmented matrix. The method is as follows.

Take the *transpose* of the secular equation, which gives

$$\tilde{H}^{(2)} - \lambda \mathbb{I} = 0,$$

where $\mathbb{I}$ is the identity matrix. Construct the augmented matrix

$$\left[\tilde{H}^{(2)} - \lambda \mathbb{I} \mid \mathbb{I} \right] = \left[\begin{array}{ccc|ccc} 0 - \lambda & 2 & 0 & 1 & 0 & 0 \\ 1 & 1 - \lambda & 0 & 0 & 1 & 0 \\ 0 & 0 & 2 - \lambda & 0 & 0 & 1 \end{array} \right],$$

where $\tilde{H}^{(2)}$ is given by the transpose of $H^{(2)}$ in Example 4.6.

Now we substitute $\lambda = 6$ into the augmented matrix and get

$$\left[\begin{array}{ccc|ccc} -6 & 2 & 0 & 1 & 0 & 0 \\ 1 & -5 & 0 & 0 & 1 & 0 \\ 0 & 0 & -4 & 0 & 0 & 1 \end{array} \right].$$

Well, actually the left section of the augmented matrix is inconsistent with modular arithmetic. We should always keep in mind that when employing modular arithmetic we should confine our integers to the positive realm; we must keep only values $0, 1, \dots, 5, 6$. Thus -6 is really $+1 \pmod{7}$, since $6 + 1 \pmod{7} = 0 \pmod{7}$. We carry out each step just the same way it would be done by computer. The augmented matrix should be

$$\left[\begin{array}{ccc|ccc} 1 & 2 & 0 & 1 & 0 & 0 \\ 1 & 2 & 0 & 0 & 1 & 0 \\ 0 & 0 & 3 & 0 & 0 & 1 \end{array} \right].$$

Now multiply the first row by $6 \pmod{7}$ and add it to the second row. This gives

$$\left[\begin{array}{ccc|ccc} 1 & 2 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 6 & 1 & 0 \\ 0 & 0 & 3 & 0 & 0 & 1 \end{array} \right]$$

for the augmented matrix. The zeroes in the second row of the left-hand side demonstrate that $\lambda = 6$ is an eigenvalue. The corresponding eigenvector is given by the second row on the right-hand side, which in column form is

$$\begin{bmatrix} 6 \\ 1 \\ 0 \end{bmatrix} \pmod{7}.$$

Normalizing the first element of the eigenvector to unity by multiplying each element by $6 \pmod{7}$ gives the eigenvector

$$\begin{bmatrix} 1 \\ 6 \\ 0 \end{bmatrix} \pmod{7}.$$

One can check that this is a solution as follows:

$$\begin{bmatrix} 0 & 1 & 0 \\ 2 & 1 & 0 \\ 0 & 0 & 2 \end{bmatrix} \begin{bmatrix} 1 \\ 6 \\ 0 \end{bmatrix} = \begin{bmatrix} 6 \\ 8 \\ 0 \end{bmatrix} = 6 \begin{bmatrix} 1 \\ 6 \\ 0 \end{bmatrix}.$$

Remember! $8 \equiv 1 \equiv 36 \pmod{7}$.

These procedures are explained in some detail in Appendix 1. The treatment of degenerate eigenvalues is also explained by example.

5.2 Dixon's method for irreducible characters

Consider the character $^{(\alpha)}\chi(A)$ of the group element A described by the irreducible matrix representative $^{(\alpha)}\Gamma(\hat{A})$. The character is the trace of the matrix, which is invariant under unitary similarity transformations. It is convenient and always possible to find a similarity transformation, $\mathbf{U}$, that diagonalizes the matrix $^{(\alpha)}\Gamma(\hat{A})$:

$$\mathbf{U}^{-1} {}^{(\alpha)}\Gamma(\hat{A}) \mathbf{U} = \begin{pmatrix} a_1 & 0 & 0 & 0 & \cdots \\ 0 & a_2 & 0 & 0 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \\ 0 & 0 & \cdots & 0 & a_{d_\alpha} \end{pmatrix} \quad (5.4)$$

where d_α is the dimension of the Irrep, and the character is given by

$$^{(\alpha)}\chi(A) = \sum_{k=1}^{d_\alpha} a_k. \quad (5.5)$$

Let the order of element A be $n(A)$, so that $A^{n(A)} = E$. Then

$$\left[\Gamma(\hat{A}) \right]^{n(A)} = \Gamma(\hat{A}^{n(A)}) = \Gamma(\hat{E}) = \mathbb{I}. \quad (5.6)$$

The superscripts (α) , which designate the Irrep, have been suppressed in order to simplify the notation a bit.

We see that the diagonal elements a_k of the diagonalized matrix representative satisfy the condition

$$(a_k)^{n(A)} = 1.$$

That is, the elements a_k are either equal to unity or are roots of unity, and each a_k may be expressed in the form

$$a_k = e^{i(2\pi n_k / n(A))}, \quad (5.7)$$

where n_k is an integer. However, this does not uniquely define a_k since

$$n'_k = n_k + mn(A),$$

with m an integer, is also a satisfactory solution. To uniquely define a_k we restrict it to be a *primitive* root of unity by requiring that

$$a_k = e^{i(2\pi n_k / n(A))}, \quad 0 \leq n_k \leq (n(A) - 1). \quad (5.8)$$

The character $\chi(A)$ can now be expressed as the polynomial

$$\chi(A) = \sum_{k=1}^{d_\alpha} a_k = \sum_{r=0}^{n(A)-1} m_\alpha(r) \xi^r, \quad (5.9)$$

where ξ is a primitive $n(A)$ th-root of unity, which means that

$$\xi^{n(A)} = 1,$$

with

$$\xi^r \neq 1, \quad 0 < r < n(A). \quad (5.10)$$

The number of times each root ξ^r appears along the diagonal is the *multiplicity*, $m_\alpha(r)$. Since the maximum number of times it can appear is given by the dimension of the matrix, we must have

$$0 \leq m_\alpha(r) \leq d_\alpha.$$

Equation (5.9), which applies to each Irrep (α), can be further simplified. We know that all elements of a class are of the same order and have the same character. Thus we can write that for the class $\mathcal{C}_i$ and Irrep (α):

$$\chi(\mathcal{C}_i) = \sum_{k=1}^{d_\alpha} a_k = \sum_{r=0}^{n_i-1} m_\alpha(r) \xi^r, \quad (5.11)$$

where n_i is the order of an element belonging to class $\mathcal{C}_i$.

A computer program for calculating characters need only use one group element from each class to determine the character of elements of the class.

Since each class of a group is of a particular order, we set n be the *least common multiple* of all the class orders ($n_1, n_2, n_3, \dots$) of the group. We define n to be the *exponent* of the group. Thus

$$R^n = E \quad \forall R \in \mathcal{G}.$$

Now let ζ be a primitive n th root of unity. Then

$$\begin{aligned} \zeta^n &= 1, \\ \zeta^r &\neq 1, \quad 0 < r < n. \end{aligned} \quad (5.12)$$

Once again the irreducible characters can be expressed as polynomials in primitive roots of unity with *integer* coefficients. Now, though, the polynomial is of degree n , which is the exponent of the group. Expressing the character for the class $\mathcal{C}_i$, we obtain

$$\chi(\mathcal{C}_i) = \sum_{k=1}^{d_\alpha} a_k = \sum_{r=0}^{n-1} m_\alpha(r) \zeta^r, \quad (5.13)$$

where the summation over a_k is for any element of the class. Note that since n is a multiple of $n(R)$ for all $R \in \mathcal{G}$, the equation for χ automatically includes all the necessary primitive $n(R)$ th roots of unity for each element R .

Example 5.2

Characters of $\mathcal{C}_{3v}$ as polynomials in primitive roots

$\mathcal{C}_{3v}$ has three classes:

$$\begin{aligned} \mathcal{C}_1 &= \{E\}, & n(\mathcal{C}_1) &= 1, \\ \mathcal{C}_2 &= \{D, F\}, & D^2 = F, D^3 = E, & n(\mathcal{C}_2) = 3, \\ \mathcal{C}_3 &= \{A, B, C\}, & A^2 = E, & n(\mathcal{C}_3) = 2. \end{aligned}$$

The exponent of the group is $n = 6$ in this trivial case.

Now consider the two-dimensional diagonal matrix Reps for the elements E and A :

$$E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad A = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}.$$

The matrices are already in diagonal form, so we can identify the primitive roots of unity by inspection. Using (5.9) we find

$$\begin{aligned} \chi(\mathcal{C}_1) = \chi(E) &= \sum_{r=0}^{n(E)-1} m(r) \xi^r = \sum_{r=0}^0 m(r) \xi^r \\ &= m(0) \xi^0 = 2 \times 1 = 2, \end{aligned}$$

since both diagonal elements of E are unity and the multiplicity is obviously 2. For $\chi(\mathcal{C}_3)$, we obtain

$$\chi(\mathcal{C}_3) = \chi(A) = \sum_{r=0}^{n(A)-1} m(r) \xi^r = \sum_{r=0}^1 m(r) \xi^r.$$

With $n(A) = 2$, we have $\zeta = e^{i(2\pi/2)} = -1$. Thus

$$\begin{aligned} \chi(\mathcal{C}_3) &= m(0) \xi^0 + m(1) \xi^1 \\ &= 1 \times (-1)^0 + 1 \times (-1)^1 = 0, \end{aligned}$$

because the roots are each of multiplicity 1 by inspection.

If we were to use (5.13), which is what we would do in the computer program whose development is outlined in this book, we would use $n = 6$, the exponent of the group, and obtain, for example,

$$\chi(\mathcal{C}_3) = \chi(A) = \sum_{r=0}^{n-1} m(r) \zeta^r = \sum_{r=0}^5 m(r) \zeta^r.$$

The primitive 6th root of unity is $\zeta = e^{i(2\pi/6)} = e^{i(\pi/3)}$, giving

$$\begin{aligned}\chi(\mathbb{C}_3) &= m(0)\zeta^0 + m(1)\zeta^1 + m(2)\zeta^2 + \cdots + m(5)\zeta^5 \\ &= m(0) + m(1)e^{i(\pi/3)} + m(2)e^{i(2\pi/3)} \\ &\quad + m(3)e^{i\pi} + m(4)e^{i(4\pi/3)} + m(5)e^{i(5\pi/3)}.\end{aligned}$$

Once again, we can determine terms by inspection, finding that only terms in ζ^0 and ζ^3 contribute, and that $m(0)$ and $m(3)$ are each unity. Thus

$$\chi(\mathbb{C}_3) = 1 \times e^0 + 1 \times e^{i\pi} = 1 - 1 = 0.$$

The trick of course is to know the multiplicities. If they are known, the calculation of the character is straightforward. Here they were known from inspection. Shortly, we will develop the algorithm for the determination of the multiplicities.

5.2.1 Integer polynomials modulo p

We have demonstrated that the characters of group elements can be expressed as polynomials in primitive roots of unity. The roots of unity are in the field of complex numbers, but the coefficients are integers. A key step in the exact calculation of characters is a *mapping of these polynomials in the field of complex numbers to the field of integers modulo a prime number p , but with identical integer coefficients modulo p .*

The mapping is given by

$$\sum_{r=0}^{n-1} m_{\alpha}(r) \zeta^r \xrightarrow{\Theta} \sum_{r=0}^{n-1} \mu_{\alpha}(r) Z^r \bmod p, \quad (5.14)$$

where Z is an *integer* and $\mu_{\alpha}(r)$ is an integer modulo a suitably chosen prime number p . Within the constraints given by the prime number p and its modulus, we have

$$m_{\alpha}(r) = \mu_{\alpha}(r). \quad (5.15)$$

We call the polynomial in Z an integer polynomial modulo p .

In the language of pure mathematics, these polynomials form *commutative rings*. We provide an introduction to these concepts in Appendix 2, along with a proof of the mapping and proofs of the key points that follow in this section. However, for those whose

interest is primarily in using group theory, the outline of the method which follows is quite sufficient.

To construct the integer polynomial we seek a prime number p which, for reasons to be demonstrated later, satisfies the conditions

$$p > 2\sqrt{g} \quad (5.16)$$

and

$$p = 1 + mn, \quad (5.17)$$

where g and n are the group order and exponent, respectively, and m is an integer. The existence of such a prime number is demonstrated through Dirichlet's theorem.

Next we define the congruence of two integers u and v , denoted by

$$u \equiv v \text{ modulo } p \quad (5.18)$$

as

$$u = v + kp, \quad (5.19)$$

where k is an integer.

For polynomials we define congruence as

$$\sum_{i=0}^n c_i x^i \equiv \sum_{i=0}^n d_i x^i \text{ mod } p, \quad \text{if } c_i \equiv d_i \text{ mod } p. \quad (5.20)$$

Remember, we are considering polynomials with integer coefficients, and it is the corresponding *coefficients* that are congruent.

Now to return to our mapping problem, we replace the primitive root ζ by an integer Z such that

$$\begin{aligned} Z^n &\equiv 1 \text{ mod } p, \\ Z^k &\not\equiv 1 \text{ mod } p, \quad 0 < k < n. \end{aligned} \quad (5.21)$$

Z is a primitive root of unity in the field of integers mod p .

Example 5.3

Integer primitive roots

For our example group, $g = 6$. Thus, we must choose a prime number $p > 2\sqrt{6}$. This requires $p \geq 5$. But, since the exponent of the group ($n = 6$) must be a divisor of $p - 1$,

we must choose $p = 1 + 6m = 7, 13, 19, \dots$, according to (5.17). Let us take the smallest allowed value, $p = 7$.

Since the exponent of the group is $n = 6$, we must pick an integer Z such that

$$Z^6 \equiv 1 \pmod{7}$$

with

$$Z^k \not\equiv 1 \pmod{7}, \quad k = 1, 2, 3, 4, 5.$$

We find Z by systematic testing, beginning with $Z = 2$:

$$\begin{aligned} 2^1 &= 2 \\ 2^2 &= 4 \\ 2^3 &= 8 \equiv 1 \pmod{7} \end{aligned}$$

Clearly $Z = 2$ is unsatisfactory. It does not meet the requirement that

$$Z^k \not\equiv 1 \pmod{7}, \quad 0 < k < 7.$$

Next we test $Z = 3$:

$$\begin{aligned} 3^1 &= 3 \\ 3^2 &= 9 \not\equiv 1 \pmod{7} \\ 3^3 &= 27 \not\equiv 1 \pmod{7} \\ 3^4 &= 81 \not\equiv 1 \pmod{7} \\ 3^5 &= 243 \not\equiv 1 \pmod{7} \\ 3^6 &= 729 \equiv 1 \pmod{7} \end{aligned}$$

Thus $Z = 3$ meets the criteria of (5.16) and (5.17).

Now consider the mapping of (5.14) applied to the character $^{(\alpha)}\chi(A)$. Clearly, it may be written as

$$\Theta \left(^{(\alpha)}\chi_i(A) \right) = \sum_{r=0}^{n-1} m_{\alpha i}(r) Z^r, \quad (5.22)$$

where i denotes the class to which A belongs and μ has been replaced by m in recognition of the identity of these coefficients as defined by (5.15). The same mapping can be applied to the class constants, namely

$$\Theta \left(^{(\alpha)}\lambda_i \right) = \frac{n e_i}{d_\alpha} \sum_{r=0}^{n-1} m_{\alpha i}(r) Z^r. \quad (5.23)$$

Consequently,

$$\Theta \left({}^{(\alpha)}\lambda_i \right) \Theta \left({}^{(\alpha)}\lambda_j \right) = \sum_{k=1}^{n_c} h_{ijk} \Theta \left({}^{(\alpha)}\lambda_k \right), \quad (5.24)$$

which, as in the original method of Burnside, leads to the set of eigenvalue equations

$$H^{(i)} \Theta \left({}^{(\alpha)}\Lambda \right) = \Theta \left({}^{(\alpha)}\lambda_i \right) \Theta \left({}^{(\alpha)}\Lambda \right). \quad (5.25)$$

We have seen how to solve this modular eigenvalue equation in Section 5.1 and more detail is given in Appendix 1.

5.2.2 Multiplicities and the character

We have shown that the character can be expressed as a sum of primitive roots of unity. For our present purposes we simplify the notation by dropping subscripts and superscripts that denote a particular class or Irrep and write the character for group element A as

$$\chi(A) = \sum_{j=0}^{n-1} m_j \xi^j. \quad (5.26)$$

Now what we want are the multiplicities, for if we knew them we could determine $\chi(A)$ numerically or even express it *exactly* in polynomial form. We can derive an equation for the coefficients m_j , the multiplicities of the roots of unity, following a standard procedure that is quite similar to that for finding the coefficients in a Fourier series expansion. But first, it is convenient to introduce an equation that is similar to (5.26), namely,

$$\chi(A^t) = \sum_{j=0}^{n-1} m_j \xi^{jt}. \quad (5.27)$$

This says that the character of a power of an element is given by a polynomial with the same multiplicities as for the character of the element itself but with each of the roots of unity raised to the same power to which the element is raised. This equation follows from expressing roots of unity as $e^{i\theta}$ and recognizing that

$$e^{i\theta_1} e^{i\theta_2} = e^{i(\theta_1+\theta_2)}.$$

Its validity is perhaps best illustrated by example.

Example 5.4

Multiplicities and the character of powers of an element

Suppose the unitary diagonal-matrix representation for A is given by

$$A = \begin{pmatrix} e^{i\alpha} & 0 & 0 \\ 0 & e^{i\alpha} & 0 \\ 0 & 0 & e^{i\beta} \end{pmatrix}.$$

Then the character is given by

$$\chi(A) = 2e^{i\alpha} + e^{i\beta}.$$

Now, the matrix Rep for A^2 , for example, is given by

$$\begin{aligned} A^2 &= \begin{pmatrix} e^{i\alpha} & 0 & 0 \\ 0 & e^{i\alpha} & 0 \\ 0 & 0 & e^{i\beta} \end{pmatrix} \begin{pmatrix} e^{i\alpha} & 0 & 0 \\ 0 & e^{i\alpha} & 0 \\ 0 & 0 & e^{i\beta} \end{pmatrix} \\ &= \begin{pmatrix} e^{2i\alpha} & 0 & 0 \\ 0 & e^{2i\alpha} & 0 \\ 0 & 0 & e^{2i\beta} \end{pmatrix}, \end{aligned}$$

and the character is given by

$$\chi(A^2) = 2e^{2i\alpha} + e^{2i\beta},$$

with the same multiplicities as for the character of A itself, as expected from (5.27).

From the modular class constants, we can compute the modular characters $\Theta \left({}^{(\alpha)}\chi_i \right)$ according to

$$\Theta \left({}^{(\alpha)}\chi_i \right) = \frac{d_\alpha}{n c_i} \Theta \left({}^{(\alpha)}\lambda_i \right), \quad (5.28)$$

if we know the dimension of the Irrep.

Using the modular equivalent of (4.52), we obtain the dimensions of the different Irreps from

$$|d_\alpha|^2 \equiv \frac{g}{\left(\sum_i \Theta(\lambda_i) \Theta(\lambda_i^{-1}) / \text{nc}(i) \right)} \pmod{p}. \quad (5.29)$$

Since $g = \sum d_\alpha^2$, the choice of $p > 2\sqrt{g}$ ensures that $p > 2d_\alpha$ so that we can determine the d_α s uniquely.

Now, knowing $\Theta\left({}^{(\alpha)}\chi_i\right)$ and Z , we can compute the multiplicities $m_{\alpha i}(r)$ from the relation

$$\begin{aligned} m_{\alpha i}(r) &= \frac{1}{n} \sum_{t=0}^{n-1} \Theta\left({}^{(\alpha)}\chi_i(A^t)\right) Z^{-rt} \bmod p \\ &= \frac{1}{n} \sum_{t=0}^{n-1} {}^{(\alpha)}\chi_i(A^t) \zeta^{-rt}. \end{aligned} \quad (5.30)$$

The proof of this equation is

$$\begin{aligned} \frac{1}{n} \sum_{t=0}^{n-1} {}^{(\alpha)}\chi_i(A^t) \zeta^{-rt} &= \frac{1}{n} \sum_{t=0}^{n-1} \left(\sum_{u=0}^{n-1} m_{\alpha i}(u) \zeta^{ut} \right) \zeta^{-rt} \\ &= \frac{1}{n} \sum_{u=0}^{n-1} m_{\alpha i}(u) \sum_{t=0}^{n-1} \zeta^{t(u-r)} \\ &= \frac{1}{n} \sum_{u=0}^{n-1} m_{\alpha i}(u) n \delta_{u,r} \\ &= m_{\alpha i}(r), \end{aligned} \quad (5.31)$$

where we have used the fact that the group element A^t has an eigenvalue ζ^{ut} occurring with the same multiplicity $m_{\alpha i}(u)$ as the eigenvalue ζ^t of the group element A , as shown by (5.29). Since $0 \leq m_{\alpha i}(r) \leq d_{\alpha} \leq p$, (5.30) determines the multiplicities $m_{\alpha i}(r)$ uniquely. Finally, one uses (5.28) to determine the irreducible characters, as demonstrated in Appendix 2.

5.3 Computer codes for Dixon's method

Dixon's method is readily amenable to computational techniques. Numerical algorithms for modulo arithmetic as well as the Gauss elimination method are easily implementable. Moreover, there are existing packages that can simplify further the implementation of Dixon's method, foremost among those is found in *Mathematica*.

Mathematica provides a computational package for number theory that contains many useful functions for this purpose. It is called `NumberTheory`NumberTheoryFunctions``. The functions that are relevant here are:

- `LCM[integer list]` : gives the least common multiple of the `integer list`.
- `Prime[n]` : gives the `nth` prime number.
- `Mod[m,n]` : gives the remainder on division of `m` by `n`, i.e. `m` modulo `n`.
- `PowerMod[a,b,n]` : gives `ab` modulo `n`.
- `PowerMod[a,-1,n]` : gives the inverse of `a` modulo `n`.
- `MultiplicativeOrder[k,n]` : gives the smallest integer `m` such that `km ≡ 1` modulo `n`.

Generating group exponent ngrp First, we generate the exponents of representative class elements, then find the lowest common multiple among them. The exponent of class i is found by satisfying the relation $LC[i, 1]^{Cexp[i]} = E$, the identity element; where $LC[i, 1]$ is the first element in the i th class array, and $Cexp[i]$ is the array containing class exponents. $m[i, j]$, the binary product of elements i and j , is used in the multiplication process.

```

Cexp={1}
Do[
  t=LC[i,1];ncexp=1;
  While[
    t≠1,t=m[[LC[[i,1]],t]];ncexp==ncexp+1
  ];
  AppendTo[Cexp,ncexp],{i,2,nc}
]
ngrp=Cexp[[2]]
Do[
  ngrp=LCM[ngrp,Cexp[[i]]],{i,3,nc}
]

```

Generating the prime number pp

```

i=2; pp=Prime[2]
While[Mod[pp,ngrp]≠1],i++;pp=Prime[i]]

```

Generating the primitive root Z

```

Z=2; mm=1
While[mm≠ngrp,Z++;mm=MultiplicativeOrder[Z,pp]]

```

Gauss's method for eigenvalue problem We denote the class-matrices by $CM[ii, i, j]$, where ii is the class index and i, j the matrix element indices. We first set up the augmented matrix, which is composed of the transpose of $CM[ii]$, together with the *augmenting* matrix $augm[i, j]$, such that eigenvectors will appear as eigenrows of $augm[i, j]$. Using $-ev$ as trial eigenvalue, which can assume integer numbers between 0 and $(pp-1)$, we determine the class-constant eigenvectors of $CM[ii]$, which now appear as rows of $augm[i, j]$. If degenerate eigenspaces are present, we repeat this procedure, but now we use $augm[i, j]$ composed of the eigenrows of the class-matrix CM and augment

it with another class-matrix, say $\mathbf{CM}'$, after projecting out the degenerate eigenspace of $\mathbf{augm}[i, j]$. We carry out the search for eigenrows only on the degenerate subspace. This process is repeated until all nondegenerate eigenvectors of the class-constant matrices are obtained. Current eigenrows are stored in **Dirac**:

1. Initialize $\mathbf{augm}[i, j]$ as eigenrows of the identity class-matrix $\mathbf{CM}[[1]]$, with degeneracy $\mathbf{nc}$.

```
nc2=2*nc
ii=1
Do[Dirac[i,j]=0,{i,1,nc},{j,1,nc}]
Do[last[i]=0,{i,1,nc}]
last[1]=nc
Do[
  Do[augm[i,j]=0,{j,1,nc}];
  augm[i,i]=1,{i,1,nc}]
```

2. Construct the matrix $c[i, j] = \sum_k \mathbf{augm}[i, k] * \mathbf{CM}^{\text{Transpose}}[k, j]$, where $\mathbf{CM}$ is the current class-matrix, and i runs over the rows of the degenerate subspace, which start with row $\mathbf{ist}$ and end at row $\mathbf{ind}=\mathbf{last}[\mathbf{ist}]$.

```
While[
  ii<nc,
  ii++;b=CM[[ii]]; b=Transpose[b];
  ist=1;
  Label[Try];
  Switch[last[ist]=ist,True,Goto[Fin]];
  ven=ist;ind=last[ist];
  Do[
    Do[
      c[i,j]=0;
      Do[c[i,j]+=augm[i,k]*b[[k,j]],
        {k,1,nc}],
      {j,1,nc}],
    {i,ist,ind}];
```

3. Start trial eigenvalues $\mathbf{ev}$, from 0 to $(\mathbf{pp}-1)$. Project out the eigenspace of known eigenvectors by constructing the matrix, $\mathbf{evd} = \mathbf{augm} * \mathbf{CM}(\text{transpose}) - \lambda * \mathbf{augm}$, which is just

the subspace orthogonal to the eigenvectors in **augm**. Construct the augmented matrix as $d = [\text{augm} \mid \text{evd}]$, and convert it to modulo **pp**. Use **flag** to give the degeneracy of the eigenvalue.

```

ev=-1;
While[
  And[ev<pp-1,ven<=ind],ev++;
  flag=0;
  Do[
    evd[i,j]=ev augm[i,j] + c[i,j],
    {i,1,nc},{j,1,nc}];
  Do[
    Do[
      k=j+nc;d[i,j]=augm[i,j];
      d[i,k]=evd[i,j],{j,1,nc}],
    {i,1,nc}];
  Do[
    d[i,j]=Mod[d[i,j],pp],{i,1,nc},
    {j,nc+1,nc2}];
  ix=ven;

```

4. Begin Gauss elimination, in modulo **pp**, over the degenerate subspace that starts at row **ist**, and ends at row **ind**. When a row of zeroes is found in **evd**, then the corresponding row in **augm** is an eigenrow. The new eigenrow is then stored in **Dirac**.

```

Do[
  jj=nc+1;
  While[And[d[i,jj]==0,jj<=nc2],jj++];
  Switch[jj<=nc2,
    True,
    inv=PowerMod[d[i,jj],-1,pp];
    Do[
      d[i,j]=Mod[inv*d[i,j],pp],
      {j,1,nc2}];

```

```

Do[
  dd=pp-d[k,jj];
  Do[
    d[k,l]=Mod[dd*d[i,l]
      +d[k,l,pp],
      {1,1,nc2}],
    {k,i+1,ind}],
  False,flag++;ven++;jx=ven-1;
  Do[
    Dirac[jx,j]=d[i,j],
    {j,1,nc}];
  ],{i,ist,ind}
];
last[ix]=jx
];

```

5. At the end of the eigenvalue search `Dirac` is used to update the `augm` matrix with the newly determined eigenrows.

```

Label[Fin];
Do[ augm[i,j]=Dirac[i,j], {i,ist,ind},{j,1,nc}];

```

6. If all nondegenerate eigenvectors have been obtained, exit the eigenvector search. Otherwise, continue reducing the remaining degenerate subspaces.

```

Switch[
  last[ist]==nc,
  True,i=0;
  While[i<nc,i++;
    Switch[last[i]!=i,
      True,Goto[Begin]]];
  qq1=1;

```

```

Switch[
    qq1==1,True,Goto[Gd]
],
False,ist=last[ist]+1;
Switch[
    last[ist]==0,
    True, Goto[Panic],
    False,Goto[Try]
];Label[Begin]
]

```

7. The final nondegenerate eigenrows are stored in `Dirac`. Normalize the eigenrow matrix `Dirac` so that the first column is composed of ones. Each row of `Dirac` will then contain an Irrep Dirac characters in modulo `pp`.

```

Label[Gd]
Do[Inv1=PowerMod[Dirac[i,1],-1,pp]
  Do[
    Dirac[i,j]=Mod[Dirac[i,j]*inv1,pp],
    {j,1,nc}
  ],{i,1,nc}
]

```

8. Use the Dirac characters to compute the dimensions of the Irreps $d(i)$, in modulo `pp`, using the relation

$$d^2(i) = g / \sum (\lambda^2(j)/r(j)),$$

where $\lambda(j)$ is the Dirac character of the j th class, and $r(j)$ the class size.

```

Do[dim2[i]=0,{i,1,nc}]
Do[
  d2=0;
  Do[
    ri=PowerMod[Length[LC[[j]]],-1,pp];

```

```

        d2=Mod[d2+Dirac[i,j]**2*ri,pp],
        {j,1,nc}
    ];
    d2=PowerMod[d2,-1,pp];
    dm=Mod[g*d2,pp];
    dim2[i]=dm,{i,1,nc}
]
Do[
    Switch[
        dim2[i]==1,
        False,j=1;dm=1;
        While[And[j<pp/2,dim2[i]!=dm],
            j++;dm=Mod[j**2,pp]];
        dim2[i]=j
        ],{i,1,nc}
]

```

9. Compute character multiplicities using the relation

$$m_{\alpha i}(r) = (1/n) \sum_{t=0}^{n-1} \Theta \left({}^{(\alpha)}\chi_i(A^t) \right) Z^{-rt} \pmod{p}$$

where α and i are Irrep and class indices, respectively, and Z is the primitive root modulo pp .

```

cip={}
chit={}
Do[
    Do[
        ri=PowerMod[Length[LC[[j]]],-1,pp];
        ch=Mod[ri*dim2[[i]]*Dirac[[i,j]],pp];
        AppendTo[chit,ch],{j,1,nc}
    ];
    AppendTo[cip,chit];chit={},{i,1,nc}
]

```



```

nm1=PowerMod[nm,-1,pp]
Do[mult[i,j,k]=0,{i,1,nc},{j,1,nc},{k,1,nn}]
Do[
  mmx=0;
  Do[
    mmx+=cip[[i,cc1[j,1]]]*zz[k,1];
    mult[i,j,k]=Mod[mmx*nm1,pp],{1,1,nc}
  ],
  {i,1,nc},{j,1,nc},{k,1,nn}
]

```

10. Use the multiplicities to compute the Irrep characters, according to the relation

$$^{(\alpha)}\chi(i) = \sum_{j=0}^{n-1} m_{\alpha i}(j) \xi^j$$

and store them in `char`.

```

Do[char[i,j]=0,{i,1,nc},{j,1,nc}]
Do[
  Do[
    char[i,j]+=mult[i,j,k]*Exp[i(2*π*(k-1)/nn),
      {k,1,nn}
    ],
    {i,1,nc},{j,1,nc}
  ]
]

```

11. Set up Irreps in ascending order of their dimensions. Store the complete one-dimensional Irreps of group elements in file Γ , and the corresponding class characters in array `charac`. The first Irrep is the identity.

```

tempo={}
Γ = {}
Do[charac[i,j]=0,{i,1,nc},{j,1,nc}]
Do[ban[i]=0;dim[i]=0,{i,1,nc}]

```

```

dim[1]=1
nrep=1
Do[AppendTo[tempo,1],{j,1,nc}];
Do[charac[1,j]=1,{j,1,nc}];
AppedTo[Γ,tempo];tempo={}
Do[
  Switch[
    And[dim2[i]==1,ban[i]==0,
    Sum[char[i,j],{j,1,nc}]!=nc],
    True,nrep++;ban[i]=1;
    dim[nrep]=dim2[i];
    Do[
      AppendTo[tempo,charac[i,indc[j]]],
      {j,1,g}];
    AppendTo[Γ,tempo];tempo={};
    Do[charac[nrep,j]=char[i,j],{j,1,nc}]
  ],{i,1,nc}
]

```

12. Add the characters of the remaining Irreps to the array **charac**, in ascending order of their dimensions.

```

i1=1; i3=nrep+1
dmax=IntegerPart[√g]
While[
  And[i1<dmax,Sum[ban[ix],{ix,nc}]<nc,i3<=nc],
  i1++;i=1;
  While[
    And[i<=nc,i3<=nc],
    Switch[
      And[dim2[i]==i1,ban[i]==0],
      True,dim[i3]=dim2[i];ban[i]=1;

```

```

Do[charac[i3,j]=char[i,j],
  {j,1,nc}];
i3++
];
i++
]
]

```

13. Print the Irrep characters in ascending order of dimensions.

```

chi=Array[charac,{nc,nc}]
Print["IRREPS PRINTED IN ASCENDING ORDER
      OF DIMENSION: "]
Print[IRREP DIMENSION: dim= ",
      dimension=Array[dim,{nc}]]
Print["IRREDUCIBLE CHARACTERS: "]
Do[
  Print[StyleForm["χ(",FontWeight→ "Bold"],
    i,"] = "
    Simplify[chi[[i]]],{i,1,nc}]
Label[Panic]

```

Appendix 1 Finding eigenvalues and eigenvectors

The basis for the computational methods that are central to computational group theory as described in this book is the solution of the eigenvalue equation

$$H^{(i)} \Lambda^{(\alpha)} = \lambda_i^{(\alpha)} \Lambda^{(\alpha)}, \quad (5.32)$$

where α denotes an Irrep and i denotes the i th class. We know from Chapter 5 how to find the set of coefficients h_{ijk} that make up the elements of the matrix $H^{(i)}$. The unknowns are the eigenvalues $\lambda_i^{(\alpha)}$ and the eigenvectors $\Lambda^{(\alpha)}$.

Suppose the matrix $H^{(i)}$ is 3×3 . Then we must find three eigenvalues and three corresponding eigenvectors as represented by three equations, one for each irreducible

representation:

$$\begin{aligned} H^{(i)} \Lambda^{(1)} &= \lambda_i^{(1)} \Lambda^{(1)} \\ H^{(i)} \Lambda^{(2)} &= \lambda_i^{(2)} \Lambda^{(2)} \\ H^{(i)} \Lambda^{(3)} &= \lambda_i^{(3)} \Lambda^{(3)} \end{aligned}$$

We can represent this set of equations in matrix form as

$$H^{(i)} V = V \boldsymbol{\lambda}, \quad (5.33)$$

where the columns of the matrix V are the eigenvectors $\Lambda^{(\alpha)}$ and $\boldsymbol{\lambda}$ is the matrix

$$\boldsymbol{\lambda} = \begin{bmatrix} \lambda_i^{(1)} & 0 & 0 \\ 0 & \lambda_i^{(2)} & 0 \\ 0 & 0 & \lambda_i^{(3)} \end{bmatrix}.$$

We can rewrite (5.33) and set its determinant equal to zero, giving

$$\left| H^{(i)} V - V \boldsymbol{\lambda} \right| = 0. \quad (5.34)$$

Of course the eigenvectors are unknown, so we will start with three basis vectors, one for each dimension, as represented by the unit matrix. Thus we take

$$V = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

as a starting set of basis vectors that span the three-dimensional space.

It is important to think of V as a matrix of vectors spanning a space, not simply as the unit matrix. The importance of this distinction will be made clear in a later section on Dixon's method, where it will have important implications for solving (5.33) in the case of degenerate eigenvalues.

Now we must address the problem of the eigenvalues. Suppose we could *guess* them. There are ways of systematically iterating an original guess so as to converge on the true value, but here we mean an *exact* guess. Of course, in general, this would be a pointless procedure. One would usually have zero probability of guessing correctly from a continuous set of possible eigenvalues. On the other hand, if the eigenvalues were known to be a subset of a reasonably sized finite set of *known* possible values, which is the case for Dixon's method, guessing might have an advantage over other methods. More accurately, rather than making guesses, one could simply try all possible eigenvalues and find which ones satisfy (5.34).

Example 5.5

Consider the matrix

$$H = \begin{bmatrix} 4 & 1 \\ 2 & 3 \end{bmatrix},$$

and suppose the possible eigenvalues are known to be integers $0 \leq \lambda \leq 10$. We could then just substitute trial values of λ into the secular equation

$$\begin{vmatrix} 4 - \lambda & 1 \\ 2 & 3 - \lambda \end{vmatrix} = 0$$

to find the actual values. One finds from direct substitution of trial values that $\lambda = 2, 5$. However, there is a more systematic way of checking, a way that in the process also yields the corresponding eigenvectors.

Write down an augmented matrix for which the left-hand side (l.h.s.) consists of the elements in the determinant of (5.34) and the right-hand side (r.h.s.) is the matrix V . For our present example we have

$$\left[\begin{array}{cc|cc} 4 - \lambda & 1 & 1 & 0 \\ 2 & 3 - \lambda & 0 & 1 \end{array} \right].$$

Now the l.h.s. of the augmented matrix will be zero if any column (or row) consists of all zeroes. Thus we can substitute possible values of λ and systematically operate on columns by standard procedures to see if it is possible to get a column of zeroes in the l.h.s. At the same time, we make identical operations on the corresponding columns in the r.h.s. of the augmented matrix.

To see how this works, we try one of the known eigenvalues, $\lambda = 2$. The augmented matrix becomes

$$\left[\begin{array}{cc|cc} 2 & 1 & 1 & 0 \\ 2 & 1 & 0 & 1 \end{array} \right]$$

for which the operations are trivial. Multiply the first column of each side of the augmented matrix by $1/2$. Then, on each side of the augmented matrix, subtract the first column from the second column. The result is

$$\left[\begin{array}{cc|cc} 1 & 0 & 1/2 & -1/2 \\ 1 & 0 & 0 & 1 \end{array} \right].$$

The column of zeroes, the second column on the l.h.s., tells us that the equations are satisfied and that $\lambda = 2$ is indeed an eigenvalue. The corresponding column on the r.h.s. is now the eigenvector belonging to the eigenvalue $\lambda = 2$. One can check that this is so by substituting into (5.32), obtaining

$$\begin{bmatrix} 4 & 1 \\ 2 & 3 \end{bmatrix} \begin{bmatrix} -1/2 \\ 1 \end{bmatrix} = 2 \begin{bmatrix} -1/2 \\ 1 \end{bmatrix},$$

carrying out the operation, and verifying that the solution is correct.

Now, in actual practice, especially when using a computer program, it is often more convenient to take the *transpose* of the matrices and operate on the *rows* of the corresponding augmented matrix to try to get a row of zeroes on the l.h.s. If that is possible, the remainder of the row on the r.h.s. contains the corresponding eigenvector.

The Gauss elimination method: a peculiar method for matrix eigenvalue problems!

The essence of Burnside's method is that the class constants can be determined by diagonalizing the class-constant matrix and then finding the group characters from the class constants, as described in Chapter 4. However, rather than try to directly diagonalize a class-constant matrix, we now work through an example problem to find the class constants for the group $\mathcal{C}_{3v}$ using the procedure we have just described for finding eigenvalues and eigenvectors. We are doing it here only for tutorial purposes, as a preliminary to Dixon's method, but without yet introducing the complications of modular arithmetic that are an ingredient of Dixon's method.

This procedure finds its roots in the method of *Gauss elimination*, which is traditionally applied to the matrix inversion problem. The inverse of a matrix $\mathbf{A}$ is found through the defining equations

$$\mathbf{A} \mathbf{X} = \mathbf{I}, \quad (5.35)$$

$$\mathbf{I} \mathbf{X} = \mathbf{A}^{-1}, \quad (5.36)$$

where $\mathbf{I}$ is the identity matrix. This can be written in augmented matrix form as

$$\left[\begin{array}{ccc|ccc} a_{11} & a_{12} & a_{13} & 1 & 0 & 0 \\ a_{21} & a_{22} & a_{23} & 0 & 1 & 0 \\ a_{31} & a_{32} & a_{33} & 0 & 0 & 1 \end{array} \right], \quad (5.37)$$

$$\left[\begin{array}{ccc|ccc} 1 & 0 & 0 & a_{11}^{-1} & a_{12}^{-1} & a_{13}^{-1} \\ 0 & 1 & 0 & a_{21}^{-1} & a_{22}^{-1} & a_{23}^{-1} \\ 0 & 0 & 1 & a_{31}^{-1} & a_{32}^{-1} & a_{33}^{-1} \end{array} \right], \quad (5.38)$$

for the case of a 3×3 matrix. The steps from equation (5.37) to equation (5.38) follow the Gauss elimination recipe.

Now, consider the matrix eigenvalue problem

$$\mathbf{X}^T [\mathbf{A}^T - \lambda \mathbf{I}] = \mathbf{0}, \quad (5.39)$$

where we have taken the transpose of $\mathbf{A}$, for reasons to be clarified shortly. If λ is replaced by $\omega \neq \lambda$, then, following the Gauss elimination method we have

$$\mathbf{X}^T [\mathbf{A}^T - \omega \mathbf{I}] = \mathbf{I}, \quad (5.40)$$

$$\mathbf{I} \mathbf{X} = [\mathbf{A}^T - \omega \mathbf{I}]^{-1}. \quad (5.41)$$

However, if now we put λ back, satisfying (5.39), the singularity of $[\mathbf{A}^T - \omega \mathbf{I}]$ implies that one or more of its rows are linear combinations of one or more of the remaining rows. The process of the Gauss elimination will then produce zero rows, the number of which will reflect the degeneracy of the eigenvalue λ . For the sake of simplicity, we use the transpose of $\mathbf{A}$ so that the eigenvectors appear as eigenrows. Upon carrying out Gauss row elimination,

we find that for every row of zeroes that appear on the l.h.s. of the augmented matrix, the corresponding row on the r.h.s. is just the eigenvector that produces the null space represented by the zero row. This scenario assumes that we know the actual eigenvalues of $\mathbf{A}$. As we demonstrated, when we work in modulo a prime number p , the eigenvalue has to be one of the integers $0 < i < p$. In this case, as we try the different integers, only true eigenvalues will produce zero rows. Usually, the Gauss elimination method is used to find the solution of a system of linear equations or to find the inverse of a matrix. Since it is usually the eigenvalues that are sought, this method is never used in a conventional matrix eigenvalue problem.

Implementation of Gauss elimination in Burnside's method

In constructing the class-constant matrices with a computer program, the form of the matrices will vary depending upon the choice of generators and the order in which they are read into the program. One possibility for the matrix $H^{(3)}$ is

$$H^{(3)} = \begin{bmatrix} 0 & 1 & 0 \\ 3 & 0 & 3 \\ 0 & 2 & 0 \end{bmatrix}.$$

Compare this with $H^{(3)}$ from Chapter 4.

Now we systematically operate on *rows* of the augmented matrix but using the *transpose* of $H^{(3)}$ and other matrices to determine eigenvalues and eigenvectors.

The augmented matrix is

$$\left[\tilde{V} \tilde{H}^{(3)} \quad -\lambda \tilde{V} \mid \tilde{V} \right] = \left[\begin{array}{ccc|ccc} -\lambda & 3 & 0 & 1 & 0 & 0 \\ 1 & -\lambda & 2 & 0 & 1 & 0 \\ 0 & 3 & -\lambda & 0 & 0 & 1 \end{array} \right].$$

Note the change in order for matrix multiplication because of the use of transposed matrices. We have used λ as a scalar because we are going to check possible values of λ one at a time. For expediency we substitute $\lambda = 3$, a known eigenvalue, to demonstrate a systematic procedure. This gives

$$\left[\begin{array}{ccc|ccc} -3 & 3 & 0 & 1 & 0 & 0 \\ 1 & -3 & 2 & 0 & 1 & 0 \\ 0 & 3 & -3 & 0 & 0 & 1 \end{array} \right].$$

Operate on the first row and multiply the first nonzero element by $-1/3$, its negative inverse. Multiply all other elements of the first row by $-1/3$. This makes +1 the first nonzero element of row one and gives

$$\left[\begin{array}{ccc|ccc} 1 & -1 & 0 & -1/3 & 0 & 0 \\ 1 & -3 & 2 & 0 & 1 & 0 \\ 0 & 3 & -3 & 0 & 0 & 1 \end{array} \right]$$

for the augmented matrix.

Row operations, like the one we have just described and performed, can be accomplished by matrix multiplication. For example, to multiply the first row by $-1/3$ is identical to operating with the matrix

$$M_1 = \begin{bmatrix} -1/3 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

Now go to the second row. If the element in the second row just below the first $+1$ in the first row is nonzero, make it zero. Here, multiply the first row by -1 and add it to the second row. This gives

$$\left[\begin{array}{ccc|ccc} 1 & -1 & 0 & -1/3 & 0 & 0 \\ 0 & -2 & 2 & 1/3 & 1 & 0 \\ 0 & 3 & -3 & 0 & 0 & 1 \end{array} \right].$$

Here we have implicitly operated with the matrix

$$M_2 = \begin{bmatrix} 1 & 0 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

Now we note that the sequence of matrix operations we have performed thus far, namely,

$$M = M_2 M_1 = \begin{bmatrix} 1 & 0 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} -1/3 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -1/3 & 0 & 0 \\ 1/3 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

is identical to the r.h.s. of the augmented matrix.

Consider the implications of what we are doing. We are making a systematic sequence of matrix multiplications with the aim of achieving a row of zeroes, if we have correctly chosen an eigenvalue.

Simultaneously, we are operating on a set of basis vectors represented by the matrix V . These matrix operations stretch, reflect, or rotate the basis vectors. If we have correctly chosen an eigenvalue, and have demonstrated that the eigenvalue equation is satisfied, we have also transformed the set of basis vectors such that at least one of them is now an eigenvector.

Let us now continue with this systematic procedure. Go to the third row, same column, to make that element zero by adding to it the appropriate multiple of the first row. Here the element is already zero, so we start over with this general procedure beginning with the second row and second column. If that element is zero, move to the third column. That is, go to the first nonzero element in the second row. Here that is -2 in the second column. Multiply the second row by the inverse of -2 to get

$$\left[\begin{array}{ccc|ccc} 1 & -1 & 0 & -1/3 & 0 & 0 \\ 0 & 1 & -1 & -1/6 & -1/2 & 0 \\ 0 & 3 & -3 & 0 & 0 & 1 \end{array} \right].$$

Now multiply the second row by -3 and add it to the third row, so as to make the second column of the third row equal to zero. This gives

$$\left[\begin{array}{ccc|ccc} 1 & -1 & 0 & -1/3 & 0 & 0 \\ 0 & 1 & -1 & -1/6 & -1/2 & 0 \\ 0 & 0 & 0 & 3/6 & 3/2 & 1 \end{array} \right].$$

The zeroes in row 3 on the l.h.s. indicate that the trial value of $\lambda = 3$ is an eigenvalue and that the r.h.s. of row 3 is the corresponding eigenvector.

As discussed in Chapter 4, we now normalize the eigenvector by making the first element equal to unity. We do this in the present case by multiplying all components of the eigenvector by 2. The solution is then

$$\lambda = 3, \quad \Lambda = \begin{bmatrix} 1 \\ 3 \\ 2 \end{bmatrix}.$$

This can be checked by applying $H^{(3)}$ to $\Lambda = [1, 3, 2]$, namely,

$$\begin{bmatrix} 0 & 1 & 0 \\ 3 & 0 & 3 \\ 0 & 2 & 0 \end{bmatrix} \begin{bmatrix} 1 \\ 3 \\ 2 \end{bmatrix} = 3 \begin{bmatrix} 1 \\ 3 \\ 2 \end{bmatrix}.$$

In a similar manner, one can demonstrate that the other two solutions are

$$\lambda = -3, \quad \Lambda = \begin{bmatrix} 1 \\ -3 \\ 2 \end{bmatrix} \quad \text{and} \quad \lambda = 0, \quad \Lambda = \begin{bmatrix} 1 \\ 0 \\ -1 \end{bmatrix}.$$

Modular arithmetic

The key point of Dixon's method is that the class constants, which are the eigenvalues of (1), are integers modulo an appropriately chosen prime number. It is that feature which makes it practical to systematically apply the Gauss elimination procedure to test trial solutions to (5.1).

As a preliminary to demonstrating Dixon's method, we present here a few definitions and some techniques for working with integers in modular arithmetic.

Two integers k and l are said to be *congruent* modulo p if they differ by an integer multiple of the integer p . For Dixon's method, p is further restricted to being a prime number. The congruence is written

$$k \equiv l \pmod{p}$$

and p is called the modulus of the congruence.

Congruent numbers are, roughly speaking, equal. The most familiar use of congruence is in specifying the time of day. We specify hours up to 12 and then start over again. The hands on the clock specify the time modulo 12.

When adding or multiplying numbers (mod p) we must restrict the resulting number to the set of integers $0, 1, \dots, p-1$. We do this, if necessary, by replacing the number

generated by its equivalent from the set of integers $0, 1, \dots, p-1$. This is convenient to do with a Fortran program by making use of the function $\text{mod}(m, p)$.

Example 5.6

Consider the integer $19 \bmod 7$.

$$\text{mod}(19, 7) = 19 - \mathbf{INT}\left(\frac{19}{7}\right) \times 7 = 19 - (2 \times 7) = 5.$$

On the other hand, the integer $i = -19 \bmod 7$, which we might expect to become -5 , actually becomes 2. Integers are always shifted by an integer multiple of p in order to bring them into the range $0 \leq i < p$.

In modular arithmetic, the sum, difference, product, or quotient of integers gives another integer such that when it is divided by p the remainder is an integer r , $0 \leq r < p$. This has an important effect on the way we determine eigenvalues in Dixon's method.

Matrix eigenvalue problem in Dixon's method

We now have the tools at hand to determine the eigenvalues of (5.32) using Dixon's method and modular arithmetic.

We begin as before by constructing an augmented matrix, only this time we use $+\lambda'$ on the l.h.s., not $-\lambda'$, and we use a prime on λ . This means that the *actual* eigenvalues λ will be the negative ($\bmod p$) of the values λ' we determine. We do this because with modular arithmetic all answers will be integers $0 \leq \lambda' < p$, where p is a prime number such that $p > 2\sqrt{g}$. In the present case we set $p = 7$. It is more convenient to have all positive integers in the augmented matrix at all stages. With $+\lambda'$ in the augmented matrix we have

$$\left[\begin{array}{ccc|ccc} \lambda' & 3 & 0 & 1 & 0 & 0 \\ 1 & \lambda' & 2 & 0 & 1 & 0 \\ 0 & 3 & \lambda' & 0 & 0 & 1 \end{array} \right] \bmod 7$$

For comparison with what we did with Burnside's method, we substitute $\lambda' = 3$ to demonstrate Dixon's method. This gives

$$\left[\begin{array}{ccc|ccc} 3 & 3 & 0 & 1 & 0 & 0 \\ 1 & 3 & 2 & 0 & 1 & 0 \\ 0 & 3 & 3 & 0 & 0 & 1 \end{array} \right] \bmod 7$$

Operate on the first row and multiply the first nonzero element by its inverse. The first nonzero element is $M_{11} = 3$ and its inverse ($\bmod 7$) is 5. Multiply all other elements of the first row by 5. This gives

$$\left[\begin{array}{ccc|ccc} 1 & 1 & 0 & 5 & 0 & 0 \\ 1 & 3 & 2 & 0 & 1 & 0 \\ 0 & 3 & 3 & 0 & 0 & 1 \end{array} \right] \bmod 7$$

for the augmented matrix.

Now go to the second row. If the element in the second row just below the first 1 in the first row is nonzero, make it zero. Here, that is the element $M_{21} = 1$. We must add to it the integer 6 to get $M_{21} \equiv 7 \equiv 0$. We can accomplish this by multiplying each element of the first row by 6 and adding it to the corresponding element of the second row to get

$$\left[\begin{array}{ccc|ccc} 1 & 1 & 0 & 5 & 0 & 0 \\ 0 & 2 & 2 & 2 & 1 & 0 \\ 0 & 3 & 3 & 0 & 0 & 1 \end{array} \right] \bmod 7$$

Next go to the third row, same column, to make that element zero by adding to it the appropriate multiple of the first row. Here the element M_{31} is already zero, so we start over with this general procedure beginning with the second row and second column. If that element is zero, move to the third column. That is, go to the first nonzero element in the second row. Here that is $M_{22} = 2$. Multiply the second row by the inverse of 2, which is 4, to get

$$\left[\begin{array}{ccc|ccc} 1 & 1 & 0 & 5 & 0 & 0 \\ 0 & 1 & 1 & 1 & 4 & 0 \\ 0 & 3 & 3 & 0 & 0 & 1 \end{array} \right] \bmod 7$$

Now multiply the second row by 4 and add it to the third row, so as to make the $M_{32} = 0$. This gives

$$\left[\begin{array}{ccc|ccc} 1 & 1 & 0 & 5 & 0 & 0 \\ 0 & 1 & 1 & 1 & 4 & 0 \\ 0 & 0 & 0 & 4 & 2 & 1 \end{array} \right] \bmod 7$$

The set of zeroes in row 3 on the l.h.s. indicates that the trial value of $\lambda' = 3$ is a solution and that the r.h.s. of the row is the corresponding eigenvector, but the eigenvalue is actually the *negative* of λ' , that is, $\lambda = -\lambda'$.

We can verify by direct substitution that the eigenvalue $\lambda \equiv -3 \equiv 4 \bmod 7$ and its corresponding eigenvector satisfy the eigenvalue equation, (5.32) We find

$$\begin{bmatrix} 0 & 1 & 0 \\ 3 & 0 & 3 \\ 0 & 2 & 0 \end{bmatrix} \begin{bmatrix} 4 \\ 2 \\ 1 \end{bmatrix} \equiv \begin{bmatrix} 2 \\ 1 \\ 4 \end{bmatrix} \equiv 4 \begin{bmatrix} 4 \\ 2 \\ 1 \end{bmatrix} \bmod 7$$

Similarly, we can find that the remaining two solutions are

$$\lambda = 0, \quad \Lambda = \begin{bmatrix} 6 \\ 0 \\ 1 \end{bmatrix} \quad \text{and} \quad \lambda = 3, \quad \Lambda = \begin{bmatrix} 4 \\ 5 \\ 1 \end{bmatrix} \bmod 7$$

We have found that $\lambda \equiv 4 \bmod 7$ is an eigenvalue with eigenvector $[4 \ 1 \ 0]$ (in row form). The eigenvector needs to be normalized such that the first component, which corresponds to the identity class, must equal unity mod 7. This can be accomplished by multiplying each component of the eigenvector by 2 mod 7, which is the inverse of 4, the first

component. A similar procedure for the remaining two eigenvectors gives the following normalized solutions.

$$\lambda = 4, \quad \Lambda = \begin{bmatrix} 1 \\ 4 \\ 2 \end{bmatrix}; \quad \lambda = 0, \quad \Lambda = \begin{bmatrix} 1 \\ 0 \\ 6 \end{bmatrix}; \quad \lambda = 3, \quad \Lambda = \begin{bmatrix} 1 \\ 3 \\ 2 \end{bmatrix} \pmod{7}$$

From inspection of these results, the reader will note that the three eigenvalues correspond to the class constants in the second row of each of the eigenvectors.

Degenerate eigenvalues

It may happen that the class-constant matrix yields degenerate eigenvalues. For example, if we had used a different set of generators, or if we used the same generators but introduced them in a different order into a computer program, the first nontrivial class-constant matrix, that is, the first class-constant matrix generated other than that for the identity class, could have been

$$H^{(2)} = \begin{bmatrix} 0 & 1 & 0 \\ 2 & 1 & 0 \\ 0 & 0 & 2 \end{bmatrix} \pmod{7}$$

The transposed augmented matrix is then

$$\left[\begin{array}{ccc|ccc} \tilde{V} \tilde{H}^{(2)} & +\lambda' \tilde{V} & \tilde{V} & & & \end{array} \right] = \left[\begin{array}{ccc|ccc} \lambda' & 2 & 0 & 1 & 0 & 0 \\ 1 & 1+\lambda' & 0 & 0 & 1 & 0 \\ 0 & 0 & 2+\lambda' & 0 & 0 & 1 \end{array} \right] \pmod{7}$$

We would now try values of λ' beginning with $\lambda' = 0$ to see if our systematic sequence of row operations would identify λ' as a solution. We would find that the first solution is obtained for $\lambda' = 1$, for which the augmented matrix after making the appropriate row operations becomes

$$\left[\begin{array}{ccc|ccc} 1 & 2 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 6 & 1 & 0 \\ 0 & 0 & 3 & 0 & 0 & 1 \end{array} \right] \pmod{7}$$

Since the actual eigenvalues λ are the negative of $\lambda' \pmod{7}$, the solution is

$$\lambda' = 1, \quad \lambda = 6, \quad \Lambda = \begin{bmatrix} 6 \\ 1 \\ 0 \end{bmatrix} \pmod{7} \quad (5.42)$$

Proceeding on, we find that there are no further solutions until $\lambda' = 5$, for which the multiplicity is 2 and the augmented matrix after having made the appropriate row operations is

$$\left[\begin{array}{ccc|ccc} 1 & 6 & 0 & 3 & 0 & 0 \\ 0 & 0 & 0 & 4 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{array} \right] \pmod{7}$$

The two eigenvectors belong to the same eigenvalue. They span the null space belonging to $\lambda' = 5$, or $\lambda = 2 \pmod{7}$ and they also define a two-dimensional vector space, a plane. Because the eigenvectors belong to a doubly degenerate eigenvalue, *any* linear combination of the two is also an eigenvector. One can check this by taking, say, the direct sum of $[4\ 1\ 0]$ and $[0\ 0\ 1]$, which is $[4\ 1\ 1]$, and showing that $H^{(2)}$ operating on this direct sum gives back the same eigenvector multiplied by the eigenvalue $\lambda = 2$. However, we seek a unique set of eigenvectors. Remember, each eigenvector corresponds to a particular Irrep. There are three of them in our example problem and each is unique. Thus we know there are two other eigenvectors in the same two-dimensional space that are linear combinations of the two we have just found, but which are unique in the following sense: Both belong to the doubly degenerate eigenvalue, $\lambda = 2$, for the eigenvalue equation

$$H^{(2)}\Lambda = \lambda_2\Lambda,$$

but each of the two eigenvectors belongs to a different (nondegenerate) eigenvalue when the eigenvalue equation to be solved is for a *different* class-coefficient matrix. These particular eigenvectors are the ones we seek.

What we are doing (or trying to do) is *equivalent* to diagonalizing a matrix. When eigenvalues are degenerate it is not always possible to diagonalize the matrix. It is the curious combination of eigenvectors and eigenvalues which are inextricably connected that makes it all possible here. To reiterate, we solved a particular eigenvalue problem and found one of the eigenvectors. By projecting out this eigenvector we reduced the vector space to two dimensions. We then found a doubly degenerate solution to the eigenvalue equation. We now move on to a *new* eigenvalue problem for which two new *nondegenerate* eigenvectors are found that are some linear combination of the two original eigenvectors that were degenerate when working with $H^{(2)}$.

The procedure at this stage is to begin anew with the next class-constant matrix, but retain the information we have learned about the eigenvectors. The algorithm that yielded the class-constant matrix $H^{(2)}$ that was just used would now yield

$$H^{(3)} = \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 2 \\ 3 & 3 & 0 \end{bmatrix}$$

We again construct the augmented matrix

$$\begin{bmatrix} \tilde{V}H^{(3)} + \lambda'\tilde{V} & \tilde{V} \end{bmatrix} \pmod{7}$$

but this time we take for our starting value of $\tilde{V}$ a matrix whose rows include the set of degenerate basis vectors we have just found, namely,

$$\tilde{V} = \begin{bmatrix} 6 & 1 & 0 \\ 4 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \pmod{7}$$

The rows are the set of eigenvectors we have just found using the class-constant matrix $H^{(2)}$. It does not matter in which order the eigenvectors are placed in the rows of $\tilde{V}$, as the reader can check by duplicating the following steps with a different ordering of the rows. We place the unique eigenvector in row 1 for convenience. We will soon eliminate it.

The general transposed augmented matrix for $H^{(3)}$ becomes

$$\left[\begin{array}{ccc|ccc} 6\lambda' & \lambda' & 21 & 6 & 1 & 0 \\ 4\lambda' & \lambda' & 15 & 4 & 1 & 0 \\ 1 & 2 & \lambda' & 0 & 0 & 1 \end{array} \right] \equiv \left[\begin{array}{ccc|ccc} 6\lambda' & \lambda' & 0 & 6 & 1 & 0 \\ 4\lambda' & \lambda' & 1 & 4 & 1 & 0 \\ 1 & 2 & \lambda' & 0 & 0 & 1 \end{array} \right] \pmod{7}$$

We again check trial values for the eigenvalues, beginning with $\lambda = 0$. For $\lambda = 0$ the augmented matrix becomes

$$\left[\begin{array}{ccc|ccc} 0 & 0 & 21 & 6 & 1 & 0 \\ 0 & 0 & 15 & 4 & 1 & 0 \\ 1 & 2 & 0 & 0 & 0 & 1 \end{array} \right] \equiv \left[\begin{array}{ccc|ccc} 0 & 0 & 0 & 6 & 1 & 0 \\ 0 & 0 & 1 & 4 & 1 & 0 \\ 1 & 2 & 0 & 0 & 0 & 1 \end{array} \right] \pmod{7}$$

The l.h.s. of the first row is already zero, and the r.h.s. of the row contains a known eigenvector belonging to a nondegenerate eigenvalue, that is, an eigenvalue of multiplicity one. Thus we *must* restrict our row operations to rows 2 and 3, which define a two-dimensional vector space containing the new eigenvalues and associated eigenvectors that we seek. The augmented matrix is then

$$\left[\begin{array}{ccc|ccc} 4\lambda' & \lambda' & 1 & 4 & 1 & 0 \\ 1 & 2 & \lambda' & 0 & 0 & 1 \end{array} \right] \pmod{7} \quad (5.43)$$

In this case, we would find that $\lambda = 0$ is not an eigenvalue, so we move on to other trial values. Carrying out row operations as before, with modular arithmetic, we find that solutions exist for $\lambda' = 3$ and $\lambda' = 4$. The actual eigenvalues are the negative of these mod 7, so the solutions are found to be

$$\left. \begin{array}{l} \lambda' = 3 \\ \lambda = 4 \end{array} \right\} \quad \Lambda = \begin{bmatrix} 2 \\ 4 \\ 1 \end{bmatrix}; \quad \left. \begin{array}{l} \lambda' = 4 \\ \lambda = 3 \end{array} \right\} \quad \begin{bmatrix} 5 \\ 3 \\ 1 \end{bmatrix} \pmod{7} \quad (5.44)$$

We can normalize the eigenvectors from (5.44) and combine them with the normalized version of (5.42) to get the following solution for the modular class constants of $\mathcal{C}_{3v}$:

$$\lambda = 6, \quad \Lambda = \begin{bmatrix} 1 \\ 6 \\ 0 \end{bmatrix}; \quad \lambda = 4, \quad \Lambda = \begin{bmatrix} 1 \\ 2 \\ 4 \end{bmatrix}; \quad \lambda = 3, \quad \Lambda = \begin{bmatrix} 1 \\ 2 \\ 3 \end{bmatrix} \pmod{7} \quad (5.45)$$

We note that the two new eigenvalues are nondegenerate. Each belongs to the third row of one of the newfound eigenvectors, because they were determined from the eigenvalue equation for $H^{(3)}$. This set of unique eigenvectors simultaneously diagonalizes *all* the class-coefficient matrices. We note that the second row of *both* of the newfound eigenvectors contains the class constants $\lambda = 2$, which were doubly degenerate eigenvalues for the eigenvalue equation for $H^{(2)}$. Here they are components of the eigenvectors, but not eigenvalues themselves.

Exercises

5.1 Assume that λ is an eigenvalue for the matrix operator

$$M = \begin{bmatrix} a & b \\ c & d \end{bmatrix}.$$

Carry out row operations in algebraic form to demonstrate explicitly that the augmented matrix provides the eigenvector belonging to λ .

5.2 Show that the eigenvectors obtained in (5.44) are linear combinations of the starting basis vectors of (5.43).

Appendix 2

In Appendix 1, the solution to the eigenvalue equation

$$H^{(i)(\alpha)} \Lambda = {}^{(\alpha)}\lambda_i {}^{(\alpha)}\Lambda \quad (5.46)$$

was described. In the example given there, the eigenvalues mod 7 were found to be $\lambda = 6, 4, 3$ with corresponding eigenvectors

$$\begin{bmatrix} 1 \\ 6 \\ 0 \end{bmatrix}, \quad \begin{bmatrix} 1 \\ 2 \\ 4 \end{bmatrix}, \quad \begin{bmatrix} 1 \\ 2 \\ 3 \end{bmatrix} \pmod{7}. \quad (5.47)$$

Each eigenvector corresponds to an Irrep, and each component of the eigenvector is a class constant λ for one of the classes in that Irrep.

A computer program must keep track of the classes and number them. Since the class-constant matrix $H^{(1)}$ is always diagonal, the computer program will begin with $H^{(2)}$. Of course, what is called $H^{(2)}$ depends on the generators chosen and the order in which they are entered into the program. In our example case, taken from Appendix 1, $H^{(2)}$ corresponds to the class of rotation operators $\{C_3, C_3^2\}$. A different choice of generators, or order of entry, could have caused $H^{(2)}$ to correspond to the class of reflection operators $\{\sigma_1, \sigma_2, \sigma_3\}$. One must be sure to keep them all straight.

We can determine the character for the elements of each class by using (5.28), which we rewrite here as

$$\Theta \left({}^{(\alpha)}\chi_i \right) \equiv \frac{d_\alpha}{\text{nc}(i)} \Theta \left({}^{(\alpha)}\lambda_i \right) \pmod{p}, \quad (5.48)$$

where Θ denotes a *modular* character. The number of elements, $\text{nc}(i)$, in each class, $\mathcal{C}_i$, is known. Only the dimension of the Irrep, d_α , is needed to determine the modular character $\Theta({}^{(\alpha)}\chi_i)$. We can find d_α using (5.29), which is

$$|d_\alpha|^2 \equiv \frac{g}{\sum_i \frac{\Theta({}^{(\alpha)}\lambda_i) \Theta({}^{(\alpha)}\lambda_i^{-1})}{\text{nc}(i)}} \pmod{p}, \quad (5.49)$$

where ${}^{(\alpha)}\lambda_i^{-1}$ means the class constant for the inverse class mod p . That is, ${}^{(\alpha)}\lambda_i$ is the class constant of the i th class. One takes an element of the i th class and finds its inverse. The inverse belongs to some class and ${}^{(\alpha)}\lambda_i^{-1}$ means the class constant for that inverse

class. However, even when we find $\Theta^{(\alpha)}\chi_i$, it will be modulo a prime number, in this case $p = 7$, and there is a bit more modular arithmetic involved before we get to the point of finding the multiplicities that allow us to express the character as a polynomial in roots of unity. We will work through an example using our example group $\mathcal{C}_{3v}$.

Dixon's method

Remembering that Dixon's method uses modular arithmetic, we evaluate (5.49) for the eigenvalue (the class constant) $\lambda = 6$ and the eigenvector $[1\ 6\ 0]$, which corresponds to the Irrep to which $\lambda = 6$ belongs.

$$|d_\alpha|^2 \equiv \frac{6}{\frac{1 \times 1}{1} + \frac{6 \times 6}{2} + \frac{0 \times 0}{3}} \pmod{7}, \quad (5.50)$$

where 1, 2, and 3 are, respectively, the numbers of elements in the classes (the orders of the classes), the eigenvector is the first of the three eigenvectors in (5.47), and the modulus 7 was determined in Appendix 1. In general, the orders of classes, the modulus, and anything else needed at this point would be included in the computer program output. The equation for d_α can be rewritten

$$\begin{aligned} |d_\alpha|^2 &\equiv \frac{6}{1 + 18 + 0} \pmod{7} \\ &\equiv \frac{6}{5} \pmod{7} \end{aligned} \quad (5.51)$$

There are numerous ways to determine d_α such that $|d_\alpha|^2 < 7$ with $d_\alpha > 0$.

Example 5.7

$$\begin{aligned} d^2 &\equiv \frac{6}{5} \equiv \frac{6}{5} \times \frac{3}{3} \equiv \frac{18}{15} \equiv \frac{14+4}{14+1} \equiv \frac{4}{1} \equiv 4 \pmod{7} \\ &\Rightarrow d_j^2 = 4 \pmod{7}. \end{aligned}$$

or

$$d^2 \equiv \frac{6}{5} \equiv \frac{6}{5-7} \equiv \frac{6}{-2} \equiv -3 \equiv 4 \pmod{7}.$$

But what is needed for computer programs is a systematic method. Fermat's theorem provides it.

Fermat's theorem

In the 1600s, Fermat discovered a beautiful and useful theorem:

Theorem: If p is a prime number that does not divide the integer a , then

$$a^{p-1} \equiv 1 \pmod{p}. \quad (5.52)$$

In general, we have an expression of the form

$$d^2 \equiv \frac{a}{b} \pmod{p}. \quad (5.53)$$

We convert the denominator to unity with the aid of Fermat's theorem. This gives

$$d^2 \equiv \frac{a}{b} \times \frac{b^{p-2}}{b^{p-2}} \equiv \frac{ab^{p-2}}{b^{p-1}} \equiv ab^{p-2} \pmod{p}. \quad (5.54)$$

We can do all this in a *Mathematica* program by making use of the function `Mod[i, j]`, which with an integer argument gives the remainder of `i` divided by `j`. Thus we have

$$\begin{aligned} d^2 &\equiv ab^{p-2} \pmod{p} \\ &= \text{Mod}[\text{ab}^{p-2}, \text{p}]. \end{aligned} \quad (5.55)$$

We evaluate fractions *at each step* by this procedure. Thus, in (5.50), we evaluate each fraction in the denominator using (5.55), and then we add all the terms in the denominator, again using modular arithmetic. We continue in this fashion, using modular arithmetic at each step, and not waiting until the end to use it.

Modular characters

Using Fermat's theorem to solve for $|d_\alpha|^2$ we find that

$$|d_\alpha|^2 \equiv 4 \pmod{7}.$$

There is an obvious solution, namely, $d_\alpha = 2$. But there are two roots, and the other one is equivalent to -2 , or 5 . In general, the roots of $d^2 \pmod{p}$ are d , $p - d$. In writing a computer program, one must be sure to find both roots, subject to the requirement that $p > 2d_\alpha$, and then choose the smaller root to ensure that d_α is uniquely and correctly determined.

Example 5.8

Suppose we have calculated

$$|d_\alpha|^2 \equiv 16 \pmod{p},$$

and we know the correct answer to be 4. What do we get for d_α using several different prime numbers for p ?

$$\begin{aligned} d_\alpha &\equiv 4, 1 \pmod{5}, \\ d_\alpha &\equiv 4, 3 \pmod{7}, \\ d_\alpha &\equiv 4, 7 \pmod{11}, \\ d_\alpha &\equiv 4, 13 \pmod{17}. \end{aligned}$$

We always get the correct root along with another that may be more or less than the correct one. By choosing $p > 2d_\alpha$ we ensure that the smaller modular root is the correct one.

More generally, we take $p > 2\sqrt{g}$ to ensure that we uniquely determine d_α for *all* Irreps.

Proof Let D equal the dimension of the largest Irrep. This Irrep appears D times in the regular representation, which is of dimension g . Thus

$$D^2 \leq g, \quad D \leq \sqrt{g}.$$

By initially choosing

$$p > 2\sqrt{g},$$

we ensure that $p > 2d_\alpha$ for any Irrep.

With a value of prime number p sufficiently large, but not larger than necessary, one can just go methodically through the squares of integers, beginning with 1, to find the first value of n such that $n^2 = d^2$. Since the two roots are symmetrical about $p/2$ one need consider only squares of n with n ranging from 1 to $(p-1)/2$.

Now we are prepared to solve for the irreducible modular characters using (5.48). Working through the case for the first of the eigenvectors in (5.47), we find

$$\Theta(\chi_1) = \frac{2}{1} \times 1 = 2,$$

$$\Theta(\chi_2) = \frac{2}{2} \times 6 = 6,$$

$$\Theta(\chi_3) = \frac{2}{3} \times 0 = 0.$$

We can now use these irreducible modular characters to calculate the multiplicities in the polynomial expression for the character.

Computing multiplicities

Now that the characters $\Theta^{(\alpha)}(\chi_i)$ are known, we can compute the multiplicities $^{(\alpha)}m_i(s)$ from (5.30). Here, we drop the Irrep designation (α) for simplicity and write

$$m_i(s) = \frac{1}{n} \sum_{t=0}^{n-1} \Theta(\chi_i(A^t)) Z^{-st} \pmod{p}, \quad (5.56)$$

where A^t is a power of any element A belonging to the class $\mathcal{C}_i$.

We begin with the trivial case of finding the multiplicities for the first class, the identity class, for the Irrep of dimension 2, which corresponds to the eigenvector $[1 \ 6 \ 0]$. Since all powers of the identity element are equal to the identity element, the irreducible modular characters

$$\Theta(\chi_1(A^t)) = \Theta(\chi_1(E^t)) = \Theta(\chi_1(E))$$

are all the same, namely, they all equal 2, as was found in the previous section. Thus,

$$m_1(s) = \frac{1}{n} \times 2 \times (Z^0 + Z^{-s} + Z^{-2s} + Z^{-3s} + Z^{-4s} + Z^{-5s}). \quad (5.57)$$

For our example case, $n = 6$ and $Z = 3$, thus,

$$m_1(0) = \frac{1}{6} \times 2 \times (3^0 + 3^0 + 3^0 + 3^0 + 3^0 + 3^0) = \frac{1}{6} \times 2 \times 6 = 2,$$

which is just what we expect for a two-dimensional Irrep for the identity element. Just as a check, let us consider another multiplicity:

$$\begin{aligned}
 m_1(1) &\equiv \frac{1}{3}(3^0 + 3^{-1} + 3^{-2} + 3^{-3} + 3^{-4} + 3^{-5}) \\
 &\equiv \frac{1}{3}\left(1 + \frac{1}{3} + \frac{1}{9} + \frac{1}{27} + \frac{1}{81} + \frac{1}{243}\right) \\
 &\equiv \frac{1}{3}\left(1 + \frac{1}{3} + \frac{1}{2} + \frac{1}{6} + \frac{1}{4} + \frac{1}{5}\right) \pmod{7} \\
 &\equiv 0.
 \end{aligned} \tag{5.58}$$

Similarly, all other values of $m_1(s)$, for $s > 0$, are found to equal zero.

Now let us consider the class $\mathcal{C}_3$, for which the irreducible modular character is zero. At first glance, one might think that the multiplicities would also be zero. But note that one sums over the modular characters of *powers* of some element belonging to the class. An element raised to some power often belongs to a different class with a nonzero character.

Our example physical realization of the class $\mathcal{C}_3$ consists of the three reflection operations of the equilateral triangle. We can use σ_1 as a representative operation. Odd powers of σ_1 are equal to σ_1 itself, but even powers are equal to the identity element E for which the irreducible modular character is 2. Thus, the modular characters in (5.56) will alternately be 2 and 0, giving

$$\begin{aligned}
 m_3(s) &\equiv \frac{1}{6}(2 \times 3^0 + 0 \times 3^{-s} + 2 \times 3^{-2s} + 0 \times 3^{-3s} + 2 \times 3^{-4s} + 0 \times 3^{-5s}), \\
 &\equiv \frac{1}{3}(3^0 + 3^{-2s} + 3^{-4s}), \pmod{7}.
 \end{aligned} \tag{5.59}$$

We can now determine the values of $m_3(s)$:

$$\begin{aligned}
 m_3(0) &\equiv \frac{1}{3}(3^0 + 3^0 + 3^0) \equiv \frac{1}{3} \times 3 \equiv 1. \\
 m_3(1) &\equiv \frac{1}{3}(3^0 + 3^{-2} + 3^{-4}) \equiv \frac{1}{3}\left(1 + \frac{1}{9} + \frac{1}{81}\right) \\
 &\equiv \frac{1}{3}\left(1 + \frac{1}{2} + \frac{1}{4}\right) \equiv \frac{1}{3}(1 + 4 + 2) \\
 &\equiv 0. \\
 m_3(2) &\equiv \frac{1}{3}(3^0 + 3^{-4} + 3^{-8}) \equiv \frac{1}{3}\left(1 + \frac{1}{81} + \frac{1}{6561}\right) \\
 &\equiv \frac{1}{3}\left(1 + \frac{1}{4} + \frac{1}{2}\right) \equiv \frac{1}{3}(1 + 2 + 4) \\
 &\equiv 0. \\
 m_3(3) &\equiv \frac{1}{3}(3^0 + 3^{-6} + 3^{-12}) \equiv \frac{1}{3}\left(1 + \frac{1}{729} + \frac{1}{531441}\right) \\
 &\equiv \frac{1}{3}\left(1 + \frac{1}{1} + \frac{1}{1}\right) \equiv \frac{1}{3}(1 + 1 + 1) \\
 &\equiv 1.
 \end{aligned}$$

The remaining values are easily found to be

$$m_2(4) = 0, \quad m_2(5) = 0.$$

Of course, in a computer program, or even when doing such a calculation by hand, one would always shift numbers at each stage to be integers in the range 0 to $p-1$. Here, large integers mod 7 have been kept at intermediate stages just to make clear the steps in the calculation.

Following the procedures just illustrated, we find the multiplicities for the class $\mathcal{C}_2$ to be

$$\begin{aligned} m_2(0) &= m_2(1) = m_2(3) = m_2(5) = 0. \\ m_2(2) &= m_2(4) = 1. \end{aligned}$$

Irreducible characters

The multiplicities are now known for expressing the irreducible characters as a polynomial in sixth-roots of unity. We have for the two-dimensional Irrep:

$$\begin{aligned} \chi(\mathcal{C}_1) &= m_1(0)e^0 = 2. \\ \chi(\mathcal{C}_2) &= m_2(2)e^{i(2\pi(2/6))} + m_2(4)e^{i(2\pi(4/6))} \\ &= e^{i(2\pi/3)} + e^{i(4\pi/3)} \\ &= \left(-\frac{1}{2} + i\frac{\sqrt{3}}{2}\right) + \left(-\frac{1}{2} - i\frac{\sqrt{3}}{2}\right) \\ &= -1. \\ \chi(\mathcal{C}_3) &= m_3(0)e^0 + m_3(3)e^{i(2\pi(3/6))} \\ &= e^0 + e^{i\pi} \\ &= 1 - 1 \\ &= 0. \end{aligned}$$

Computation project

Use the sample programs given in this chapter together with other sample programs presented in Chapters 2 and 4 to construct a complete program to determine the characters of finite groups. Use the program you develop to determine the Irreps of the point-groups $\mathcal{C}_{4v}$ and $\mathcal{C}_{6v}$.

6

Group action and symmetry projection operators

In the first part of this chapter we introduce some concepts regarding the action of symmetry group operators on objects, sets, and number fields; and we define the terminology involved. This is followed in the second part by the definition of *symmetry projection operators*, and description of the methodology for their construction. We also demonstrate how the emerging ideas of group action enter into the operational structure of the projection operators.

6.1 Group action

We would like to stress the fact that the application of group theory to a physical system entails defining the changes effected by the operators of its symmetry group on its constituent elements. In other words, describing the group action on the system. So far, we have presented ample, but particular, examples of this action, such as geometric rotations of, and permutations among the system constituents. However, it is now desirable to present some concepts in group actions that transcend the particulars we have considered previously. These concepts are particularly evident in geometric situations; we find such examples in crystallography, where basic equivalence relations naturally emerge, and become algorithmically approachable.

Let us examine the case of a group $\mathcal{G}$ acting on a set of points M ; we then note the following:

- (i) **$\mathcal{G}$ -set** The action of $\mathcal{G}$ on M is a mapping where every element $g \in \mathcal{G}$ takes a point $m \in M$ to the point $m' = gm \in M$ such that

$$\begin{cases} g_2(g_1 m) = (g_2 g_1) m, \quad \forall g_1, g_2 \in \mathcal{G}, \\ E m = m, \end{cases} \quad \forall m \in M. \quad (6.1)$$

We note that on the left-hand side the action map is applied twice, once for g_1 and then for g_2 , while on the right-hand side it is applied only once, for the group product $g_1 g_2 = g_3$.

The action of $\mathcal{G}$ on M qualifies M as a $\mathcal{G}$ -set.

- (ii) **Orbit** When any element $g \in \mathcal{G}$ acts on M , such that $g m_1 = m_2$, the two elements $m_1, m_2 \in M$ are said to lie in the same *orbit*. Thus, a $\mathcal{G}$ -orbit $\mathcal{O}_{\mathcal{G}}(m)$ is the subset of points $\{g m \mid \forall g \in \mathcal{G}\}$.

It is then clear that different orbits generated by the action of $\mathcal{G}$ on M are either identical or disjoint subsets of M . The $\mathcal{G}$ -orbits,

$$\mathcal{O}_{\mathcal{G}}(m) := \{gm \mid g \in \mathcal{G}\} \forall m \in M$$

partition M into pairwise disjoint subsets.

Example 6.1

The action of C_{2v} on the water molecule

We find from Figure 6.1 that when we apply the operations of C_{2v} to the H_2O molecule, i.e. to the set $[H_1, H_2, O]$, O is left invariant, while H_1 and H_2 are interchanged, or permuted, under the action of the two-fold rotation C_2 and the reflection σ_y , but they are left unchanged by σ_x and, of course, E . Therefore, the action of C_{2v} results in two C_{2v} -orbits:

- A two-member orbit $\mathcal{O}_{\mathcal{G}}(H_1) = [H_1, H_2]$, and
- A one-member orbit $\mathcal{O}_{\mathcal{G}}(O) = [O]$.

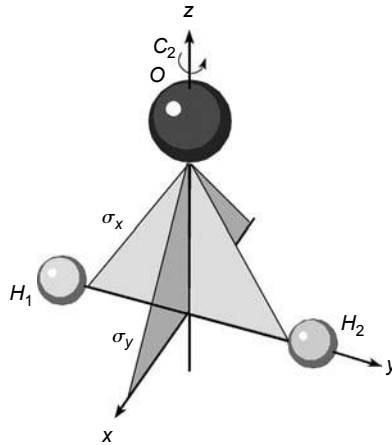


Fig. 6.1. The water molecule and its symmetry.

Example 6.2

Orbits under the action of C_{4v} on a square sheet

Typical orbits generated by the action of C_{4v} on the continuous set of points forming a square are shown in Figure 6.2; we find four types of orbits: namely, one 8-member orbit, two 4-member orbits, and one 1-member orbit.

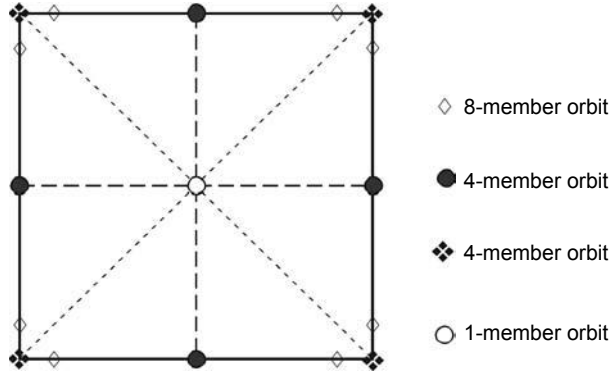


Fig. 6.2. Some orbits of the action of C_{4v} on a square.

Being in the same orbit is an equivalence relation on M , sometimes denoted by $\sim_{\mathcal{G}}$. The set $M/\sim_{\mathcal{G}}$ of equivalence classes or orbits is usually denoted by $\mathcal{G}\backslash M$ (and called the quotient $M \bmod \mathcal{G}$).

In mathematics, an orbit is a very general group-theoretical term describing any set of objects that are mapped onto each other by the action of a group. However, we will present in Chapters 10–12 more tangible manifestations of orbits associated with crystallographic symmetry and the Irreps of space-groups:

- An orbit can be identified with a lattice because it is generated by the action of its space-group on any single point in a Euclidean space.
- Another orbit is identified as a *Wyckoff position* or *set* when the action is due to a crystallographic point-group.
- In the classification of space-group Irreps, Chapter 11, an orbit is manifest in the *star of the wavevector*.

- (iii) **Stabilizer** Sometimes the action of some elements of $\mathcal{G}$ on $m \in M$ leaves m unchanged. We then identify the set of these operators as the *stabilizer* of the element m in $\mathcal{G}$,

$$G_m := \{g \in \mathcal{G} | gm = m\}.$$

Clearly, G_m is a subgroup of $\mathcal{G}$ of order g_m , namely, $G_m \subseteq \mathcal{G}$. The orbit to which m belongs contains g/g_m members; for each member we identify a stabilizer subgroup of $\mathcal{G}$ of order g_m . The collection of stabilizers of these members constitute conjugacy subgroups of G_m in $\mathcal{G}$, as will be explained in Chapter 8. The intersection of all conjugacy classes of stabilizers G_m with $m \in M$ is called the *kernel* of the action, and is a normal subgroup of $\mathcal{G}$.

Sometimes the stabilizer is referred to as an *isotropy group*; however, we reserve this label to describe subgroups associated with the Landau theory of phase transitions, presented in Chapter 17.

Example 6.3

The stabilizers associated with the orbit points of Example 6.2

8-member orbit	$\rightarrow \{E\}$
4-member orbit	$\rightarrow \{E, \sigma_v\} \rightarrow \{E, \sigma_x\}, \{E, \sigma_y\}$ (conjugate subgroups),
4-member orbit	$\rightarrow \{E, \sigma_d\} \rightarrow \{E, \sigma_{xy}\}, \{E, \sigma_{\bar{x}y}\}$ (conjugate subgroups),
1-member orbit	$\rightarrow C_{4v}$.

- The 1-member orbit, with C_{4v} as a stabilizer, is called a *fixed-point* orbit.
 - The 8-member orbit, with $\{E\}$ as a stabilizer, is called a *principal* orbit.
-

In different applications of symmetry discussed in later chapters, we will encounter manifestations of stabilizers under different guises; for example, in crystallographic applications we identify stabilizers under the name *site-symmetry* groups in real space; while for wavevectors in reciprocal space they are known as the *little groups of the wavevectors*.

- (iv) **Orbit type** Orbits with the same conjugacy classes of stabilizers are said to be of the same type.
-

Example 6.4

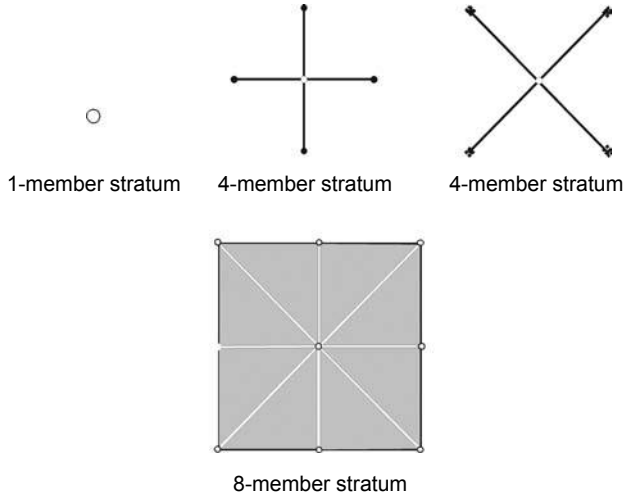
The square center (open circle) is a fixed-point orbit, it is the only such point on the square sheet. We also find that the two 4-member orbits cited above are not of the same type, since they belong to the distinct conjugacy classes $\{E, \sigma_v\}$ and $\{E, \sigma_d\}$.

- (v) **Stratum** A stratum is the union of orbits of the same type that result from a group action.
-

Example 6.5

Square-sheet strata

We identify the strata, starting from top left, as a fixed-point origin, a $\{E, \sigma_v\}$ -type stratum, and a $\{E, \sigma_d\}$ -type stratum. The remaining orbits are of the principal type and form a single stratum.

Fig. 6.3. Strata of the action of C_{4v} on a square sheet.

6.2 Symmetry projection operators

Given a vector in ordinary three-dimensional space, it is sometimes necessary to know its *projection* onto a plane or onto another vector. These ideas are familiar from analytic geometry. They are generalized in quantum mechanics where the ordinary vector becomes a *state* vector, or *state* function $|\Psi\rangle$, using the ket-bra notation, in Hilbert space. For example, if a set of orthonormal functions $\{|\phi_n\rangle\}$ forms a complete basis for a Hilbert space, it is possible to perform a decomposition, or projection, of a state function $|\Psi\rangle$ onto the constituent basis functions by employing the set of projection operators $\hat{P}_n$:

$$\hat{P}_n |\Psi\rangle = |\phi_n\rangle \langle \phi_n | \Psi \rangle = c_n |\phi_n\rangle, \quad (6.2)$$

so that

$$|\Psi\rangle = \sum_n |\phi_n\rangle \langle \phi_n | \Psi \rangle = \sum_n c_n |\phi_n\rangle. \quad (6.3)$$

The projection operator can be viewed as a generalization of the idea of resolving a vector into its components along the basis vectors of a Cartesian coordinate system. In group theory it resolves a *state vector*, a function, into components that transform according to the rows of the different Irreps of the symmetry group. In contrast to quantum mechanical projection operators, in Hilbert spaces, and in vector projections in Cartesian spaces, this projection is independent of the particular basis set of functions that may be associated with the Irreps. These symmetry projection operators are constructed from the matrix representatives of Irreps.

6.2.1 Construction of the symmetry transfer operators

Let us consider a basis set $\{({}^\nu\phi_k)\}$ for an Irrep (ν) of a group $\mathcal{G}$. If we operate on one of the basis functions, $({}^\nu\phi_k)$, with the operator $\hat{R}$, we generate a linear combination of the set of basis functions given by

$$\hat{R}({}^\nu\phi_k) = \sum_l ({}^\nu\phi_l) ({}^\nu\Gamma_{lk}(R)), \quad (6.4)$$

where the coefficients are elements of the k th row of $({}^\nu\Gamma(R))$. Making use of the matrix orthogonality relations given by (4.27),

$$\frac{d_\mu}{g} \sum_R ({}^\mu\Gamma_{ij}(R)) ({}^\nu\Gamma_{j'i'}^{-1}(R)) = \delta_{\mu\nu} \delta_{ii'} \delta_{jj'}, \quad (6.5)$$

we multiply (6.5) by $(d_\mu/g)({}^\mu\Gamma_{ji}^{-1}(R))$ and sum over R , to get

$$\begin{aligned} \frac{d_\mu}{g} \sum_R ({}^\mu\Gamma_{ji}^{-1}(R)) \hat{R}({}^\nu\phi_k) &= \sum_l ({}^\nu\phi_l) \frac{d_\mu}{g} \sum_R ({}^\mu\Gamma_{ji}^{-1}(R)) ({}^\nu\Gamma_{lk}(R)) \\ &= \sum_l ({}^\nu\phi_l) \delta_{\nu\mu} \delta_{il} \delta_{jk} \\ &= ({}^\nu\phi_i) \delta_{\nu\mu} \delta_{jk}. \end{aligned} \quad (6.6)$$

It is now possible to define a *symmetry transfer operator* $({}^\mu)\hat{P}_{ij}$ as

$$({}^\mu)\hat{P}_{ij} = \frac{d_\mu}{g} \sum_{\hat{R}} ({}^\mu\Gamma_{ji}^{-1}(R)) \hat{R}, \quad i \neq j. \quad (6.7)$$

The matrix element $({}^\mu\Gamma_{ji}^{-1}(R))$ is just a number, perhaps a complex number. The operator $\hat{R}$ that follows can be expressed in *any* Rep engendered by $\hat{R}$ on an arbitrary complete set of basis functions in the Hilbert space of the physical system invariant under $\mathcal{G}$. The nature and procedure of construction of the operator $\hat{R}$ will be demonstrated in the examples that follow.

We find that

$$({}^\mu)\hat{P}_{ij}^\dagger ({}^\nu)\hat{P}_{i'j'} = \delta_{\mu\nu} \delta_{ii'} ({}^\mu)\hat{P}_{jj'}. \quad (6.8)$$

The restriction $i \neq j$ in (6.7) is a reminder that $({}^\mu)\hat{P}_{ij}$ is an off-diagonal operator. It is a symmetry transfer operator which changes the symmetry properties from one row of the Irrep (ν) to another row of the same Irrep, as described by the equation

$$({}^\mu)\hat{P}_{ij} ({}^\nu)\phi_k = ({}^\nu)\phi_i \delta_{\nu\mu} \delta_{jk}. \quad (6.9)$$

If $\nu = \mu$, $k = j$, then

$$^{(\mu)}\hat{P}_{ij} \ ^{(\mu)}\phi_j = ^{(\mu)}\phi_i. \quad (6.10)$$

That is, the symmetry transfer operator $^{(\mu)}\hat{P}_{ij}$ operating on a function $^{(\mu)}\phi_j$ belonging to the j th row of the μ th Irrep yields its orthogonal partner belonging to the i th row.

Thus, if *one* of the basis functions is known we can find all its *partners* by using the symmetry transfer operator. An example follows.

Example 6.6

We treat a system with C_{3v} symmetry, and consider the function, $\phi_2 = x^2 - y^2$, which transforms according to the second row of its two-dimensional Irrep $^{(3)}\Gamma$. Operating with the symmetry transfer operator

$$\begin{aligned} ^{(3)}\hat{P}_{21} &= \frac{2}{6} \sum_R ^{(3)}\Gamma_{21}^{-1}(R) \hat{R} \\ &= \frac{1}{3} \left\{ ^{(3)}\Gamma_{21}^{-1}(E) \hat{E} + ^{(3)}\Gamma_{21}^{-1}(\sigma_1) \hat{\sigma}_1 + ^{(3)}\Gamma_{21}^{-1}(\sigma_2) \hat{\sigma}_2 \right. \\ &\quad \left. + ^{(3)}\Gamma_{21}^{-1}(\sigma_3) \hat{\sigma}_3 + ^{(3)}\Gamma_{21}^{-1}(C_3) \hat{C}_3 + ^{(3)}\Gamma_{21}^{-1}(C_3^2) \hat{C}_3^2 \right\} \\ &= \frac{1}{3} \left[0(\hat{E} + \hat{\sigma}_1) - \frac{\sqrt{3}}{2}(\hat{C}_3^2 + \hat{\sigma}_2) + \frac{\sqrt{3}}{2}(\hat{C}_3 + \hat{\sigma}_1) \right] \end{aligned}$$

should produce its partner function, which belongs to the first row of $^{(3)}\Gamma$.

We remind ourselves of the procedure by considering the action of $\hat{C}_3$ on ϕ_2 . Following the prescription of Section 3.2, we replace x and y in $\phi_2(x, y) = x^2 - y^2$ by the corresponding components x' and y' as determined by

$$\begin{bmatrix} x' \\ y' \end{bmatrix} = C_3^{-1} \begin{bmatrix} x \\ y \end{bmatrix} = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix}.$$

We find after a bit of algebra that

$$\begin{aligned} \hat{C}_3(x^2 - y^2) &= \hat{\sigma}_3(x^2 - y^2) = \frac{-1}{2}x^2 + \frac{1}{2}y^2 + \sqrt{3}xy, \\ \hat{C}_3^2(x^2 - y^2) &= \hat{\sigma}_2(x^2 - y^2) = \frac{-1}{2}x^2 + \frac{1}{2}y^2 - \sqrt{3}xy. \end{aligned}$$

We obtain

$$\begin{aligned} ^{(3)}\hat{P}_{12}(x^2 - y^2) &= \frac{1}{3} \left\{ 2 \times 0 \times (x^2 - y^2) \right. \\ &\quad \left. - 2 \times \frac{\sqrt{3}}{2} \left(\frac{-1}{2}x^2 + \frac{1}{2}y^2 - \sqrt{3}xy \right) \right. \\ &\quad \left. + 2 \times \frac{\sqrt{3}}{2} \left(\frac{-1}{2}x^2 + \frac{1}{2}y^2 + \sqrt{3}xy \right) \right\} \\ &= 2xy. \end{aligned}$$

Thus $2xy$ is the partner function of $x^2 - y^2$ and the two form a basis for $^{(3)}\Gamma$.

In general, if we know just one basis function for an Irrep, we can find all the partner basis functions by using the appropriate symmetry transfer operators.

Construction of the operator $\hat{R}$

At this point we try to clarify the physical role played by the operator $\hat{R}$ when applying (6.7) to a physical problem. In a typical problem we may be interested in the entire Hilbert space of the system, or in some closed subspace. In any case, we can choose a basis set that spans the relevant space. We partition the relevant space into subspaces that belong to different rows, indexed k , of Irreps (ν). We also allow for the possible multiple occurrence of subspaces belonging to Irrep (ν), and label these (ν)-subspaces with the index s . Thus we designate the basis as $\Phi := \{^{(\nu)}\phi_{ks}\}$. A familiar example of such multiple occurrence can be found, say, in the p -states of a hydrogen atom; they may be 2p, 3p, 4p, ... but they all transform like the basis Y_l^m !

Now, we expand an arbitrary state vector Ψ in the relevant Hilbert space/subspace of the physical system, in terms of the basis set $\{^{(\nu)}\phi_{ks}\}$ that span the Hilbert space. We obtain

$$\Psi = \sum_{\nu, k, s} ^{(\nu)} c_{ks} ^{(\nu)} \phi_{ks}, \quad (6.11)$$

where k and s index the rows of Irrep (ν) and the subspaces that transform according to Irrep (ν). Operating on Ψ by the symmetry transfer operator $^{(\mu)}\hat{P}_{ij}$ gives

$$\begin{aligned} ^{(\mu)}\hat{P}_{ij} \Psi &= ^{(\mu)}\hat{P}_{ij} \sum_{\nu, k, s} ^{(\nu)} c_{ks} ^{(\nu)} \phi_{ks} = \sum_{\nu, k, s} ^{(\nu)} c_{ks} ^{(\mu)} \hat{P}_{ij} ^{(\nu)} \phi_{ks} \\ &= \sum_{\nu, k, s} ^{(\nu)} c_{ks} ^{(\nu)} \phi_{is} \delta_{\nu\mu} \delta_{jk} = \sum_s ^{(\mu)} c_{js} ^{(\mu)} \phi_{is}, \end{aligned} \quad (6.12)$$

where we used (6.9). We find that $^{(\mu)}\hat{P}_{ij}$ selects the $^{(\mu)}\phi_{js}$ s from Ψ and converts them to $^{(\mu)}\phi_{is}$ s.

6.2.2 The Wigner projection operator

By setting $j = i$, we can define a projection operator known as the *Wigner projection operator* $^{(\mu)}P_{ii}$ as

$$^{(\mu)}\hat{P}_{ii} \Psi = ^{(\mu)} c_i ^{(\mu)} \phi_i. \quad (6.13)$$

It is of fundamental importance. In addition to its many applications in physical problems, it will play a key role in developing the irreducible matrix Reps.

We identify $^{(\mu)}\hat{P}_{ii}$ as the projection operator associated with the i th row of the μ th Irrep, the (μ, i) th symmetry of $\mathcal{G}$, or the Wigner projection operator. The projection operator selects the component of an arbitrary vector Ψ along $^{(\mu)}\phi_i$, which may be thought of as

the component along a unit vector $^{(\mu)}\phi_i$ inasmuch as $^{(\mu)}\phi_i$ is from an orthonormal basis set. It is clear that when the projection operator is applied to a general function, it will yield either zero or a basis function that is unnormalized, in general.

Example 6.7

We consider the operation of the Wigner projection operators belonging to the $^{(3)}\Gamma$ of C_{3v} , acting on:

(i) The function

$$\mathcal{F}(x, y, z) = x + y + z + xz + x^2.$$

Here, we must do something a bit different from Example 6.1. In that example we operated on a *known* basis function belonging to one row of an Irrep, and converted it to a basis function belonging to a different row of the Irrep. Here, we are considering a rather general function, or Hilbert space vector, and we want to project out basis functions that belong to a particular row of an Irrep. One way of doing the projection is to follow a procedure analogous to what was done in Section 3.2.

The prescription To project $^{(\mu)}\hat{P}_{ii}$ onto $\mathcal{F}(x, y, z)$, write the parts of the function $\mathcal{F}$ as the components of a vector and let the projection operator

$$^{(\mu)}\hat{P}_{ii} = \frac{d_\mu}{g} \sum_{\hat{R}} ^{(\mu)}\Gamma_{ii}^{-1}(\hat{R}) \hat{R} \quad (6.14)$$

act on each component separately. This generates a new function $\mathcal{F}'$, some (or all) of whose components might be zero. The components of this new function are basis functions that belong to the Irrep $^{(\mu)}\Gamma$.

For $^{(3)}\Gamma$ of C_{3v} , we take $i = 1$ and refer to Section 3.2 for the action of individual operators $\hat{R}$ on the various parts of the function $\mathcal{F}$. By choosing $i = 1$ we find basis functions that *belong* to the first row of $^{(3)}\Gamma$.

$$\begin{aligned} ^{(3)}\hat{P}_{11} \mathcal{F} &= \frac{d_3}{g} \sum_{\hat{R}} ^{(3)}\Gamma_{11}^{-1}(\hat{R}) \hat{R} \begin{bmatrix} x \\ y \\ z \\ xz \\ x^2 \end{bmatrix} \\ &= \frac{2}{6} \left\{ (1) \hat{E} \begin{bmatrix} x \\ y \\ z \\ xz \\ x^2 \end{bmatrix} + (-1) \hat{\sigma}_1 \begin{bmatrix} x \\ y \\ z \\ xz \\ x^2 \end{bmatrix} + \left(\frac{1}{2}\right) \hat{\sigma}_2 \begin{bmatrix} x \\ y \\ z \\ xz \\ x^2 \end{bmatrix} \right\} \end{aligned}$$

$$\begin{aligned}
& + \left(\frac{1}{2}\right) \hat{\sigma}_3 \begin{bmatrix} x \\ y \\ z \\ xz \\ x^2 \end{bmatrix} + \left(\frac{-1}{2}\right) \hat{C}_3 \begin{bmatrix} x \\ y \\ z \\ xz \\ x^2 \end{bmatrix} + \left(\frac{-1}{2}\right) \hat{C}_3^2 \begin{bmatrix} x \\ y \\ z \\ xz \\ x^2 \end{bmatrix} \Bigg\} \\
& = \frac{1}{3} \left\{ \begin{bmatrix} x \\ y \\ z \\ xz \\ x^2 \end{bmatrix} - \begin{bmatrix} -x \\ y \\ z \\ -xz \\ x^2 \end{bmatrix} \right. \\
& \quad + \frac{1}{2} \begin{bmatrix} \frac{1}{2}x - \frac{\sqrt{3}}{2}y \\ -\frac{\sqrt{3}}{2}x - \frac{1}{2}y \\ z \\ \left(\frac{1}{2}x - \frac{\sqrt{3}}{2}y\right)z \\ \left(\frac{1}{2}x - \frac{\sqrt{3}}{2}y\right)^2 \end{bmatrix} + \frac{1}{2} \begin{bmatrix} \frac{1}{2}x + \frac{\sqrt{3}}{2}y \\ +\frac{\sqrt{3}}{2}x - \frac{1}{2}y \\ z \\ \left(\frac{1}{2}x + \frac{\sqrt{3}}{2}y\right)z \\ \left(\frac{1}{2}x + \frac{\sqrt{3}}{2}y\right)^2 \end{bmatrix} \\
& \quad \left. - \frac{1}{2} \begin{bmatrix} \frac{-1}{2}x - \frac{\sqrt{3}}{2}y \\ +\frac{\sqrt{3}}{2}x - \frac{1}{2}y \\ z \\ \left(\frac{-1}{2}x - \frac{\sqrt{3}}{2}y\right)z \\ \left(\frac{-1}{2}x - \frac{\sqrt{3}}{2}y\right)^2 \end{bmatrix} - \frac{1}{2} \begin{bmatrix} -\frac{1}{2}x + \frac{\sqrt{3}}{2}y \\ -\frac{\sqrt{3}}{2}x - \frac{1}{2}y \\ z \\ \left(\frac{-1}{2}x + \frac{\sqrt{3}}{2}y\right)z \\ \left(\frac{-1}{2}x + \frac{\sqrt{3}}{2}y\right)^2 \end{bmatrix} \right\} \\
& = \frac{1}{3} \begin{bmatrix} 3x \\ 0 \\ 0 \\ 3xz \\ 0 \end{bmatrix} = \begin{bmatrix} x \\ 0 \\ 0 \\ xz \\ 0 \end{bmatrix}.
\end{aligned}$$

We have found two basis functions $\{x, xz\}$ that belong to the first row of $^{(3)}\Gamma$ for the group C_{3v} . We might *expect* from Section 3.2 that x^2 would be a basis function. Perhaps it belongs to the second row of $^{(3)}\Gamma$.

- (ii) The function, $\mathcal{F} = x^2 + y^2 + xy$, and check to see if any parts of this function serve as basis functions belonging to the second row of $^{(3)}\Gamma$.

$$\begin{aligned}
^{(\mu)}\hat{P}_{22}\mathcal{F} &= \frac{d_\mu}{g} \sum_{\hat{R}} ^{(\mu)}\Gamma_{22}^{-1}(\hat{R}) \hat{R} \begin{bmatrix} x^2 \\ y^2 \\ xy \end{bmatrix} \\
&= \frac{2}{6} \left\{ (1) \hat{E} \begin{bmatrix} x^2 \\ y^2 \\ xy \end{bmatrix} + (1) \hat{\sigma}_1 \begin{bmatrix} x^2 \\ y^2 \\ xy \end{bmatrix} + \left(\frac{-1}{2}\right) \hat{\sigma}_2 \begin{bmatrix} x^2 \\ y^2 \\ xy \end{bmatrix} \right.
\end{aligned}$$

$$\begin{aligned}
& + \left(\frac{-1}{2} \right) \hat{\sigma}_3 \begin{bmatrix} x^2 \\ y^2 \\ xy \end{bmatrix} + \left(\frac{-1}{2} \right) \hat{C}_3 \begin{bmatrix} x^2 \\ y^2 \\ xy \end{bmatrix} + \left(\frac{-1}{2} \right) \hat{C}_3^2 \begin{bmatrix} x^2 \\ y^2 \\ xy \end{bmatrix} \Bigg\} \\
& = \frac{1}{3} \left\{ \begin{bmatrix} x^2 \\ y^2 \\ xy \end{bmatrix} + \begin{bmatrix} x^2 \\ y^2 \\ -xy \end{bmatrix} + \frac{-1}{2} \begin{bmatrix} \left(\frac{1}{2}x - \frac{\sqrt{3}}{2}y \right)^2 \\ \left(\frac{-\sqrt{3}}{2}x - \frac{1}{2}y \right)^2 \\ \left(\frac{1}{2}x - \frac{\sqrt{3}}{2}y \right) \left(\frac{-\sqrt{3}}{2}x - \frac{1}{2}y \right) \end{bmatrix} \right. \\
& \quad - \frac{1}{2} \begin{bmatrix} \left(\frac{1}{2}x + \frac{\sqrt{3}}{2}y \right)^2 \\ \left(\frac{\sqrt{3}}{2}x - \frac{1}{2}y \right)^2 \\ \left(\frac{1}{2}x + \frac{\sqrt{3}}{2}y \right) \left(\frac{\sqrt{3}}{2}x - \frac{1}{2}y \right) \end{bmatrix} - \frac{1}{2} \begin{bmatrix} \left(\frac{-1}{2}x - \frac{\sqrt{3}}{2}y \right)^2 \\ \left(\frac{\sqrt{3}}{2}x - \frac{1}{2}y \right)^2 \\ \left(\frac{-1}{2}x - \frac{\sqrt{3}}{2}y \right) \left(\frac{\sqrt{3}}{2}x - \frac{1}{2}y \right) \end{bmatrix} \\
& \quad \left. - \frac{1}{2} \begin{bmatrix} \left(\frac{-1}{2}x + \frac{\sqrt{3}}{2}y \right)^2 \\ \left(\frac{-\sqrt{3}}{2}x - \frac{1}{2}y \right)^2 \\ \left(\frac{-1}{2}x + \frac{\sqrt{3}}{2}y \right) \left(\frac{-\sqrt{3}}{2}x - \frac{1}{2}y \right) \end{bmatrix} \right\} \\
& = \frac{1}{3} \begin{bmatrix} \frac{3}{2}(x^2 - y^2) \\ \frac{3}{2}(y^2 - x^2) \\ 0 \end{bmatrix} = \begin{bmatrix} (x^2 - y^2) \\ (y^2 - x^2) \\ 0 \end{bmatrix},
\end{aligned}$$

where a factor of 1/2 has been dropped in the last matrix in order to get the conventional normalization. Clearly, any numerical multiplier will be carried through all steps of the projection process, so the projected basis functions are not generally normalized. We have projected out the basis function $(x^2 - y^2)$ as belonging to the second row of $^{(3)}\Gamma$ for the group $\mathcal{C}_{3v}$. In Chapter 3, we recognized that it was necessary to take the appropriate linear combination of x^2 and y^2 to get a basis function belonging to a *unitary* Rep. Here, the use of unitary projection operators automatically gave us the correct basis function, apart from a scaling factor.

Hermiticity and idempotency: the eigenvalue problem

The Wigner projection operators are Hermitian and idempotent, namely

$$^{(\mu)}\hat{P}_{ii}^\dagger = ^{(\mu)}\hat{P}_{ii}, \quad (6.15)$$

$$^{(\mu)}\hat{P}_{ii}^2 = ^{(\mu)}\hat{P}_{ii}. \quad (6.16)$$

Let us introduce an arbitrary complete set of basis vectors in the Hilbert space of the system

$$\Psi = \{\phi_1, \phi_2, \dots\},$$

which engenders a Rep of $\mathcal{G}$

$$\hat{R}\Psi = \Psi\Gamma(R), \quad R \in \mathcal{G}.$$

$\Gamma(R)$ is then substituted for $\hat{R}$ in the expression of $^{(\mu)}P_{ii}$, and we obtain

$$^{(\mu)}\hat{P}_{ii} \Psi = \Psi \frac{d_{\mu}}{g} \sum_{R \in \mathcal{G}} ^{(\mu)}\Gamma_{ii}^*(R) \Gamma(R) = \Psi ^{(\mu)}\mathbf{P}_i. \quad (6.17)$$

The matrix $^{(\mu)}\mathbf{P}_i$ satisfies [5]:

- (i) (6.15), which guarantees the existence of a unitary transformation $\mathcal{U}$ that diagonalizes $^{(\mu)}\mathbf{P}_i$, and
- (ii) (6.16), which tells us that the eigenvalues can only be 1 or 0 !!

The eigenvalue problem

We then write

$$\mathcal{U}^\dagger ^{(\mu)}\mathbf{P}_i \mathcal{U} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \quad (6.18)$$

or

$$^{(\mu)}\mathbf{P}_i \mathcal{U} = \mathcal{U} \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} = (\mathbf{u}, \mathbf{0}), \quad (6.19)$$

where $\mathbf{u}$ is the rectangular part of $\mathcal{U}$ containing eigencolumns with unit eigenvalues,

$$^{(\mu)}\mathbf{P}_i \mathbf{u} = \mathbf{u}. \quad (6.20)$$

Adopting this approach ensures that the ensuing symmetrized vector, i.e. the eigencolumns of $\mathbf{u}$, are independent.

Example 6.8

We consider the case of vibrational modes of the water molecule. The H_2O molecule has C_{2v} symmetry, with the symmetry operations shown in Figure 6.4.

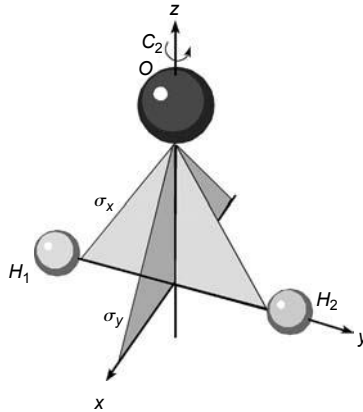


Fig. 6.4. The water molecule and its symmetry.

Hilbert space The relevant Hilbert space is that of infinitesimal displacements of the O and two H atoms, of dimension 9; it is spanned by the vector

$$\mathbf{d} = \begin{bmatrix} \mathbf{d}_{H_1} & \mathbf{d}_{H_2} & \mathbf{d}_O \end{bmatrix} \\ = \begin{bmatrix} x_{H_1} & y_{H_1} & z_{H_1} & x_{H_2} & y_{H_2} & z_{H_2} & x_O & y_O & z_O \end{bmatrix},$$

where, for example, $\mathbf{d}_{H_1} = [x_{H_1} \ y_{H_1} \ z_{H_1}]$ describes the displacements of the hydrogen atom 1, as shown in Figure 6.4.

Rep engendered by C_{2v} We find that the local displacements of each atom, $\mathbf{d}_i = [x_i \ y_i \ z_i]$, will transform, under the operations of C_{2v} , according to the matrices:

$$\mathbb{I} \mathbf{d}_i = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \mathbf{d}_i, \quad C_2 \mathbf{d}_i = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \mathbf{d}_i, \\ \sigma_x \mathbf{d}_i = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \mathbf{d}_i, \quad \sigma_y \mathbf{d}_i = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \mathbf{d}_i.$$

In addition, we should remember that the action of C_{2v} on the H_2O molecule induced permutations among the set $[H_1, H_2, O]$, which can be described by the matrices

$$C_2 \begin{pmatrix} H_1 \\ H_2 \\ O \end{pmatrix} = \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{pmatrix} H_1 \\ H_2 \\ O \end{pmatrix}, \\ \sigma_x \begin{pmatrix} H_1 \\ H_2 \\ O \end{pmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{pmatrix} H_1 \\ H_2 \\ O \end{pmatrix}, \\ \sigma_y \begin{pmatrix} H_1 \\ H_2 \\ O \end{pmatrix} = \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{pmatrix} H_1 \\ H_2 \\ O \end{pmatrix}.$$

Combining these into a single Rep that includes the effect of symmetry operations of C_{2v} on both the atoms and the local coordinate systems attached to the atoms, we obtain

$$\mathbf{I} = \begin{bmatrix} \mathbb{I} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbb{I} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbb{I} \end{bmatrix}, \quad \mathbf{C}_2 = \begin{bmatrix} \mathbf{0} & C_2 & \mathbf{0} \\ C_2 & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & C_2 \end{bmatrix}, \\ \boldsymbol{\sigma}_x = \begin{bmatrix} \sigma_x & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \sigma_x & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \sigma_x \end{bmatrix}, \quad \boldsymbol{\sigma}_y = \begin{bmatrix} \mathbf{0} & \sigma_y & \mathbf{0} \\ \sigma_y & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \sigma_y \end{bmatrix},$$

where C_2 , σ_x and σ_y are the 3×3 matrices define above, and $\mathbf{0}$ is the 3×3 null matrix.

The Irreps of $\mathcal{C}_{2v}$ can be simply determined by the inspection method, and are given in Table 6.1.

Table 6.1. *Character table for $\mathcal{C}_{2v}$.*

	E	C_2	σ_x	σ_y
$(1)\Gamma$	1	1	1	1
$(2)\Gamma$	1	1	-1	-1
$(3)\Gamma$	1	-1	1	-1
$(4)\Gamma$	1	-1	-1	1

As an example, let us construct the projection operator $(1)P_{11}$ using (6.14),

$$\begin{aligned}
 (1)P_{11} &= \frac{1}{4} [\mathbf{I} + \mathbf{C}_2 + \sigma_x + \sigma_y] \\
 &= \begin{bmatrix} \mathbb{I} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbb{I} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbb{I} \end{bmatrix} + \begin{bmatrix} \mathbf{0} & C_2 & \mathbf{0} \\ C_2 & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & C_2 \end{bmatrix} + \begin{bmatrix} \sigma_x & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \sigma_x & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \sigma_x \end{bmatrix} + \begin{bmatrix} \mathbf{0} & \sigma_y & \mathbf{0} \\ \sigma_y & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \sigma_y \end{bmatrix} \\
 &= \frac{1}{4} \begin{bmatrix} \mathbb{I} + \sigma_x & C_2 + \sigma_y & \mathbf{0} \\ C_2 + \sigma_y & \mathbb{I} + \sigma_x & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbb{I} + \sigma_x + C_2 + \sigma_y \end{bmatrix} \\
 &= \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1/2 & 0 & 0 & -1/2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1/2 & 0 & 0 & 1/2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1/2 & 0 & 0 & 1/2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1/2 & 0 & 0 & 1/2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}
 \end{aligned}$$

Diagonalization of $(1)P_{11}$ gives

$$(1)\mathbf{u} = \begin{bmatrix} 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

with

$${}^{(4)}\mathbf{u} = \begin{bmatrix} 1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \end{bmatrix}$$

From the rows of these projection matrices we obtain the following linearly independent symmetrized vectors:

$${}^{(1)}\Gamma : \begin{cases} |1, 1\rangle = \frac{1}{\sqrt{2}} [0, 1, 0; 0, -1, 0; 0, 0, 0], \\ |1, 2\rangle = \frac{1}{\sqrt{2}} [0, 0, 1; 0, 0, 1; 0, 0, 0], \\ |1, 3\rangle = [0, 0, 0; 0, 0, 0; 0, 0, 1], \end{cases}$$

$${}^{(2)}\Gamma : |2, 1\rangle = \frac{1}{\sqrt{2}} [1, 0, 0; -1, 0, 0; 0, 0, 0],$$

$${}^{(3)}\Gamma : \begin{cases} |3, 1\rangle = \frac{1}{\sqrt{2}} [0, 1, 0; 0, 1, 0; 0, 0, 0], \\ |3, 2\rangle = \frac{1}{\sqrt{2}} [0, 0, 1; 0, 0, -1; 0, 0, 0], \\ |3, 3\rangle = [0, 0, 0; 0, 0, 0; 0, 1, 0], \end{cases}$$

$${}^{(4)}\Gamma : \begin{cases} |4, 1\rangle = \frac{1}{\sqrt{2}} [1, 0, 0; 1, 0, 0; 0, 0, 0], \\ |4, 2\rangle = [0, 0, 0; 0, 0, 0; 1, 0, 0]. \end{cases}$$

Molecular motion must include three degrees of freedom associated with the center-of mass (COM), and another three describing the rotations about the COM.

The COM translation transforms as a vector; it engenders the three-dimensional vector Rep ${}^{(\vee)}\Gamma$. The reduction of ${}^{(\vee)}\Gamma$ in terms of the $\mathcal{C}_{3v}$ Irreps is

$${}^{(\vee)}\Gamma = {}^{(1)}\Gamma + {}^{(3)}\Gamma + {}^{(4)}\Gamma.$$

Moreover, it requires that the constituent atoms have identical displacement vectors. Thus, we can write

$$\begin{aligned} |{}^{(\vee)}\Gamma, 1\rangle &:= \frac{1}{\sqrt{3}} [1, 0, 0; 1, 0, 0; 1, 0, 0] = \frac{1}{\sqrt{3}} [\sqrt{2} |4, 1\rangle + |4, 2\rangle], \\ |{}^{(\vee)}\Gamma, 2\rangle &:= \frac{1}{\sqrt{3}} [0, 1, 0; 0, 1, 0; 0, 1, 0] = \frac{1}{\sqrt{3}} [\sqrt{2} |3, 1\rangle + |3, 3\rangle], \\ |{}^{(\vee)}\Gamma, 3\rangle &:= \frac{1}{\sqrt{3}} [0, 0, 1; 0, 0, 1; 0, 0, 1] = \frac{1}{\sqrt{3}} [\sqrt{2} |1, 2\rangle + |1, 3\rangle]. \end{aligned}$$

Comment on representations of angular momenta

The angular momentum $\mathbf{L}$ of a particle about a point is given by $\mathbf{L} = \mathbf{r} \times \mathbf{p}$, where $\mathbf{r}$ and $\mathbf{p}$ are its position and linear momentum vectors, respectively. Since both $\mathbf{r}$ and $\mathbf{p}$ change sign under spatial inversion, $\mathbf{L}$ does not change sign under such operation. It is an *axial vector* – it transforms like a vector under proper rotations. We can consider an improper rotation $\bar{R}$ as a combination of a proper rotation and an inversion, $\bar{R} = RI = IR$; and we find that

$$^{(v)}\chi(\bar{R}) = -^{(v)}\chi(R).$$

Since the determinants of proper and improper rotations in three dimensions are $+1$ and -1 , respectively, the characters of an axial vector Rep can be derived from those of a polar vector Rep with the relation

$$^{(a)}\chi(\bar{R}) = \det |\bar{R}| ^{(v)}\chi(\bar{R}).$$

The characters for the three-dimensional axial vector Rep, of which the rotational angular momentum of the water molecule is a basis, are then given by

$$\chi(E) = 3, \quad \chi(C_2) = -1, \quad \chi(\sigma_x) = \chi(\sigma_y) = -1.$$

A reduction of this three-dimensional Rep in terms of the one-dimensional Irreps of C_{2v} gives

$$^{(a)}\Gamma = ^{(2)}\Gamma \oplus ^{(3)}\Gamma \oplus ^{(4)}\Gamma.$$

The corresponding symmetrized vectors are

$$\begin{aligned} |^{(a)}\Gamma, 1\rangle &= \frac{1}{\sqrt{2}} [1, 0, 0; -1, 0, 0; 0, 0, 0] = |2, 1\rangle, \\ |^{(a)}\Gamma, 2\rangle &= \frac{1}{\sqrt{3}} \left[0, \frac{1}{2}, -\frac{\sqrt{3}}{2}; 0, \frac{1}{2}, \frac{\sqrt{3}}{2}; 0, -1, 0 \right] \\ &= \frac{1}{\sqrt{3}} \left[\frac{1}{\sqrt{2}} |3, 1\rangle - \sqrt{\frac{3}{2}} |3, 2\rangle - |3, 3\rangle \right], \\ |^{(a)}\Gamma, 3\rangle &= \frac{1}{\sqrt{3}} [-1, 0, 0; -1, 0, 0; 1, 0, 0] \\ &= \frac{1}{\sqrt{3}} [|4, 2\rangle - \sqrt{2} |4, 1\rangle]. \end{aligned}$$

We can anticipate that, in the most general case, the matrix $\Gamma(R)$ will be of dimension $3N \times 3N$, where N is the number of particles in the system. For the case of molecular vibration of the H_2O molecule, we found that it would be 9×9 . A complete analysis of this system will be given in Chapter 15.

- The Wigner projection operator $^{(\mu)}\hat{P}_{ii}$ can be used to project-out of a general function a basis function that transforms as the i th row of Irrep (μ) .
- The symmetry transfer operator $^{(\mu)}\hat{P}_{ij}$ can then be used to generate all the partner basis functions.

Program for generating projection operators for molecular vibrations

The input information required is:

(i) Generators of the point-group:

- Irrep matrices **GM**, rotation matrices **Rot**, and permutations **P** of the point-group generators;
- Number of generators **NG**, number of Irreps **NC**, and number of permutation entries.

This is contained in the point-group file, for example **C2v.m**.

- (ii) Atomic position vectors are contained in **RR[[i,j]]**, where **i** denotes either atomic species or orbit, and **j**, member atoms of species or orbit **i**. Thus, there are two ways to enter the required atomic positions data: you may record all atomic positions, classifying them by species, or you may enter orbit representatives, identifying them as first members of their respective orbits. In the latter case, you have to provide for the generation of the remaining members of each orbit with the aid of rotation matrices.
- (iii) The total number of atoms is **NAT**, the number of atomic species is **NSP**, or the number of orbits **NOR**.
- (iv) The number of atoms of species (or orbit) **i** is **ATYPE[[i]]**.
- (v) In case species are specified and not orbits, then orbits have to be generated.

Ultimately, we classify the atomic positions into *orbits*. Sometimes different orbits may belong to the same elemental species. In the case of the H₂O molecule, the two H atoms occupy equivalent positions and fall in the same orbit, since they can be interchanged by the action of the operators of C_{2v} .

Program MOLSYM

Required input data and *Mathematica* packages:

```
<< C:/path/point-group.m
<< C:/path/mol.m
<< DiscreteMath'Combinatorica'
<< LinearAlgebra'MatrixManipulation'
```

1. Generate all the symmetry aspects of the point-group:
Rotation matrices, Irrep matrices, and characters.

```

Rot[1] = IdentityMatrix[3];
Initiate matrix Ireps in list Irrep, Irrep dimensions in dmu
REP = {};
Do[
  Switch[dmu[[i]] == 1,
    True, Do[AppendTo[REP, 1], {j, 1, g}],
    False,
    Do[
      AppendTo[REP, IdentityMatrix[dmu[[i]]]],
      {j, 1, g}
    ]
  ], {i, 1, NC}
];
Irrep = Partition[REP, g];
L = {Range[NP]};
Do[
  AppendTo[L, P[[i]]];
  Do[
    Irrep[[j, i + 1]] = GM[[j, i], {j, 2, NC}
  ], {i, 1, NG}
];
Array[L, {NG + 1}];
nel = Length[L];
f := Permute[L[[i]], L[[j]]];
While[TrueQ[Length[L] < g],
  For[i = 1, i < g, i++,
    For[j = 1, j < (Length[L] + 1), j++,
      Switch[FreeQ[L, f], True,
        AppendTo[L, f]; nel++;
        Rot[nel] = Rot[i].Rot[j];
        Do[
          Switch[dmu[[mu]] == 1,
            True,

```

```

Irrep[[mu, nel]] = Irrep[[mu, i]] * Irrep[[mu, j]],
      ch[mu, nel] = Irrep[[mu, nel]],
      False,
Irrep[[mu, nel]] = Irrep[[mu, i]] * Irrep[[mu, j]];
      ch[mu, nel] = Tr[Irrep[[mu, nel]]]
      ], {mu, 2, NC}
    ]
  ]
]
]

```

List `Irrep` now contains all matrix Irreps, for all group elements.
List `ch` contains Irrep characters.

2. Symmetry of atomic positions:

Operate on the atomic positions by group rotations and construct the permutations among equivalent atoms under the action of these operations. The permutation matrices are stored in `PERMA`. These matrices also define the molecule's orbits.

• Generate permutation matrices:

```

PERMA = {Range[NAT]}; NPER = {};
Do[
NOA = 0;
Do[
  Do[
    RP = Rot[kk]·RR[ik, jk]; kx = 0; park = 0;
    While[And[kx < ATYPE[[ik]], park == 0], kx++;
      RDIF = RP - RX[ik, kx];
      Switch[RDIF . RDIF < 0.01,
        True, lx = NOA + kx;
        AppendTo[NPER, lx]; park = 1
      ]
    ], {jk, 1, ATYPE[[ik]]}
  ];
];

```



```

NOA += ATYPE[[ik]], {ik, 1, NSM}
];
AppendTo[PERMA, NPER]; NPER = {}, {kk, 2, g}];
Pro is initially a 3NAT x 3NAT zero matrix

Do[
  Pro = {};

```

3. Construction of Irrep projection operators:

```

ZRO = 0*IdentityMatrix[3]; Sympro = {};
Do[
  dmux[imu] = 0, {imu, 1, NC}
]; Do[
  AppendTo[Pro, ZRO],
  {i, 1, NAT}, {j, 1, NAT}
]; Pro = Partition[Pro, NAT];

• Construct projection operator P(mu, i) in Pro
Do[
  Do[
    ic = PERMA[[kk, ir]];
    Switch[dmu[[mu]] == 1,
      True,
      Pro[[ir, ic]] += ch[mu, kk] * Rot[kk],
      False,
      Pro[[ir, ic]] += Irrep[[mu, kk, nu, nu]] * Rot[kk]
    ], {kk, 1, g}
  ], {ir, 1, NAT}
];
Do[
  Do[
    Do[
      im = 3* (ir - 1) + i;

```

```

Do[
  jm = 3*(ic - 1) + j;
  Proj[im, jm] = dmu[mu] * Pro[[ir, ic, i, j]]/g,
  {j, 1, 3}
], {ic, 1, NAT}
], {i, 1, 3}
], {ir, 1, NAT}
];
Project = Array[Proj, {3*NAT, 3*NAT}];
EGV = Eigenvalues[Project];
EV = Eigenvectors[Project];
Do[
  Switch[EGV[[ig]] == 1,
    True, dmu[mu]++; AppendTo[Sympro, EV[[ig]]]
  ], {ig, 1, 3*NAT}
], {"", {nu, 1, dmu[mu]}}
], {mu, 1, NC}
]
];
Print[
  "Symmetry-adapted eigenvectors: ",
  MatrixForm[Sympro]
]

```

6.2.3 The Irrep projection operator

Often only the characters of Irreps are known. For this case it is useful to define yet another projection operator, the *Irrep projection operator* $^{(\mu)}\hat{P}$ as

$$\begin{aligned}
 ^{(\mu)}\hat{P} &= \sum_i ^{(\mu)}\hat{P}_{ii} \\
 &= \frac{d_\mu}{g} \sum_i \sum_{\hat{R}} ^{(\mu)}\Gamma_{ii}^{-1}(\hat{R}) \hat{R} \\
 &= \frac{d_\mu}{g} \sum_{\hat{R}} ^{(\mu)}\chi(\hat{R}) \hat{R},
 \end{aligned} \tag{6.21}$$

where use has been made of (6.14).

Operating on a function Ψ , the Irrep projection operator produces a vector function in the subspace of the Irrep $^{(\mu)}\Gamma$ given by

$$\begin{aligned} {}^{(\mu)}\hat{P} \Psi &= \sum_i {}^{(\mu)}\hat{P}_{ii} \Psi = \frac{d_\mu}{g} \sum_{\hat{R}} {}^{(\mu)}\chi(\hat{R}) \hat{R} \Psi \\ &= \sum_i {}^{(\mu)}c_i {}^{(\mu)}\phi_i. \end{aligned} \quad (6.22)$$

This is a *sum* of the basis functions that span the subspace of the Irrep.

Again, a unitary transformation $\mathcal{U}$ that diagonalizes $^{(\mu)}\mathbf{P}$ according to (6.18) does exist, and gives the symmetrized eigenvectors $^{(\mu)}\mathbf{u}$ that form a basis set for the subspace $^{(\mu)}$, namely,

$${}^{(\mu)}\mathbf{P}_i {}^{(\mu)}\mathbf{u} = {}^{(\mu)}\mathbf{u}. \quad (6.23)$$

Example 6.9

Let us consider the action of the Irrep projection operator

$${}^{(3)}\hat{P} = \frac{2}{6} \left((2)\hat{E} + (0)\hat{\sigma}_1 + (0)\hat{\sigma}_2 + (0)\hat{\sigma}_3 + (-1)\hat{C}_3 + (-1)\hat{C}_3^{-1} \right)$$

of C_{3v} on the functions of Example 6.3. We find

$$\begin{aligned} {}^{(3)}\hat{P} \begin{bmatrix} x \\ y \\ z \\ xz \\ x^2 \end{bmatrix} &= \frac{1}{3} \left(2\hat{E} \begin{bmatrix} x \\ y \\ z \\ xz \\ x^2 \end{bmatrix} - \hat{C}_3 \begin{bmatrix} x \\ y \\ z \\ xz \\ x^2 \end{bmatrix} - \hat{C}_3^2 \begin{bmatrix} x \\ y \\ z \\ xz \\ x^2 \end{bmatrix} \right) \\ &= \frac{1}{3} \left\{ \begin{bmatrix} 2x \\ 2y \\ 2z \\ 2xz \\ 2x^2 \end{bmatrix} - \begin{bmatrix} -\frac{1}{2}x - \frac{\sqrt{3}}{2}y \\ +\frac{\sqrt{3}}{2}x - \frac{1}{2}y \\ z \\ \left(\frac{-1}{2}x - \frac{\sqrt{3}}{2}y\right)z \\ \left(\frac{-1}{2}x - \frac{\sqrt{3}}{2}y\right)^2 \end{bmatrix} - \begin{bmatrix} \frac{-1}{2}x + \frac{\sqrt{3}}{2}y \\ \frac{-\sqrt{3}}{2}x - \frac{1}{2}y \\ z \\ \left(\frac{-1}{2}x + \frac{\sqrt{3}}{2}y\right)z \\ \left(\frac{-1}{2}x + \frac{\sqrt{3}}{2}y\right)^2 \end{bmatrix} \right\} \\ &= \frac{1}{3} \begin{bmatrix} 3x \\ 3y \\ 0 \\ 3xz \\ \frac{3}{2}(x^2 - y^2) + \sqrt{3}xy \end{bmatrix} = \begin{bmatrix} x \\ y \\ 0 \\ xz \\ \frac{1}{2}(x^2 - y^2) + \frac{1}{\sqrt{3}}xy \end{bmatrix}. \end{aligned}$$

$$\begin{aligned}
({}^{(3)}\hat{P} \begin{bmatrix} x^2 \\ y^2 \\ xy \end{bmatrix}) &= \frac{1}{3} \left(2\hat{E} \begin{bmatrix} x^2 \\ y^2 \\ xy \end{bmatrix} - \hat{C}_3 \begin{bmatrix} x^2 \\ y^2 \\ xy \end{bmatrix} - \hat{C}_3^2 \begin{bmatrix} x^2 \\ y^2 \\ xy \end{bmatrix} \right) \\
&= \frac{1}{3} \left\{ \begin{bmatrix} 2x^2 \\ 2y^2 \\ 2xy \end{bmatrix} - \begin{bmatrix} \left(\frac{-1}{2}x - \frac{\sqrt{3}}{2}y\right)^2 \\ \left(\frac{\sqrt{3}}{2}x - \frac{1}{2}y\right)^2 \\ \left(\frac{-1}{2}x - \frac{\sqrt{3}}{2}y\right)\left(\frac{\sqrt{3}}{2}x - \frac{1}{2}y\right) \end{bmatrix} \right. \\
&\quad \left. - \begin{bmatrix} \left(\frac{-1}{2}x + \frac{\sqrt{3}}{2}y\right)^2 \\ \left(\frac{-\sqrt{3}}{2}x - \frac{1}{2}y\right)^2 \\ \left(\frac{-1}{2}x + \frac{\sqrt{3}}{2}y\right)\left(\frac{-\sqrt{3}}{2}x - \frac{1}{2}y\right) \end{bmatrix} \right\} \\
&= \frac{1}{3} \begin{bmatrix} \frac{3}{2}(x^2 - y^2) + \sqrt{3}xy \\ \frac{3}{2}(y^2 - x^2) + \sqrt{3}xy \\ \frac{1}{2}xy \end{bmatrix} = \begin{bmatrix} (x^2 - y^2) + \sqrt{\frac{1}{3}}xy \\ (y^2 - x^2) + \sqrt{\frac{1}{3}}xy \\ \frac{1}{3}xy \end{bmatrix}.
\end{aligned}$$

We notice that in both cases, if we start with a pure basis function of $({}^{(3)}\Gamma)$, we end up with a pure basis function, and when the initial function is not properly symmetrized, such as x^2 , we end up with a linear combination of the symmetry adapted basis functions of $({}^{(3)}\Gamma)$.

The Irrep projection operator obeys the idempotency property

$$({}^{(\mu)}\hat{P})^* ({}^{(\nu)}\hat{P}) = \delta_{\mu\nu} ({}^{(\mu)}\hat{P}),$$

which is to be expected from a projection operator. In the case of one-dimensional Irreps, $d_\mu = 1$, the projection operator is called a *primitive operator*, because it projects onto a one-dimensional subspace. Since, in general, $({}^{(\mu)}\hat{P})$ will produce a general vector (function) in the irreducible space (μ) , further resolution into row components has to be achieved by corresponding Wigner projection operators.

6.3 The regular projection matrices: the simple characteristic

Next we construct the Wigner projection matrix for the Hilbert space of the regular Rep.

$$({}^{(\mu)}\hat{P}_{ii}^{(\text{reg})}) = \frac{d_\mu}{g} \sum_{\hat{R}} ({}^{(\mu)}\Gamma_{ii}^{-1}(\hat{R})) ({}^{(\text{reg})}\Gamma(\hat{R})), \quad (6.24)$$

which yields the (μ, i) th symmetry type. Note that here we have specified the general operator $\hat{R}$ of (6.7) to be of a particular form, namely, the $g \times g$ regular Rep matrix. If we

sum over i we obtain a $g \times g$ matrix projection operator called the **simple characteristic**, defined as

$${}^{(\mu)}\hat{P}^{(\text{reg})} = \sum_{i=1} {}^{(\mu)}\hat{P}_{ii}^{\text{reg}}. \quad (6.25)$$

This can be expressed in a more useful form as follows:

$$\begin{aligned} {}^{(\mu)}\hat{P}^{(\text{reg})} &= \frac{d_\mu}{g} \sum_i \sum_{\hat{R}} {}^{(\mu)}\Gamma_{ii}^{-1}(\hat{R}) {}^{(\text{reg})}\Gamma(\hat{R}) \\ &= \frac{d_\mu}{g} \sum_{\hat{R}} {}^{(\mu)}\chi^*(\hat{R}) {}^{(\text{reg})}\Gamma(\hat{R}) \\ &= \frac{d_\mu}{g} \sum_{\mathcal{C}_i} \left\{ {}^{(\mu)}\chi^*(\mathcal{C}_i) \sum_{\hat{R} \in \mathcal{C}_i} {}^{(\text{reg})}\Gamma(\hat{R}) \right\} \\ &= \frac{d_\mu}{g} \sum_i^{N_c} {}^{(\mu)}\chi^*(\mathcal{C}_i) {}^{(\text{reg})}\mathbf{C}_i. \end{aligned}$$

$${}^{(\mu)}\hat{P}^{\text{reg}} = \frac{d_\mu}{g} \sum_i^{N_c} {}^{(\mu)}\chi^*(\mathcal{C}_i) {}^{(\text{reg})}\mathbf{C}_i, \quad (6.26)$$

where ${}^{(\text{reg})}\mathbf{C}_i$ is the regular Rep of the class matrix operator. This differs from (6.24) in that the general operator $\hat{R}$ has been replaced by the class matrix operator of the class to which $\hat{R}$ belongs and the summation is now over classes.

It is clear from (6.26) that ${}^{(\mu)}\hat{P}^{\text{reg}}$ is a $g \times g$ matrix that is a particular linear combination of the regular class matrices. Apart from an overall normalizing factor of d_μ/g , the coefficient for each regular class matrix is the complex character of that class in the μ th Irrep. Now, the elements of the regular class matrices are zeroes or ones as defined in (4.18) of Section 4.3, namely,

$${}^{(\text{reg})}\Gamma_{jk}(\hat{R}_i) = \begin{cases} 1, & \text{if } \hat{R}_j \hat{R}_k^{-1} = \hat{R}_i, \\ 0, & \text{otherwise.} \end{cases}$$

Thus, if we multiply a class matrix by its complex character, the new matrix consists of matrix elements that are either zero or the complex character of the class in the μ th Irrep. Thus, from the definition of ${}^{(\mu)}\hat{P}^{\text{reg}}$ in (6.26), we obtain the following simple expression for its elements:

$${}^{(\mu)}\hat{P}_{lm}^{\text{reg}} = \frac{d_\mu}{g} {}^{(\mu)}\chi(\hat{R}_l^{-1} \hat{R}_m) = \frac{d_\mu}{g} {}^{(\mu)}\chi({}^{(\text{reg})}\Gamma_{lm}). \quad (6.27)$$

This is particularly useful for computational purposes. The simple characteristics of the different Irreps can be easily constructed from the irreducible characters determined by Dixon's method. An example calculation also elucidates (6.26) and (6.27).

Example 6.10

Class matrices for C_{3v}

$$\begin{aligned}
 {}^{(\text{reg})}\mathbf{C}_1 &= {}^{(\text{reg})}\Gamma(E) = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \\
 {}^{(\text{reg})}\mathbf{C}_2 &= {}^{(\text{reg})}\Gamma(\sigma_1) + {}^{(\text{reg})}\Gamma(\sigma_2) + {}^{(\text{reg})}\Gamma(\sigma_3) \\
 &= \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \end{bmatrix} + \begin{bmatrix} 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \end{bmatrix} \\
 &\quad + \begin{bmatrix} 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \end{bmatrix} \\
 &= \begin{bmatrix} 0 & 1 & 1 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 & 1 & 1 \\ 1 & 0 & 0 & 0 & 1 & 1 \\ 1 & 0 & 0 & 0 & 1 & 1 \\ 0 & 1 & 1 & 1 & 0 & 0 \\ 0 & 1 & 1 & 1 & 0 & 0 \end{bmatrix} \\
 {}^{(\text{reg})}\mathbf{C}_3 &= {}^{(\text{reg})}\Gamma(C_3) + {}^{(\text{reg})}\Gamma(C_3^2) \\
 &= \begin{bmatrix} 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} + \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{bmatrix}
 \end{aligned}$$

$${}^{(2)}\hat{P}^{\text{reg}} = \frac{1}{6} \begin{pmatrix} 1 & -1 & -1 & -1 & 1 & 1 \\ -1 & 1 & 1 & 1 & -1 & -1 \\ -1 & 1 & 1 & 1 & -1 & -1 \\ -1 & 1 & 1 & 1 & -1 & -1 \\ 1 & -1 & -1 & -1 & 1 & 1 \\ 1 & -1 & -1 & -1 & 1 & 1 \end{pmatrix}$$

The simple characteristics can be easily generated in *Mathematica* by the following function:

Using the array `Preg[mu,i,j]` for the elements of the projection operators: ${}^{(\mu)}\hat{P}^{\text{reg}}$, we generate these elements as follows:

```
Do[Preg[mu,i,j]=dm[mu]*charac[indc[m[[LI[[i]]],j]]]/g,
  {j,1,g},{i,1,g},{mu,1,nc}]
```

where `indc[k]` is the class to which element `k` belongs,
and `LI[[i]]` is the inverse of element `i`.

Keeping in mind that

$$\frac{1}{g} \sum_{i=1}^{N_c} \text{nc}(i) {}^{(\mu)}\chi^*(i) {}^{(\nu)}\chi(i) = \delta_{\mu\nu},$$

and

$${}^{(\text{reg})}\chi(i) = \sum_{\mu=1}^{N_c} d_{\mu} {}^{(\mu)}\chi(i),$$

where i stands for class i , we can now take the trace of the simple characteristic

$$\text{Tr}^{(\mu)}\hat{\mathbf{P}}^{\text{reg}} = \frac{d_{\mu}}{g} \sum_{i=1}^{N_c} {}^{(\mu)}\chi^*(i) \text{Tr} \mathbf{C}^{\text{reg}}(i), \quad (6.28)$$

but the trace of the regular class-constant matrix is just the trace of the regular Rep of any element of the class multiplied by the number of elements in the class, $\text{nc}(i)$. Thus,

$$\begin{aligned} \text{Tr}^{(\mu)}\hat{\mathbf{P}}^{\text{reg}} &= \frac{d_{\mu}}{g} \sum_{i=1}^{N_c} {}^{(\mu)}\chi^*(i) \text{nc}(i) \chi^{\text{reg}}(i) \\ &= \frac{d_{\mu}}{g} \sum_{i=1}^{N_c} {}^{(\mu)}\chi^*(i) \text{nc}(i) \sum_{\nu=1}^{N_c} d_{\nu} {}^{(\nu)}\chi(i), \end{aligned} \quad (6.29)$$

where the last summation follows from recognizing that the trace of an element in the regular Rep is the sum of the characters for each Irrep multiplied by the multiplicity of that Irrep in the regular Rep. Thus (6.29) can be rewritten as

$$\text{Tr}^{(\mu)}\hat{\mathbf{P}}^{\text{reg}} = \frac{d_{\mu}}{g} \sum_{\nu=1}^{N_c} d_{\nu} \sum_{i=1}^{N_c} {}^{(\mu)}\chi^*(i) \text{nc}(i) {}^{(\nu)}\chi(i). \quad (6.30)$$

Using the orthogonality theorem for characters, (4.34), we now have

$$\mathrm{Tr}^{(\mu)} \hat{\mathbf{P}}^{\mathrm{reg}} = d_\mu^2. \quad (6.31)$$

The simple characteristics are, therefore, singular matrices of rank d_μ^2 . As projection operators they are also idempotent and Hermitian,

$$({}^{(\mu)} \hat{\mathbf{P}}^{\mathrm{reg}})^2 = {}^{(\mu)} \hat{\mathbf{P}}^{\mathrm{reg}},$$

and the columns are eigenvectors with unit eigenvalues. This provides a check that the calculated simple characteristic is *probably* correct.

Example 6.11

Direct matrix multiplication demonstrates that ${}^{(3)} \hat{\mathbf{P}}^{\mathrm{reg}}$ from Example 6.10 is idempotent. Operating on the first column of ${}^{(3)} \hat{\mathbf{P}}^{\mathrm{reg}}$ by ${}^{(3)} \hat{\mathbf{P}}^{\mathrm{reg}}$ itself, we find that the column is an eigenvector with unit eigenvalue:

$$\begin{aligned} \frac{1}{3} \begin{bmatrix} 2 & 0 & 0 & 0 & -1 & -1 \\ 0 & 2 & -1 & -1 & 0 & 0 \\ 0 & -1 & 2 & -1 & 0 & 0 \\ 0 & -1 & -1 & 2 & 0 & 0 \\ -1 & 0 & 0 & 0 & 2 & -1 \\ -1 & 0 & 0 & 0 & -1 & 2 \end{bmatrix} \begin{bmatrix} 2 \\ 0 \\ 0 \\ 0 \\ -1 \\ -1 \end{bmatrix} \\ = \frac{1}{3} \begin{bmatrix} 6 \\ 0 \\ 0 \\ 0 \\ -3 \\ -3 \end{bmatrix} = 1 \begin{bmatrix} 2 \\ 0 \\ 0 \\ 0 \\ -1 \\ -1 \end{bmatrix} \end{aligned}$$

Since idempotency requires that the columns of ${}^{(\mu)} \hat{\mathbf{P}}^{\mathrm{reg}}$ are also eigencolumns of ${}^{(\mu)} \hat{\mathbf{P}}^{\mathrm{reg}}$, with unit eigenvalues, it follows that the order of the set of linearly independent eigencolumns would be given by its trace, i.e. d_μ^2 . Consequently, we should be able to find a rectangular reduction matrix ${}^{(\mu)} \hat{T}$ of order $g \times d_\mu^2$ by looking for d_μ^2 orthogonalized eigencolumns of ${}^{(\mu)} \hat{\mathbf{P}}^{\mathrm{reg}}$ using a Schmidt orthogonalization procedure, which can be simplified by the use of the idempotency and hermiticity of ${}^{(\mu)} \hat{\mathbf{P}}^{\mathrm{reg}}$.

Exercises

6.1 Determine the orbits, stabilizers, and strata of the action of

$$\mathcal{G} := \left\{ \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}, \right\},$$

on the xy -plane.

- 6.2 With reference to Example 6.3, to which rows of ${}^{(3)}\Gamma$ do the functions $\{yz, xy\}$ belong, if any?
- 6.3 The valence electron orbitals of a water molecule consist of one 1s-orbital on each H atom, and the three-fold degenerate 2p-orbital manifold centered on the O atom. Under the C_{2v} symmetry group operations, the permutations among the atoms are the same as those considered in Example 6.8. However, the function-space is now different as it consists of electron wavefunctions.
- (i) Determine the Rep engendered by C_{2v} on the set of electron states.
 - (ii) Derive the symmetry-adapted states of the water molecule.
- 6.4 The ammonia molecule NH_3 has C_{3v} symmetry. Determine:
- (i) Its symmetry-adapted vibrational modes.
 - (ii) Its symmetry-adapted molecular orbitals. (Again, consider s-orbitals centered on the H atoms, and a p-manifold on the N atom.

In the following problems we consider molecules which contain carbon atoms. The four valence electrons of a carbon atom occupy both the 2s and 2p states, which have to be included in each set of orbitals of these molecules.

- 6.5 Repeat Exercise 6.4. for the case of a planar molecule of the form AB_3 , such as CO_3^{2-} , which has D_{3h} symmetry.
- 6.6 In the methane molecule, CH_4 , the C atom is located at the center of a tetrahedron, while the H atoms are at its apices. Repeat Exercise 6.4 for this molecule.
- 6.7 Repeat Exercise 6.4. for the benzene molecule. It consists of six carbon atoms forming the apices of a hexagon and six hydrogen atoms bound radially, thus having D_{6h} symmetry.

7

Construction of the irreducible representations

In this chapter we use the method of projection operators, presented in Chapter 6, to develop a general procedure for calculating all the Irreps of an arbitrary finite group. The method was first proposed by Stig Flodmark and Esko Blokker [6, 7, 8, 9, 10, 11].

The essence of this method is to establish a general procedure for obtaining the matrices of an Irrep (α) from the matrices of the regular Rep with the aid of projection matrices. Thus, for an Irrep of dimension d_α , we need to construct a matrix ${}^{(\alpha)}\Phi$ of dimension $g \times d_\alpha$, such that when it operates on a matrix ${}^{(\text{reg})}\Gamma(R)$ of the regular Rep we obtain ${}^{(\alpha)}\Gamma(R)$, namely,

$${}^{(\alpha)}\Phi^\dagger {}^{(\text{reg})}\Gamma(R) {}^{(\alpha)}\Phi = {}^{(\alpha)}\Gamma(R), \quad \forall R \in \mathcal{G}. \quad (7.1)$$

The construction of such a projection matrix is achieved by using the simple characteristic matrix of the Irrep α , introduced in the preceeding chapter, to project d_α linearly independent vectors from the eigenvectors of the regular Rep matrices. In the remaining part of this chapter, we describe how to utilize the permutative character of the regular Rep matrices to obtain their eigenvector, and how to project out the symmetrized eigenvector components that belong to the subspace of the Irrep α .

7.1 Eigenvectors of the regular Rep

A close examination of the matrices of the regular Rep reveals that they have the simple structure of *permutation matrices*. This is no surprise, when we consider the structure of the regular matrices in terms of the *rearrangement theorem*. As a consequence, their eigenvectors can be simply produced through determining their cycle structure.

If $\mathbf{u}_\lambda$ is an eigenvector of ${}^{(\text{reg})}\Gamma(\hat{R}_k)$, then the operation

$${}^{(\text{reg})}\Gamma(\hat{R}_k) \mathbf{u}_\lambda = \mathbf{u}' = \lambda \mathbf{u}_\lambda \quad (7.2)$$

yields a vector $\mathbf{u}'$ in which the elements, $(u_1, u_2, \dots, u_g)$, are permuted, and such that

$$u_i = u'_i / \lambda. \quad (7.3)$$

Moreover, the *cycle structure* of $\hat{R}_k$ means that the permutations are partitioned into subsets, where the elements of each subset are permuted only among themselves. We also should recall that *group elements in the same class have the same cycle structure*.

We can construct independent eigenvectors of ${}^{(\text{reg})}\Gamma(\hat{R}_k)$ by choosing the only nonzero elements of $\mathbf{u}_\lambda$ to be the *subset* corresponding to one of the permutation cycles of $\hat{R}_k$. And, according to (7.2), when we choose the first element of such a subset to be equal to one, all others must equal powers of λ .

The eigenvalue λ may assume any of the powers of $\xi = e^{(2\pi i/\ell_{\text{cycle}})}$, where ℓ_{cycle} is the permutation cycle length. Since n , the group exponent, is a divisor of ℓ_{cycle} , $\xi = \zeta^{n/\ell_{\text{cycle}}}$. Each allowed value has a corresponding eigenvector in which only the elements corresponding to one permutation cycle are different from zero and equal to powers of λ . Working through all powers of ζ and all cycles, one can quickly construct a complete set of g linearly independent eigencolumns. That is already more than we need. We need choose only one eigenvalue λ and construct its eigencolumns.

Example 7.1

Construction of eigencolumns belonging to ${}^{(\text{reg})}\Gamma(\hat{\sigma}_1)$ of $\mathcal{C}_{3v}$

From Example 4.1 we know that

$${}^{(\text{reg})}\Gamma(\hat{\sigma}_1) = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \end{pmatrix}.$$

Let this matrix Rep operate on a general column vector, yielding

$$\begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \end{pmatrix} \begin{bmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \\ u_5 \\ u_6 \end{bmatrix} = \begin{bmatrix} u_2 \\ u_1 \\ u_6 \\ u_5 \\ u_4 \\ u_3 \end{bmatrix}.$$

We see that the effect of ${}^{(\text{reg})}\Gamma(\hat{\sigma}_1)$ operating on a vector is to permute the elements among themselves according to the permutation cycles (12)(36)(45).

The element σ_1 is of order 2, so are its cycle lengths, so the possible eigenvalues are powers of $\xi = e^{(2\pi i/2)}$, namely, $\lambda = \pm 1$. It is clear then that there exist three independent eigencolumns, for *each* eigenvalue, of the form

$$\begin{bmatrix} u_1 \\ u_2 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} = \begin{bmatrix} 1 \\ \lambda \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}, \quad \begin{bmatrix} 0 \\ 0 \\ u_3 \\ 0 \\ 0 \\ u_6 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ \lambda \end{bmatrix}, \quad \begin{bmatrix} 0 \\ 0 \\ 0 \\ u_4 \\ u_5 \\ 0 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \\ \lambda \\ 0 \end{bmatrix},$$

if we choose the first element to be unity. Letting λ take both its values, ± 1 , we obtain the following six eigenvectors, which span the six-dimensional space of $\mathcal{C}_{3v}$:

$$\begin{bmatrix} 1 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}, \begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 1 \end{bmatrix}, \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \end{bmatrix}, \begin{bmatrix} 1 \\ -1 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}, \begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ -1 \end{bmatrix}, \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \\ -1 \\ 0 \end{bmatrix}.$$

Let's try one more. What happens if we choose C_3 ? We know from Example 4.1 that

$${}^{(\text{reg})}\Gamma(\hat{C}_3) = \begin{pmatrix} 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}.$$

Letting this operate on a general vector we find

$$\begin{pmatrix} 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \begin{bmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \\ u_5 \\ u_6 \end{bmatrix} = \begin{bmatrix} u_5 \\ u_3 \\ u_4 \\ u_2 \\ u_6 \\ u_1 \end{bmatrix},$$

corresponding to the same permutation cycle structure (156)(234) that we found in Example 2.1. This gives us two independent eigencolumns. Since C_3 is of order 3, possible eigenvalues are powers of $\zeta = e^{(2\pi i/3)}$. Two independent eigencolumns, with three different eigenvalues for each, once again yields six eigencolumns to span the six-dimensional space of $\mathcal{C}_{3v}$. They are:

$$\begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \\ e^{i(2\pi/3)} \\ e^{i(4\pi/3)} \end{bmatrix}, \begin{bmatrix} 0 \\ 1 \\ e^{i(2\pi/3)} \\ e^{i(4\pi/3)} \\ 0 \\ 0 \end{bmatrix}, \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \\ e^{i(4\pi/3)} \\ e^{i(2\pi/3)} \end{bmatrix}, \begin{bmatrix} 0 \\ 1 \\ e^{i(4\pi/3)} \\ e^{i(2\pi/3)} \\ 0 \\ 0 \end{bmatrix}, \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \\ 1 \\ 1 \end{bmatrix}, \begin{bmatrix} 0 \\ 1 \\ 1 \\ 1 \\ 0 \\ 0 \end{bmatrix}.$$

7.1.1 Computer generation of eigenvectors of the regular Rep

The algorithm used in generating an eigenvector of ${}^{(\text{reg})}\Gamma(\hat{R}_k)$ is based on determining its cycle structure when considered as the permutation of g objects. Each cycle generates a number of eigenvectors equal to the cycle length, with corresponding eigenvalues λ equal to powers of the primitive root $\xi = e^{(2\pi i/\ell_{\text{cycle}})}$. We select only one of these eigenvectors. It is constructed by setting nonzero values, only at the locations of the cycle elements: placing

1 in the first location of the given cycle, and assigning to the remaining locations of the cycle powers of the eigenvalue λ . Notice that the values of λ are confined to the set of powers of $\zeta = e^{(2\pi i/n)}$, where n is the group exponent.

- (i) To determine the cycle structure, we make use of the fact that the nonzero locations, ij , in $^{(\text{reg})}\Gamma(\hat{R}_k)$ satisfy the relation $\hat{R}_k^{-1} \hat{R}_i = \hat{R}_j$. Hence, in effect, when $^{(\text{reg})}\Gamma(\hat{R}_k)$ operates on a vector it replaces the entry in the i location by that in the j location. Since the elements of a class have the same cycle structure, we choose $\hat{R}_k$ as the first element in each class. The following program generates the eigenvectors for the representative element $\text{LC}[[i,1]]$ of class i . Cycle lengths are stored in `Lcycle`, the cycle structures in `loops`, and number of cycles in `nocycl[i-1]`.

```
lpl={}; Lcycle={}
inv=LI1[[LC[[i,1]]]]; plp=0;
Do[flag[j]=0,{j,1,g}];
first=1; llp=0; cnt=1; elm=0;
While[
  And[first<=g,cnt<=g],
  While[And[first<g,flag[first]==1],first++];
  flag[first]=1;mrow=first;
  While[elm!=first,
    elm=m[[1,inv,mrow]];
    loops[i-1,cnt]=elm; cnt++; llp++;
    flag[elm]=1;mrow=elm
  ];
  plp++; AppendTo[lpl,llp]; llp=0
];
nocycl[i-1]=plp; AppendTo[Lcycle,lpl]; lpl={}
```

- (ii) Each eigenvector of $^{(\text{reg})}\Gamma(\hat{R}_k)$ is constructed from one of its cycles. For each cycle, we choose the value in its first location to be 1, successive locations will then be assigned progressive powers of $\xi = e^{(2\pi i/\ell_{\text{cycle}})}$.

```
nov=0; iv=1;
While[nov<nocycl[i-1], nov++;
  Switch[nov>1,True, iv=iv+Lcycle[[i-1,nov-1]]];
  Do[rvec[nov,i]=0,{i,1,g}];
  rvec[nov,iv]=1;nrt=1; pp=iv+Lcycle[[i-1,nov]];
```

```

j=iv;ex=Exp[i(2π/Lcycle[[i-1,nov]])];
While[j<pp,l1=loops[[i-1,j]];
Switch[l1≠iv,True,nrt=nrt*ex;
      rvec[nov,l1]=nrt];
j++] ]

```

7.2 The symmetry structure of the regular Rep eigenvectors

Suppose we find a unitary transformation that produces an Irrep equivalent to the Irrep $^{(\alpha)}\Gamma$ where only the matrix representative $^{(\alpha)}\Gamma(\hat{R}_k)$ of the *specific* group operator $\hat{R}_k$ is found in diagonal form, i.e. with eigenvalues, $^{(\alpha)}\lambda_1, ^{(\alpha)}\lambda_2, \dots, ^{(\alpha)}\lambda_{d_\alpha}$. (Note that no claim is made that any other $^{(\alpha)}\Gamma(\hat{R}_i)$, $i \neq k$, are diagonal.) Then, recalling from our approach to Dixon's method that if n is the exponent of the group $\mathcal{G}$, with element $\hat{R}_k \in \mathcal{G}$,

$$(\hat{R}_k)^n = \hat{E}.$$

Thus, we must have

$$\left(^{(\alpha)}\Gamma(\hat{R}_k)\right)^n = ^{(\alpha)}\Gamma(\hat{E}),$$

from which we conclude that each eigenvalue $^{(\alpha)}\lambda_k$ of $^{(\alpha)}\Gamma(\hat{R}_k)$ will be one of the numbers $(\zeta^0, \zeta^1, \zeta^2, \dots, \zeta^{n-1})$ with

$$\zeta = e^{(2\pi i/n)}.$$

Since the regular Rep is completely decomposable into group Irreps, it is also true that each of the eigenvalues λ of $^{(\text{reg})}\Gamma(\hat{R}_k)$ is equal to one of the numbers $(\zeta^0, \zeta^1, \zeta^2, \dots, \zeta^{n-1})$.

We seek a transformation of the regular Rep that reduces it *completely*, not just to *block*-diagonal form, but to *diagonal* form. Of course, each Irrep $^{(\alpha)}\Gamma$ occurs d_α times along the main diagonal, but we even assume that the d_α matrices of each Irrep $^{(\alpha)}$ along the main diagonal are *exactly* equal, not just equivalent. We denote this special $g \times g$ Rep by $^{(\text{reg})}\Gamma_D(\hat{R}_k)$ to distinguish it from the ordinary regular Rep $^{(\text{reg})}\Gamma$.

Example 7.2

The matrix $^{(\text{reg})}\Gamma_D(\hat{C}_3)$ for $\mathcal{C}_{3v}$

It would be of the form

$$^{(\text{reg})}\Gamma_D(\hat{C}_3) = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & e^{i(2\pi/3)} & 0 & 0 & 0 \\ 0 & 0 & 0 & e^{-i(2\pi/3)} & 0 & 0 \\ 0 & 0 & 0 & 0 & e^{i(2\pi/3)} & 0 \\ 0 & 0 & 0 & 0 & 0 & e^{-i(2\pi/3)} \end{pmatrix}$$

The space $^{(\text{reg})}\mathcal{V}$ of the $g \times g$ Rep $^{(\text{reg})}\Gamma_D$ is spanned by g vectors. The space comprises d_α identical irreducible subspaces associated with each Irrep (α) of the group $\mathcal{G}$. We write the basis vectors of the i th subspace of Irrep (α) , $^{(\alpha)}\mathcal{V}^i$, as $^{(\alpha)}V^i$ such that

$$\begin{aligned} \hat{R}_k^{(\alpha)} V^i &= \hat{R}_k \begin{bmatrix} ^{(\alpha)}v_1^i \\ ^{(\alpha)}v_2^i \\ \dots \\ ^{(\alpha)}v_{d_\alpha}^i \end{bmatrix} \\ &= [^{(\alpha)}v_1^i, ^{(\alpha)}v_2^i, \dots, ^{(\alpha)}v_{d_\alpha}^i] ^{(\alpha)}\Gamma^i(\hat{R}_k), \end{aligned} \quad (7.4)$$

for $i = 1, 2, \dots, d_\alpha$. To reiterate, we note that the Irrep $^{(\alpha)}\Gamma$ is of dimension d_α . Since each Irrep of dimension d_α appears d_α times along the diagonal of the regular Rep, there are d_α identical subspaces. Thus, (7.4) holds for $i = 1, 2, \dots, d_\alpha$.

For the complete g -dimensional space of $^{(\text{reg})}\Gamma_D$ we have

$$\begin{aligned} \hat{R}_k [^{(1)}V^1, ^{(1)}V^2, \dots, ^{(1)}V^{d_1}, ^{(2)}V^1, \dots, ^{(\text{nc})}V^1, \dots, ^{(\text{nc})}V^{d_{\text{nc}}}] \\ = [^{(1)}V^1, \dots, ^{(\text{nc})}V^{d_{\text{nc}}}] ^{(\text{reg})}\Gamma_D(\hat{R}_k), \end{aligned} \quad (7.5)$$

where the *sets* of basis vectors $^{(\alpha)}V^i$ range over all Irreps, of which there are nc, the number of classes.

Example 7.3

For the element $\hat{C}_3$ of the group $\mathcal{C}_{3v}$, which has three classes and hence three Irreps, of which two are one-dimensional and one is two-dimensional, (7.5) becomes

$$\hat{C}_3 [^{(1)}V^1, ^{(2)}V^1, ^{(3)}V^1, ^{(3)}V^2] = [^{(1)}V^1, ^{(2)}V^1, ^{(3)}V^1, ^{(3)}V^2] ^{(\text{reg})}\Gamma_D(\hat{C}_3).$$

We assume that $^{(\alpha)}\Gamma(\hat{R}_k)$, the matrix representative of $\hat{R}_k$ in (7.5), is diagonal, not just block diagonalized. We also assume that $^{(\alpha)}\Gamma_{11}(\hat{R}_k)$ is a *nondegenerate eigenvalue* λ , so when $\hat{R}_k$ operates on the first basis vector the eigenvalue equation is simply

$$\hat{R}_k^{(\alpha)} v_1^i = \lambda^{(\alpha)} v_1^i, \quad (7.6)$$

for $i = 1, 2, \dots, d_\alpha$. Because an Irrep of dimension d_α occurs d_α times in the regular Rep, so must the eigenvalue λ occur at least d_α times for either $^{(\text{reg})}\Gamma_D(\hat{R}_k)$ or $^{(\text{reg})}\Gamma(\hat{R}_k)$. It occurs probably even more times in $\Gamma^{\mathcal{R}}(\hat{R}_k)$ and $^{(\text{reg})}\Gamma(\hat{R}_k)$, as other Irreps $^{(\beta)}\Gamma(\hat{R}_k)$ can also have this eigenvalue, even several times, since for other Irreps we do not require that λ be nondegenerate.

The general form of the eigenvector of $^{(\text{reg})}\Gamma(\hat{R}_k)$, belonging to eigenvalue λ , is then

$$v_\lambda = \sum_{i=1}^{d_\alpha} a_i^{(\alpha),i} v_1^i + \sum_{\beta \neq \alpha} \sum_{i=1}^{d_\beta} \sum_k b_{\beta ik}^{(\beta),i} v_k, \quad (7.7)$$

where the summation in the second term runs over all β , ($\beta \neq \alpha$) for which $^{(\beta)}\Gamma(\hat{R}_k)$ has eigenvalue λ , and the summation over k is to allow for degenerate eigenvalues λ in $^{(\beta)}\Gamma(\hat{R}_k)$. We find that contributions from the last term in (7.7) disappear in the process of acting on v_λ with the Irrep projection operator $^{(\alpha)}\hat{P}$. Thus there is no need for the reader uninterested in every mathematical fine point to be concerned with this term.

7.3 Symmetry projection on regular Rep eigenvectors

A symmetrized vector $^{(\alpha)}V_\lambda$ in the subspace of the Irrep (α), is now obtained by applying the Irrep projection operator,

$$^{(\alpha)}\hat{\mathbf{P}} = \frac{d_\alpha}{g} \sum_{m=1}^g {}^{(\alpha)}\chi^*(\hat{\mathbf{R}}_m) \hat{\mathbf{R}}_m, \quad (7.8)$$

to $\mathbf{u}_\lambda$, since all contributions of the second term in (7.7) are canceled, and we obtain

$$^{(\alpha)}\hat{\mathbf{P}} \mathbf{u}_\lambda = \sum_{i=1}^{d_\alpha} a_i {}^{(\alpha)}v_1^i = {}^{(\alpha)}w_1. \quad (7.9)$$

The nondegeneracy of λ is easily established. If the number of independent vectors obtained after projection of the independent eigenvectors of the eigenvalue λ is larger than d_α , then λ is degenerate and one must choose another eigenvalue or another group element to start with. We then find that

$$\hat{\mathbf{R}}_m {}^{(\alpha)}w_1 = \hat{\mathbf{R}}_m \sum_{i=1}^{d_\alpha} a_i {}^{(\alpha)}v_1^i = \sum_{s=1}^{d_\alpha} {}^{(\alpha)}w_s {}^{(\alpha)}\Gamma(\hat{\mathbf{R}}_m)_{s1} = {}^{(\alpha)}\phi_m, \quad (7.10)$$

with

$$^{(\alpha)}w_s = \sum_{i=1}^{d_\alpha} \alpha_i {}^{(\alpha)}v_s^i, \quad (7.11)$$

where $\hat{R}_m \neq \hat{R}_k$. (Recall that $\hat{R}_k$ is the *specific* element of the previous sections with diagonal Rep $^{(\alpha)}\Gamma_D(\hat{R}_k)$.) So the vectors $^{(\alpha)}w_s$, $s = 1, 2, \dots, d_\alpha$ also span an irreducible space $^{(\alpha)}\Omega$, transforming according to $^{(\alpha)}\Gamma$. The vectors $^{(\alpha)}\phi_1 \equiv {}^{(\alpha)}w_1$, and $^{(\alpha)}\phi_m$ lie in the space $^{(\alpha)}\Omega$. By operating with different elements $\hat{R}_m$ ($m = 2, 3, \dots, g$) on $^{(\alpha)}\phi_1 = {}^{(\alpha)}w_1$, we finally obtain d_α linearly independent vectors $^{(\alpha)}\phi_d$, $d = 1, 2, \dots, d_\alpha$ and these form a basis $^{(\alpha)}\Phi = ({}^{(\alpha)}\phi_1, \dots, {}^{(\alpha)}\phi_{d_\alpha})$ of $^{(\alpha)}\Omega$. The linear independence is checked by orthonormalizing each newly produced $^{(\alpha)}\phi_d$ to the previous ones by Schmidt's procedure. Since this basis of $^{(\alpha)}\Omega$ is just as good as the basis $^{(\alpha)}\mathbf{W} = ({}^{(\alpha)}w_1, \dots, {}^{(\alpha)}w_{d_\alpha})$ it will transform as $^{(\alpha)}\Gamma$:

$$\hat{\mathbf{R}}_p {}^{(\alpha)}\Phi = {}^{(\alpha)}\Phi {}^{(\alpha)}\Gamma(\hat{\mathbf{R}}_p), \quad (7.12)$$

The matrices $^{(\alpha)}\Gamma(\hat{\mathbf{R}}_p)$ differ from those corresponding to $^{(\alpha)}\mathbf{W}$ only by a linear transformation. Since we constructed $^{(\alpha)}\Phi$ as an orthonormal basis, we immediately obtain the

unitary Irrep $^{(\alpha)}\Gamma$:

$$^{(\alpha)}\Gamma(\hat{R}_p) = ^{(\alpha)}\Phi^\dagger \text{}^{(\text{reg})}\Gamma(R_p) ^{(\alpha)}\Phi, \quad (7.13)$$

where Φ is a $g \times d_\alpha$ rectangular matrix.

Example 7.4

Finding the two-dimensional $^{(3)}\Gamma$ Irrep of $\mathcal{C}_{3v}$

We begin by finding the orthonormal basis $^{(3)}\Phi$ that belongs to the subspace of the two-dimensional Irrep $^{(3)}\Gamma$ of the group $\mathcal{C}_{3v}$. From Example 6.6 we know the *simple characteristic* of the two-dimensional Irrep of the group $\mathcal{C}_{3v}$ is

$$^{(3)}\hat{P}^{\text{reg}} = \frac{1}{3} \begin{pmatrix} 2 & 0 & 0 & 0 & -1 & -1 \\ 0 & 2 & -1 & -1 & 0 & 0 \\ 0 & -1 & 2 & -1 & 0 & 0 \\ 0 & -1 & -1 & 2 & 0 & 0 \\ -1 & 0 & 0 & 0 & 2 & -1 \\ -1 & 0 & 0 & 0 & -1 & 2 \end{pmatrix}.$$

If we were to operate on each of the eigencolumns from Example 7.3 with $^{(3)}\hat{P}^{\text{reg}}$, we would find that the first set of six eigencolumns do not belong to the subspace of the two-dimensional Irrep of $^{(3)}\Gamma$. This simple exercise is left to the reader. However, if we choose the first eigencolumn from the second set of six eigencolumns we find

$$\frac{1}{3} \begin{pmatrix} 2 & 0 & 0 & 0 & -1 & -1 \\ 0 & 2 & -1 & -1 & 0 & 0 \\ 0 & -1 & 2 & -1 & 0 & 0 \\ 0 & -1 & -1 & 2 & 0 & 0 \\ -1 & 0 & 0 & 0 & 2 & -1 \\ -1 & 0 & 0 & 0 & -1 & 2 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \\ e^{i(2\pi/3)} \\ e^{i(4\pi/3)} \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \\ e^{i(2\pi/3)} \\ e^{i(4\pi/3)} \end{pmatrix},$$

thus demonstrating that we have found an eigencolumn belonging to $^{(3)}\Gamma$. However, there is some ambiguity in the last set of eigencolumns in Example 7.1, because columns 1 and 3, as well as columns 2 and 4, are not orthogonal to each other. This is because they belong to the *doubly degenerate* two-dimensional Irrep $^{(3)}\Gamma$.

There is a systematic procedure that we can adopt in order to find the second eigencolumn that we need to span the two-dimensional subspace of $^{(3)}\Gamma$. We operate on the first eigencolumn with other operations of the group in order to generate a *partner* eigencolumn. We choose $^{(\text{reg})}\Gamma(\hat{\sigma}_1)$, which we know from Example 7.2, obtaining

$$\begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \\ e^{i(2\pi/3)} \\ e^{i(4\pi/3)} \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \\ e^{i(4\pi/3)} \\ e^{i(2\pi/3)} \\ 0 \\ 0 \end{pmatrix}.$$

We now have an eigencolumn that is independent of and orthogonal to the first, and which is a partner to it. These two eigencolumns thus form a basis for the two-dimensional Irrep $^{(3)}\Gamma$, which we can normalize and write as

$$^{(3)}\Phi = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 & 0 \\ 0 & 1 \\ 0 & e^{i(4\pi/3)} \\ 0 & e^{i(2\pi/3)} \\ e^{i(2\pi/3)} & 0 \\ e^{i(4\pi/3)} & 0 \end{pmatrix}.$$

Now we can generate the full two-dimensional Irrep $^{(3)}\Gamma$ by following the prescription of (7.13) for each element of the group. We find for $^{(3)}\Gamma(\hat{\sigma}_1)$, with

$$^{(3)}\Phi^\dagger = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 & 0 & 0 & 0 & e^{-i(2\pi/3)} & e^{-i(4\pi/3)} \\ 0 & 1 & e^{-i(4\pi/3)} & e^{-i(2\pi/3)} & 0 & 0 \end{pmatrix},$$

that

$$^{(3)}\Gamma(\hat{\sigma}_1) = ^{(3)}\Phi^\dagger \text{ (reg) } \Gamma(\hat{\sigma}_1) ^{(3)}\Phi = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.$$

Continuing in this fashion for all other elements of the group, we find:

$$\begin{aligned} ^{(3)}\Gamma(\hat{E}) &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, & ^{(3)}\Gamma(\hat{\sigma}_1) &= \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \\ ^{(3)}\Gamma(\hat{\sigma}_2) &= \begin{pmatrix} 0 & e^{-i(2\pi/3)} \\ e^{i(2\pi/3)} & 0 \end{pmatrix}, & ^{(3)}\Gamma(\hat{\sigma}_3) &= \begin{pmatrix} 0 & e^{i(2\pi/3)} \\ e^{-i(2\pi/3)} & 0 \end{pmatrix}, \\ ^{(3)}\Gamma(\hat{C}_3) &= \begin{pmatrix} e^{i(2\pi/3)} & 0 \\ 0 & e^{-i(2\pi/3)} \end{pmatrix}, & ^{(3)}\Gamma(\hat{C}_3^2) &= \begin{pmatrix} e^{-i(2\pi/3)} & 0 \\ 0 & e^{i(2\pi/3)} \end{pmatrix}. \end{aligned}$$

7.4 Computer construction of Irreps with $d_\alpha > 1$

(i) Normalized symmetry-projected basis vector

The simple characteristic matrix defined in Chapter 6 is used to construct the symmetry-projected vector **svec**, which belongs to the **nrep** Irrep, from the eigenvector **rvec** of the regular Rep. After normalization it is stored as the first column of the $\mathbf{g} \times \mathbf{d}_{\text{nrep}}$ matrix **sympmp**.

```

Do[svec[i]=0,{i,1,g}];
Do[
    elm=m[[1,i,LI[[j]]]];
    elm=indc[elm];svec[i]+=charac[nrep,elm]*rvec[j],
    {i,1,g},{j,1,g}
];
norm=Sum[svec[i]*Conjugate[svec[i]],{i,1,g}];
Do[symp[i,1]=svec[i]/sqrt[norm],{i,1,g}]

```

(ii) **Construction of remaining Irrep basis vectors by application of other group elements**

Since group elements that are powers of the element k will have the same eigenvector of the regular Rep, they should be ignored in this procedure. This is implemented by an array `ban` which assigns a value 1 to such group elements.

```

Do[ban[i]=0,{i,1,g}];
ban[1]=1;ban[LC[[class,1]]]=1;ix=1;
elpwr=LC[[class,1]];expo=LC1[[class]]-1;
While[ix<expo,
    elmpwr=m[[1,elpwr,LC[[class,1]]]];
    ban[elpwr]=1,ix++
];
nsymm=1;dl=dim[nrep];iy=1;
While[nsymm<dl,Label[Try];
    While[ban[iy]==1,iy++];
    ban[iy]=1;
    Do[
        my=m[[1,LI[[iy]],i]];
        svec[i]=symp[my,nsymm],{i,1,g}
    ];
    Do[
        scalar=0;

```

```

Do[scalar+=Conjugate[symp[j,i]]*svec[j],
  {j,1,g}];
Switch[Abs[scalar]<0.001,
  False,
  Switch[Abs[scalar-1]<0.001,
    True,iy++;Goto[Try],
    False,
    Do[
      svec[kk]=svec[kk]-scalar*symp[kk,i],
      {kk,1,g}];
      norm=0;
      Do[
        norm+=svec[kk]*Conjugate[svec[kk]],
        {kk,1,g}];
        norm=sqrt[norm];
        Switch[norm<0.001,
          True,Goto[Try]
        ];
        Do[svec[kk]=svec[kk]/norm,
          {kk,1,g}]
      ]
    ],
  {i,1,nsymm}];
nsymm++;
Do[symp[j,nsymm]=svec[j],{j,1,g}]
];

```

(iii) **Generate the Irrep using (13)**

```

Do[hermsymp[i,j]=Conjugate[symp[j,i]},{i,1,d1},{j,1,g}];
temps={}; Do[rep[j,k]=0,{j,1,d1},{k,1,d1}];

```

```

Do[Switch[j==k,True,rep[j,k]=1],{i,1,d1},{j,1,d1}];
AppendTo[temps,Irrep=Array[rep,{d1,d1}];
Do[rep[j,k]=0,{j,1,d1},{k,1,d1}];
Do[
Do[
grp=m[[1,LI[[iv]],j]];
Do[
gensym[j,k]=symp[grp,k],{k,1,d1}
],{j,1,g}
];
Do[
Do[
rep[i,j]+=hermsymp[i,k]*gensym[k,j],{k,1,g},
{i,1,d1},{j,1,d1}
];
Irrep=Array[rep,{d1,d1}];
AppendTo[temps,Irrep];
Do[rep[j,k]=0,{j,1,d1},{k,1,d1},
{iv,2,lgen}
];
Do[ban[i]=0,{i,1,g}];
Do[ban[i]=1,{i,1,lgen}];jx=2;
While[Sum[ban[i],{i,g}]<g,
mm=m[[1,2,jx]];
Switch[ban[mm]==0,True,
Do[
Do[
rep[j,k]+=temps[[2,j,1]]*temps[[jx,1,k]],
{1,1,d1}
],
{j,1,d1},{k,1,d1}
];
];

```

```

Irrep=Array[rep,{dl,dl}];
AppendTo[temps,Irrep]; Do[rep[j,k]=0,{j,1,dl},{k,1,dl}];
ban[mm]=1];
jx++; AppendTo[gamma,temps];temps={} ]

```

7.5 Summary of the method

- Form a nondegenerate eigencolumn of $^{(\text{reg})}\Gamma(\hat{R}_k)$.
- Operate on it with the projection matrix $^{(\alpha)}\hat{P}^{\text{reg}}$.
- Operate on the projected column with different matrices $\Gamma^{\text{reg}}(\hat{R}_m)$ and orthonormalize, obtaining d_α orthonormal columns, which form the matrix $^{(\alpha)}\Phi$.
- Generate the Irrep (α) according to (7.13).

We illustrate the method with another example.

Example 7.5

The group $\mathcal{C}_{4v}$

The multiplication table is

E	C_4	C_2	C_4^3	σ_x	σ_y	$\sigma_{d_{xy}}$	$\sigma_{d_{\bar{x}y}}$
1	2	3	4	5	6	7	8
2	3	4	1	8	7	5	6
3	4	1	2	6	5	8	7
4	1	2	3	7	8	6	5
5	7	6	8	1	3	2	4
6	8	5	7	3	1	4	2
7	6	8	5	4	2	1	3
8	5	7	6	2	4	3	1

It has a two-dimensional Irrep with characters $(2, 0, -2, 0, 0, 0, 0, 0)$. According to (6.27)

$$^{(5)}\hat{P}^{\text{reg}} = (1/2) \begin{pmatrix} 1 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & -1 & 0 & 0 & 0 & 0 \\ -1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 1 \end{pmatrix}.$$

Element $\hat{C}_4$ is of order 4, so $\zeta = \exp(2\pi i/4) = i$ and possible eigenvalues are $(1, i, -1, -i)$.

$${}^{(\text{reg})}\Gamma(\hat{C}_4) = \begin{pmatrix} 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \end{pmatrix}.$$

When ${}^{(\text{reg})}\Gamma(\hat{C}_4)$ operates on an eigenvector, it permutes the first four and the last four elements among themselves, according to the permutation cycles $(1432)(5768)$. This leads to two different eigencolumns

$$\begin{pmatrix} v_1 \\ \lambda^3 v_1 \\ \lambda^2 v_1 \\ \lambda v_1 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \quad \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ v_5 \\ \lambda^2 v_5 \\ \lambda v_5 \\ \lambda^3 v_5 \end{pmatrix}$$

for each value of $\lambda = (1, i, -1, -i)$. Thus we obtain eight independent eigencolumns. We now choose the first type with $v_1 = 1$ and for a particular λ . This gives a column with elements

$$(1, \lambda^3, \lambda^2, \lambda, 0, 0, 0, 0).$$

Now operate on this column by ${}^{(5)}P^{\text{reg}}$ to obtain

$$(1 - \lambda^2)(1, -\lambda, -1, \lambda, 0, 0, 0, 0).$$

This shows immediately that eigencolumns for $\lambda = 1, -1$ do not belong to the subspace ${}^{(5)}V$. We choose one of the remaining eigenvalues, $\zeta = i$, so that we obtain the column

$$(1, -i, -1, i, 0, 0, 0, 0).$$

When operating with ${}^{(\text{reg})}\Gamma(\hat{C}_2)$ and ${}^{(\text{reg})}\Gamma(\hat{C}_4^3)$ we obtain a constant times the same column. But operating with ${}^{(\text{reg})}\Gamma(\hat{\sigma}_5)$ we obtain a new column

$$(0, 0, 0, 0, 1, -1, -i, i)$$

which is independent of and even orthogonal to the first column. So

$${}^{(5)}\Phi = (1/2) \begin{pmatrix} 1 & 0 \\ -i & 0 \\ -1 & 0 \\ i & 0 \\ 0 & 1 \\ 0 & -1 \\ 0 & -i \\ 0 & i \end{pmatrix}$$

Performing the projection of (7.13), we obtain the Irrep matrices:

$$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix}, \quad \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix}$$

$$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}, \quad \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix}.$$

Suppose that we had started with element C_2 . The regular Rep of this element permutes the elements in an eigencolumn according to the cycles: (13) (24) (56) (78). This leads to four different types of columns with possible eigenvalues $\lambda = 1, -1$. After projection with ${}^{(5)}\hat{P}^{\text{reg}}$ there remain the four vectors with $\lambda = -1$. So $\lambda = -1$ occurs twice in ${}^{(5)}\Gamma(C_2)$ and C_2 is not a good element to start with.

Exercise

7.1 In Chapter 2 or 3 it was found that the matrix

$$S = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ i & -i \end{pmatrix}$$

diagonalized the matrix $\hat{C}_3^2$. Use the inverse process to “undiagonalize” the set of six matrices found in Example 7.2 and show that this similarity transformation produces a set of six matrices that form an Irrep of the group $\mathcal{C}_{3v}$.

8

Product groups and product representations

8.1 Introduction

So far, we have presented the concepts and methodology required for the construction of Irreps of finite groups. However, if we are to deal with groups of infinitely countable order, such as the space-groups, we find that new strategies are required for their construction. These strategies rely on the concepts of induction and subduction of group representations that we develop here and in the following chapter. First, we need to introduce new group theoretical entities such as subgroups, cosets, and invariant subgroups, upon which we construct the methodology for generating the Irreps of space-groups. In addition, as we will see, they take many guises in different applications.

8.2 Subgroups and cosets

A *subgroup* $\mathcal{H}$, of order h , of a group $\mathcal{G}$, denoted by $\mathcal{H} \subset \mathcal{G}$, is a subset of h elements of $\mathcal{G}$ that is itself a group under the binary composition law associated with $\mathcal{G}$. Two trivial subgroups of a given group $\mathcal{G}$ can be identified: $\mathcal{G}$ itself and the group of the identity E . Any other subgroup is called *proper*.

Example 8.1

The point-group $\mathcal{C}_{3v}$ has four proper subgroups: $\mathcal{C}_3 = \{E, C_3, C_3^2\}$, and $\{E, \sigma_1\}$, $\{E, \sigma_2\}$, $\{E, \sigma_3\} \equiv \mathcal{C}_s$.

We now use the concept of a subgroup to define *cosets* as follows: For $\mathcal{H} \subset \mathcal{G}$,

$$\left. \begin{array}{ll} \text{left coset} & R_i \mathcal{H}, \\ \text{right coset} & \mathcal{H} R_i, \end{array} \right\} R_i \in \mathcal{G}, R_i \notin \mathcal{H}. \quad (8.1)$$

Based on this definition of left and right cosets, the following properties must hold for cosets:

- (i) The elements of $\mathcal{H}$ itself comprise the left (right) coset $E\mathcal{H}$ ($\mathcal{H}E$).
- (ii) The left (right) coset $R_i\mathcal{H}$ ($\mathcal{H}R_i$) contains the element R_i ;
 - its elements are all distinct from each other, for if two elements of the coset are equal:

$$R_i H_k = R_i H_l \xrightarrow{\text{implies}} H_k = H_l, \quad H_k, H_l \in \mathcal{H}, \quad (8.2)$$

- its elements are different from those of $\mathcal{H}$ as implied by the definition of a group:

$$H_k = R_i H_l \implies R_i = H_k H_l^{-1} \in \mathcal{H}. \quad (8.3)$$

- (iii) If we choose another element $R_j \in \mathcal{G}$, $R_j \notin \mathcal{H}$, and $R_j \notin R_i\mathcal{H}$, we find that the elements of the coset $R_j\mathcal{H}$ are also distinct from those of $\mathcal{H}$ and $R_i\mathcal{H}$.

Proof For $R_i, R_j \in \mathcal{G}$,

- We may have $R_i^{-1}R_j = H_k \in \mathcal{H}$; then $R_j = R_i H_k$ and $R_j\mathcal{H} = R_i H_k\mathcal{H} = R_i\mathcal{H}$ and the two left cosets are identical.
 - Conversely, if there is an element common between the two cosets, say $R_i H_k = R_j H_l$, then $R_i^{-1}R_j = H_k H_l \in \mathcal{H}$.
- (iv) Every element of the group $\mathcal{G}$ is in some left (right) coset and no element is in more than one left (right) coset, so that any two cosets are either identical or disjoint.
 - (v) Every left (right) coset contains the same number of elements, this number being equal to the order of $\mathcal{H}$, h .
 - (vi) **Lagrange's theorem** If $\mathcal{H}$ is a subgroup of $\mathcal{G}$, its order h is a factor of the order g of $\mathcal{G}$. The integer g/h is called the index of $\mathcal{H}$ in $\mathcal{G}$.

If g is a prime number, then $\mathcal{G}$ has only trivial subgroups.

Coset representatives

Therefore, a group $\mathcal{G}$ can be *decomposed into unique* left (right) cosets of one of its subgroups $\mathcal{H} \subset \mathcal{G}$: Choose $R_1 = E$, $E\mathcal{H} = \mathcal{H}$. Next, choose R_2 from the set of elements $\mathcal{G} - \mathcal{H}$, followed by R_3 from the set $\mathcal{G} - \mathcal{H} - R_2\mathcal{H}$, and so on until all the elements of the group $\mathcal{G}$ are exhausted. We then obtain the decomposition

$$\boxed{\mathcal{G} = \sum_{i=1}^{g/h} R_i \mathcal{H}.} \quad (8.4)$$

The elements R_i are called *coset representatives*. A representative of coset i may be chosen as any element from coset i ; however, once chosen it will be elevated to the level of representative and given the notation R_i .

Example 8.2

The group C_{3v} has the following coset structures with respect to its subgroups:

Table 8.1. *Decomposition of C_{3v} into left and right cosets (i, j, k cyclic).*

Subgroup	Index	Left coset representative	Decomposition
$\{E, \sigma_i\}$	3	E, σ_j, σ_k	$E \{E, \sigma_i\} + \sigma_j \{E, \sigma_i\} + \sigma_k \{E, \sigma_i\}$ $= \{E, \sigma_i\} + \{\sigma_j, C_3^{-1}\} + \{\sigma_k, C_3\}$
$\{E, C_3, C_3^{-1}\}$	2	E, σ_i	$E \{E, C_3, C_3^{-1}\} + \sigma_i \{E, C_3, C_3^{-1}\}$ $= \{E, C_3, C_3^{-1}\} + \{\sigma_i, \sigma_j, \sigma_k\}$
Subgroup	Index	Right coset representative	Decomposition
$\{E, \sigma_i\}$	3	E, σ_j, σ_k	$\{E, \sigma_i\} E + \{E, \sigma_i\} \sigma_j + \{E, \sigma_i\} \sigma_k$ $= \{E, \sigma_i\} + \{\sigma_j, C_3\} + \{\sigma_k, C_3^{-1}\}$
$\{E, C_3, C_3^{-1}\}$	2	E, σ_i	$\{E, C_3, C_3^{-1}\} E + \{E, C_3, C_3^{-1}\} \sigma_i$ $= \{E, C_3, C_3^{-1}\} + \{\sigma_i, \sigma_k, \sigma_j\}$

We denote the set of left (right) cosets by $\mathcal{G} : \mathcal{H}$ ($\mathcal{H} : \mathcal{G}$).

8.2.1 Conjugate subgroups

The reader may find discussions of *conjugate subgroups* in references [12, 13, 14, 15]. Multiplying (8.4) by R_k^{-1} from the right, where R_k is a representative of the k th coset, we obtain

$$\begin{aligned}
 \mathcal{G} &= \mathcal{G} R_k^{-1} = \sum_{i=1}^{g/h} R_i \mathcal{H} R_k^{-1} \\
 &= \sum_{i=1}^{g/h} R_i (R_k^{-1} R_k) \mathcal{H} R_k^{-1} \\
 &= \sum_{i=1}^{g/h} R_i R_k^{-1} (R_k \mathcal{H} R_k^{-1}) \\
 &= \sum_{i=1}^{g/h} R_i R_k^{-1} \mathcal{H}^{\{k\}} = \sum_{l=1}^{g/h} R_l \mathcal{H}^{\{k\}}, \tag{8.5}
 \end{aligned}$$

which is a decomposition of $\mathcal{G}$ in terms of the left cosets of the *conjugate subgroup* $\mathcal{H}^{\{k\}} = R_k \mathcal{H} R_k^{-1}$, with $R_i R_k^{-1} = R_l$ its left coset representatives.

It is straightforward to show that $\mathcal{H}^{\{k\}}$ obeys group properties. For example, closure is demonstrated as follows: let $H_1^{\{k\}}, H_2^{\{k\}} \in \mathcal{H}^{\{k\}}$, such that $H_1^{\{k\}}\{k\} = \mathbf{R}_k H_1 \mathbf{R}_k^{-1}$ and $H_2^{\{k\}} = \mathbf{R}_k H_2 \mathbf{R}_k^{-1}$, where $H_1, H_2 \in \mathcal{H}$, then

$$\begin{aligned} H_1^{\{k\}} H_2^{\{k\}} &= \mathbf{R}_k H_1 \mathbf{R}_k^{-1} \mathbf{R}_k H_2 \mathbf{R}_k^{-1} \\ &= \mathbf{R}_k H_1 H_2 \mathbf{R}_k^{-1} = \mathbf{R}_k H_3 \mathbf{R}_k^{-1} = H_3^{\{k\}} \in \mathcal{H}^{\{k\}}. \end{aligned}$$

The first line of (8.5) shows that any element of $\mathcal{G}$ can be represented as a product

$$R = \mathbf{R}_i H \mathbf{R}_k^{-1}, \quad (8.6)$$

or, operating from the left by $\mathbf{R}_i^{-1}$ and from the right by $\mathbf{R}_k$, that

$$H = \mathbf{R}_i^{-1} R \mathbf{R}_k. \quad (8.7)$$

We now elaborate on the important concept of *conjugate subgroups*, since we will show in Chapter 12 that conjugate subgroups and their conjugate Irreps allow us to direct, specifically, the method of induced representations to the generation of induced Irreps.

Conjugate subgroups are defined by the relationships:

$$\begin{aligned} \mathcal{H}^{\{j\}} &= \mathbf{R}_j \mathcal{H} \mathbf{R}_j^{-1}, \\ \tilde{\mathcal{H}}^{\{j\}} &= \mathbf{R}_j^{-1} \mathcal{H} \mathbf{R}_j. \end{aligned}$$

(8.8)

The subgroups $\mathcal{H}^{\{j\}}$ and $\tilde{\mathcal{H}}^{\{j\}}$ are conjugate to $\mathcal{H}$.

Example 8.3

The subgroup $\mathcal{H}^{\{1\}} = \{E, \sigma_1\}$ has conjugate subgroups

$$\begin{aligned} \mathcal{H}^{\{2\}} &= \sigma_2 \{E, \sigma_1\} \sigma_2^{-1} = \{E, \sigma_3\}, \\ \mathcal{H}^{\{3\}} &= \sigma_3 \{E, \sigma_1\} \sigma_3^{-1} = \{E, \sigma_2\}. \end{aligned}$$

Thus, conjugate subgroups are a set of subgroups related to each other by a conjugacy operation, or similarity transformation, involving a group element.

Conjugacy classes of subgroups

The set of all subgroups conjugate to $\mathcal{H} \subset \mathcal{G}$, is called the *conjugacy class* of $\mathcal{H}$ in $\mathcal{G}$, and is denoted by

$$[\mathcal{H}]_{\mathcal{G}} = \{R\mathcal{H}R^{-1}, R \in \mathcal{G}\},$$

Conjugacy classes play a prominent role in applications of group-theoretical concepts in condensed matter physics, especially in crystallography, where they form the backbone of lattice and space-group classification.

Example 8.4

As shown in Figure 8.1, C_{3v} contains four conjugacy classes, while C_{4v} has eight conjugacy classes. The number of conjugate subgroups is indicated in square parentheses, when it exceeds one.

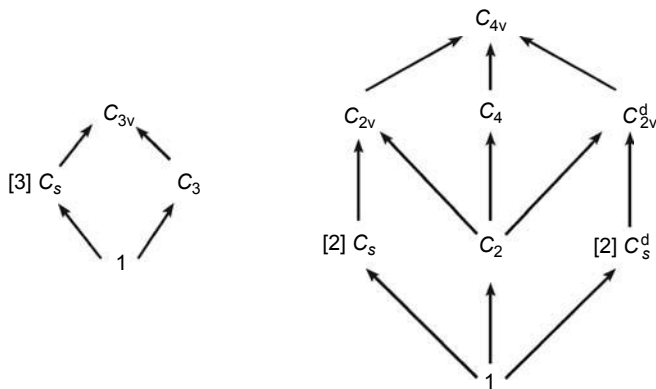


Fig. 8.1. Conjugacy classes of the groups C_{3v} and C_{4v} .

We note that for C_{nv} when n is a prime number, as in the case of C_{3v} , there are four conjugacy classes including 1 and the whole group. Moreover, for n even, there are pairs of conjugacy classes which belong to the same geometric class, such as C_s and C_s^d , and C_{2v} and C_{2v}^d , in the case of C_{4v} .

8.2.2 Self-conjugate (invariant or normal) subgroups and their quotient groups

The reader may find discussions of *normal subgroups* in references [12, 13, 14, 15, 16]. The process of subgroup conjugation may sometimes lead to the generation of conjugate subgroups, all of which are identical to the original subgroup. Such a subgroup is called a *normal*, *invariant*, or *self-conjugate* subgroup. It has no distinct conjugate subgroups! Conversely, a subgroup $\mathcal{N}$ of a group $\mathcal{G}$ is *invariant* or *normal*, denoted by $\mathcal{N} \triangleleft \mathcal{G}$, if

$$R_i \mathcal{N} R_i^{-1} = \mathcal{N}, \quad \forall R_i \in \mathcal{G}.$$

An invariant subgroup $\mathcal{N}$ of order n , of a group $\mathcal{G}$ of order g , has the following properties:

- (i) The conjugacy operation implies that $\mathcal{N}$ consists of complete classes.
- (ii) All left and right cosets coincide,

$$R_i \mathcal{N} = \mathcal{N} R_i, \quad \forall R_i \in \mathcal{G},$$

and $\mathcal{N}$ comprises entire conjugacy classes of $\mathcal{G}$.

(iii) The left (right) cosets of $\mathcal{N}$ form a group with binary multiplication defined by

$$(R_i \mathcal{N})(R_j \mathcal{N}) = (R_i R_j) \mathcal{N}, \quad \forall R_i, R_j \in \mathcal{G}. \quad (8.9)$$

This group, $\mathcal{Q}$, is called the **quotient** or **factor** group, and is symbolized by

$$\mathcal{Q} = \mathcal{G}/\mathcal{N}, \quad (8.10)$$

and has the following properties:

- (a) Its order q is equal to the index of $\mathcal{N}$ in $\mathcal{G}$, $q = g/n$.
- (b) In contrast to the usual subgroups of $\mathcal{G}$, the elements of the quotient group $\mathcal{Q}$ of a normal subgroup $\mathcal{N}$ of $\mathcal{G}$ are cosets and not individual elements of $\mathcal{G}$.
- (c) The identity of $\mathcal{G}/\mathcal{N}$ is the subgroup $\mathcal{N}$ itself.
- (d) The group of cosets of the invariant subgroup $\mathcal{N}$ is isomorphic to the elements of the group $\mathcal{Q}$, such that $Q_i = R_i \mathcal{N}$.

The relation of the quotient group $\mathcal{Q}$ to the covering group $\mathcal{G}$ may be regarded as a homomorphism, which in this particular case is called an *epimorphism*.¹

The existence of a normal subgroup is of great importance to the structure of groups. Groups that have invariant Abelian subgroups are *composite* groups, those that have non-Abelian invariant subgroups are called *semi-simple*, while those that do not have invariant subgroups are termed *simple*.

Example 8.5

Table 8.1 shows that $\mathcal{C}_{3v}$ has one invariant Abelian subgroup $\mathcal{C}_3 = \{E, C_3, C_3^2\}$, hence it is composite. The corresponding decomposition is

$$\mathcal{C}_{3v} = \{E, C_3, C_3^2\} + \sigma_v \{E, C_3, C_3^2\}, \quad (8.11)$$

where σ_v can be any one of the three reflection operations. The factor group $\mathcal{C}_{3v}/\mathcal{C}_3$ is isomorphic with $\mathcal{C}_s = \{E, \sigma_v\}$.

In view of (8.10), we may envision constructing $\mathcal{C}_{3v}$ by defining a product of the invariant subgroup and the quotient group, namely,

$$\begin{aligned} \mathcal{C}_{3v} &= \{E, \sigma_v\} \wedge \{E, C_3, C_3^2\} \\ &= \{E, C_3, C_3^2\} + \sigma_v \{E, C_3, C_3^2\}. \end{aligned}$$

As we will see in the following section, such a prescription for constructing $\mathcal{C}_{3v}$ as a product of an invariant and a noninvariant subgroup is called a semidirect product, denoted by $\wedge$.

¹ An epimorphism ϕ is a homomorphic map of a group $(\mathcal{G}, \circ)$ onto a group $(\mathcal{H}, *)$, $\phi : \mathcal{G} \rightarrow \mathcal{H}$ such that $\forall G_i, G_j \in \mathcal{G}$, $\phi(G_i) * \phi(G_j) = G_i \circ G_j$. $\mathcal{G}$ may then be larger than $\mathcal{H}$.

Groups, supergroups, and normalizers

The reader may find further discussion in references [12, 17]. We can reverse the group-subgroup relation $\mathcal{H} \subset \mathcal{G}$ and, instead, consider the relation $\mathcal{G} \supset \mathcal{H}$ as $\mathcal{G}$ being a super- or covering-group of $\mathcal{H}$. In that sense, we introduce the *normalizer* $\mathcal{N}(\mathcal{H}|\mathcal{G})$ of a group $\mathcal{H}$ with respect to one of its supergroups $\mathcal{G}$ as the set of all elements $g \in \mathcal{G}$ that map $\mathcal{H}$ onto itself by conjugation:

$$\mathcal{N}(\mathcal{H}|\mathcal{G}) := \{g \in \mathcal{G} | g\mathcal{H}g^{-1} = \mathcal{H}\}. \quad (8.12)$$

The normalizer $\mathcal{N}(\mathcal{H}|\mathcal{G})$ is always a group intermediate between $\mathcal{H}$ and $\mathcal{G}$:

$$\mathcal{H} \subseteq \mathcal{N}(\mathcal{H}|\mathcal{G}) \subseteq \mathcal{G}; \quad \text{and} \quad \mathcal{H} \triangleleft \mathcal{N}(\mathcal{H}|\mathcal{G}). \quad (8.13)$$

It is the largest such intermediate group that contains $\mathcal{H}$ as a normal subgroup. Therefore, it describes to a certain extent, depending on the choice of $\mathcal{G}$, the symmetry of the group $\mathcal{H}$.

If $\mathcal{N}(\mathcal{H}|\mathcal{G}) = \mathcal{G}$, then $\mathcal{H}$ is an invariant subgroup of $\mathcal{G}$, i.e. $\mathcal{H} \triangleleft \mathcal{G}$. Moreover, $\mathcal{H}$ is a *maximal invariant subgroup* of $\mathcal{G}$ if $\mathcal{G}$ does not have another invariant subgroup that contains $\mathcal{H}$.

Example 8.6

A simple illustration of the concept of a normalizer may be found in the case of the group $\mathcal{C}_3$ and its supergroup $\mathcal{D}_{3h}$. The latter contains the subgroup $\mathcal{D}_3$, which is a normalizer of $\mathcal{C}_3$, since $\mathcal{C}_3$ is an invariant subgroup in $\mathcal{D}_3$. Incidentally, $\mathcal{D}_3$ is a maximal invariant subgroup of $\mathcal{D}_{3h}$ and $\mathcal{C}_3$ is a maximal invariant subgroup of $\mathcal{D}_3$.

8.3 Direct outer-product groups

Further discussion on direct outer-product groups may be found in [12, 13, 14, 15, 17]. The group $\mathcal{D}_{3h}$ presents a perfect and lucid example for describing the construction of outer-product groups. In contrast to $\mathcal{C}_{3v}$, we find that $\mathcal{D}_{3h}$ contains two disjoint normal subgroups: $\mathcal{D}_3$, which is isomorphic to $\mathcal{C}_{3v}$, and $\mathcal{S} = \{E, \sigma_h\}$, with σ_h a reflection through a plane normal to the three-fold axis. We note that we can construct $\mathcal{D}_{3h}$ as

$$\begin{aligned} \mathcal{D}_{3h} &= \{E, \sigma_h\} \otimes \{E, \mathcal{C}_3, \mathcal{C}_3^2, U_1, U_2, U_3\} \\ &= \{E, \mathcal{C}_3, \mathcal{C}_3^2, U_1, U_2, U_3, \sigma_h, \sigma_h \mathcal{C}_3, \sigma_h \mathcal{C}_3^2, \sigma_h U_1, \sigma_h U_2, \sigma_h U_3\} \\ &= \{E, \mathcal{C}_3, \mathcal{C}_3^2, U_1, U_2, U_3, \sigma_h, \mathcal{S}_3, \mathcal{S}_3^2, \sigma_1, \sigma_2, \sigma_3\} \\ &= \mathcal{S} \otimes \mathcal{D}_3 = \mathcal{D}_3 \otimes \mathcal{S}, \end{aligned}$$

where $\otimes$ denotes a *direct product* operation.

We now generalize this idea and declare that a group $\mathcal{G}$ is said to be the direct product of its subgroups $\mathcal{H}_1, \mathcal{H}_2, \dots, \mathcal{H}_n$,

$$\mathcal{G} = \mathcal{H}_1 \otimes \mathcal{H}_2 \otimes \dots \otimes \mathcal{H}_n \quad (8.14)$$

if:

- (i) The elements of each subgroup commute with all elements of every other subgroup.
- (ii) Every element of $\mathcal{G}$ is defined in terms of a unique product of elements, one from each of the subgroups, $R = H^1 H^2 \dots H^n$, where $H^i \in \mathcal{H}_i$.
- (iii) The only common element among the subgroups is the identity.

Conversely, we find that if $\mathcal{G} = \mathcal{H}_1 \otimes \mathcal{H}_2 \dots \otimes \mathcal{H}_n$, then,

- (i) $\mathcal{H}_1, \mathcal{H}_2, \dots, \mathcal{H}_n$ are all invariant subgroups of $\mathcal{G}$, namely, $\mathcal{N}_1 = \mathcal{H}_1, \mathcal{N}_2 = \mathcal{H}_2, \dots, \mathcal{N}_n = \mathcal{H}_n$.
- (ii) The number of classes in $\mathcal{G}$ is the product of the number of classes of its constituent direct-product invariant subgroups.

If $\mathcal{G} = \mathcal{N}_1 \otimes \mathcal{N}_2$, and both $\mathcal{N}_1$ and $\mathcal{N}_2$ are Abelian, then $\mathcal{G}$ is also Abelian.

There are two ways for the manifestation of a direct-product group:

- (i) A direct implementation is evidently obtained through its mathematical definition, which is demonstrated by the case of $\mathcal{D}_{3h}$. We may also consider, as a second example, the case of the dihedral group

$$\begin{aligned} \mathcal{D}_2 &= \{E, C_2, C_{2x}, C_{2y}\} \\ &= \{E, C_{2x}\} \otimes \{E, C_{2y}\} = \{E, C_{2x}C_{2y}, EC_{2x}, EC_{2y}\} \\ &= \{E, C_{2y}\} \otimes \{E, C_{2x}\} = \{E, C_{2y}C_{2x}, C_{2x}E, C_{2y}E\}, \end{aligned}$$

since $C_{2x}C_{2y} = C_{2y}C_{2x} = C_2$.

- (ii) Another realization of a direct-product group arises as a consequence of the physical aspects of a system, namely, when a physical system possesses completely uncoupled sets of dynamical variables such that its Hamiltonian consists of the sum of noninteracting terms, disjoint in their respective variables, in the form

$$H = \sum_i H_i. \quad (8.15)$$

A typical example is found in one-electron Hamiltonians where magnetic field and spin-orbit coupling terms are absent, and the spatial and spin degrees of freedom are decoupled, namely,

$$H = H(\mathbf{r}) + H(\sigma). \quad (8.16)$$

Each of the component Hamiltonians has a group of symmetry operations associated with it, $\mathcal{N}_1 \equiv \mathcal{N}_r$ for the first term and $\mathcal{N}_2 \equiv \mathcal{N}_\sigma$ for the second. As a consequence, the corresponding wavefunctions of this system are just linear combinations of products of spatial and spin wavefunctions,

$$\Psi(\mathbf{r}, \sigma) = \Phi(\mathbf{r})\chi(\sigma).$$

where $\mathcal{N}_r$ and $\mathcal{N}_\sigma$ operate, exclusively, on the spatial and spin degrees of freedom, respectively. The former leaves $\chi(\sigma)$ unchanged, and the latter leaves $\Phi(\mathbf{r})$ unchanged.

Thus, if we apply the composite symmetry operation

$$\begin{aligned} R_{\mathbf{r}} R_{\sigma} \Psi(\mathbf{r}, \sigma) &= R_{\mathbf{r}} R_{\sigma} \Phi(\mathbf{r}) \chi(\sigma) = R_{\mathbf{r}} \Phi(\mathbf{r}) R_{\sigma} \chi(\sigma) \\ &= \Phi(R_{\mathbf{r}}^{-1} \mathbf{r}) \chi(R_{\sigma}^{-1} \sigma) = R_{\sigma} R_{\mathbf{r}} \Psi(\mathbf{r}, \sigma), \end{aligned} \quad (8.17)$$

we find that all the operations in one group commute with all the operations in the other group; and the covering group of the Hamiltonian is just a direct product of the two groups, each product element being the product of an element from $\mathcal{N}_{\mathbf{r}}$ with an element from $\mathcal{N}_{\sigma}$, without restrictions.

Sometimes both invariant subgroups $\mathcal{N}_1$ and $\mathcal{N}_2$ are isomorphic to a group $\mathcal{N}$, and the direct product becomes $\mathcal{N}_1 \otimes \mathcal{N}_2 = \mathcal{N} \otimes \mathcal{N}$. We notice, in such a case, that $\mathcal{N} \otimes \mathcal{N}$ contains a subgroup isomorphic to $\mathcal{N}$, namely, the “diagonal” subgroup comprising the elements $N_i N_i$, which is not necessarily a normal subgroup of $\mathcal{N} \otimes \mathcal{N}$.

8.3.1 Representations of direct outer-product groups: Kronecker-product representations

We now consider how to construct representations of an outer-product group $\mathcal{G}$ in terms of the representations of its constituent normal subgroups $\mathcal{T}$ and $\mathcal{S}$. Although the procedure described below applies to general representations, we focus on the case of Irreps. In other words, we explain how to construct Irreps of $\mathcal{G}$ from the Irreps of $\mathcal{T}$ and $\mathcal{S}$.

Let $^{(\mu)}\Delta$ and $^{(\nu)}\Lambda$ be Irreps of $\mathcal{T}$ and $\mathcal{S}$, respectively, with $^{(\mu)}\psi_i$ ($i = 1, \dots, d_{\mu}$) and $^{(\nu)}\phi_k$ ($k = 1, \dots, d_{\nu}$) as basis sets, then

$$\begin{aligned} T \ ^{(\mu)}\psi_i &= \sum_j \ ^{(\mu)}\psi_j \ ^{(\mu)}\Delta_{ji}(T), \\ S \ ^{(\nu)}\phi_k &= \sum_l \ ^{(\nu)}\phi_l \ ^{(\nu)}\Lambda_{lk}(S). \end{aligned} \quad (8.18)$$

We now show that the $d_{\mu}d_{\nu}$ functions $^{(\mu)}\psi_i^{(\nu)}\phi_k$ form the basis for an Irrep of $\mathcal{G}$. Multiplying the two equations (8.18), we obtain

$$\begin{aligned} T S \ ^{(\mu)}\psi_i \ ^{(\nu)}\phi_k &= T \ ^{(\mu)}\psi_i S \ ^{(\nu)}\phi_k \\ &= \sum_{jl} \ ^{(\mu)}\psi_j \ ^{(\nu)}\phi_l \ ^{(\mu)}\Delta_{ji}(T) \ ^{(\nu)}\Lambda_{lk}(S). \end{aligned} \quad (8.19)$$

On the other hand, setting $R = TS$, and regarding $^{(\mu \otimes \nu)}\Psi_{ik} = ^{(\mu)}\psi_i \ ^{(\nu)}\phi_k$ as the components of a basis set, we write

$$R \ ^{(\mu)}\psi_i \ ^{(\nu)}\phi_k = R \ ^{(\mu \otimes \nu)}\Psi_{ik} = \sum_{jl} \ ^{(\mu \otimes \nu)}\Psi_{jl} \ ^{(\mu \otimes \nu)}\Gamma_{jl,ik}(R). \quad (8.20)$$

We then identify

$$^{(\mu \otimes \nu)}\Gamma_{jl,ik}(TS) = ^{(\mu)}\Delta_{ji}(\hat{T}) \ ^{(\nu)}\Lambda_{lk}(\hat{S}), \quad (8.21)$$

which is just the definition of the *Kronecker product* of the matrices Δ and Λ . Symbolically, we write

$$^{(\mu \otimes \nu)}\Gamma(TS) = ^{(\mu)}\Delta(T) \otimes ^{(\nu)}\Lambda(S). \quad (8.22)$$

To find the character of TS we sum the diagonal elements in (8.22):

$$^{(\mu \otimes \nu)}\chi(TS) = ^{(\mu)}\chi(T) ^{(\nu)}\chi(S). \quad (8.23)$$

Example 8.7

To illustrate how the notation works, let us consider the case where the representations $d_\mu = d_\nu = 2$. Symbolically, we write

$$\begin{aligned} T \begin{bmatrix} ^{(\mu)}\psi_1 \\ ^{(\mu)}\psi_2 \end{bmatrix} &= \begin{bmatrix} ^{(\mu)}\psi_1 & ^{(\mu)}\psi_2 \end{bmatrix} \begin{bmatrix} ^{(\mu)}\Delta_{11} & ^{(\mu)}\Delta_{12} \\ ^{(\mu)}\Delta_{21} & ^{(\mu)}\Delta_{22} \end{bmatrix}, \\ S \begin{bmatrix} ^{(\nu)}\phi_1 \\ ^{(\nu)}\phi_2 \end{bmatrix} &= \begin{bmatrix} ^{(\nu)}\phi_1 & ^{(\nu)}\phi_2 \end{bmatrix} \begin{bmatrix} ^{(\nu)}\Lambda_{11} & ^{(\nu)}\Lambda_{12} \\ ^{(\nu)}\Lambda_{21} & ^{(\nu)}\Lambda_{22} \end{bmatrix}, \\ TS \begin{bmatrix} \psi_1\phi_1 \\ \psi_1\phi_2 \\ \psi_2\phi_1 \\ \psi_2\phi_2 \end{bmatrix} &= \begin{bmatrix} \psi_1\phi_1 & \psi_1\phi_2 & \psi_2\phi_1 & \psi_2\phi_2 \end{bmatrix} \\ &\quad \times \begin{bmatrix} \Delta_{11}\Lambda_{11} & \Delta_{11}\Lambda_{21} & \Delta_{21}\Lambda_{11} & \Delta_{21}\Lambda_{21} \\ \Delta_{11}\Lambda_{12} & \Delta_{11}\Lambda_{22} & \Delta_{21}\Lambda_{12} & \Delta_{21}\Lambda_{22} \\ \Delta_{12}\Lambda_{11} & \Delta_{12}\Lambda_{21} & \Delta_{22}\Lambda_{11} & \Delta_{22}\Lambda_{21} \\ \Delta_{12}\Lambda_{12} & \Delta_{12}\Lambda_{22} & \Delta_{22}\Lambda_{12} & \Delta_{22}\Lambda_{22} \end{bmatrix} \\ &= \begin{bmatrix} \psi_1\phi_1 & \psi_1\phi_2 & \psi_2\phi_1 & \psi_2\phi_2 \end{bmatrix} \\ &\quad \times \begin{bmatrix} \Gamma_{11,11} & \Gamma_{12,11} & \Gamma_{21,11} & \Gamma_{22,11} \\ \Gamma_{11,12} & \Gamma_{12,12} & \Gamma_{21,12} & \Gamma_{22,12} \\ \Gamma_{11,21} & \Gamma_{12,21} & \Gamma_{21,21} & \Gamma_{22,21} \\ \Gamma_{11,22} & \Gamma_{12,22} & \Gamma_{21,22} & \Gamma_{22,22} \end{bmatrix}. \end{aligned} \quad (8.24)$$

It is then obvious from this example that (8.21) and (8.23) are satisfied, that is $\Gamma_{jl,ik} = \Delta_{ji}\Lambda_{lk}$, and

$$^{(\mu \otimes \nu)}\chi(TS) = ^{(\mu)}\chi(T) ^{(\nu)}\chi(S).$$

A key point To find the characters of the Irreps of the direct-product group $\mathcal{G}$ of $\mathcal{T}$ and $\mathcal{S}$ we take the products of the characters of $\mathcal{T}$ and $\mathcal{S}$.

To prove the *irreducibility* of these representations we use the character orthonormalization relations (4.32),

$$\frac{1}{g} \sum_R {}^{(\mu)}\chi(R) {}^{(\nu)}\chi(R^{-1}) = \delta_{\mu\nu},$$

to obtain

$$\begin{aligned} \frac{1}{ts} \sum_{T \times S} \left| {}^{(\mu \otimes \nu)}\chi(TS) \right|^2 &= \frac{1}{ts} \sum_{T, S} \left| {}^{(\mu)}\chi(T) \right|^2 \left| {}^{(\nu)}\chi(S) \right|^2 \\ &= \left[\frac{1}{t} \sum_T \left| {}^{(\mu)}\chi(T) \right|^2 \right] \left[\frac{1}{s} \sum_S \left| {}^{(\nu)}\chi(S) \right|^2 \right] \\ &= 1. \end{aligned} \tag{8.25}$$

The *completeness* of the set of Irreps is tested by Burnside's theorem

$$\sum_{\mu \otimes \nu} (d_{\mu \otimes \nu})^2 = \sum_{\mu, \nu} (d_{\mu})^2 (d_{\nu})^2 = tq = g, \tag{8.26}$$

that is, we can construct all the Irreps of $\mathcal{G}$ from the Irreps of $\mathcal{T}$ and $\mathcal{S}$.

Example 8.8

Irreps of $\mathcal{O}(3)$

The *orthogonal group* $\mathcal{O}(3)$ consists of all operations in Euclidean space $\mathcal{E}(3)$ that leave one point and all angles and distances invariant. It will be discussed in detail in Chapters 10 and 11. The full isotropic symmetry group in three dimensions is obtained from the direct product of the group of proper rotations $\mathcal{SO}(3)$, the *special orthogonal group of order 3*, and the inversion group $\mathcal{C}_i = \{\hat{E}, \hat{I}\}$. The group $\mathcal{C}_i$ has two one-dimensional Irreps:

	$\hat{E}$	$\hat{I}$
$(+)\Gamma$	1	1
$(-)\Gamma$	1	-1

The Irreps of $\mathcal{SO}(3)$ are engendered from spherical harmonic bases $|j, m\rangle$, where each manifold j engenders an Irrep. We know from quantum mechanics that the rotation operators $R(\hat{\mathbf{n}}, \phi)$ are expressed in terms of the angular momentum operator $\mathbf{J}$ as

$$R(\hat{\mathbf{n}}, \phi) = e^{-i\mathbf{J} \cdot \hat{\mathbf{n}}\phi},$$

which we will also derive in Chapter 10. The Irreps of $\mathcal{SO}(3)$ are then generated as

$${}^{(j)}\Gamma_{m'm}(R) = \langle j, m' | e^{-i\mathbf{J} \cdot \hat{\mathbf{n}}\phi} | j, m \rangle,$$

using the matrix elements of J_z and $J_{\pm}$. These matrix elements are sometimes called *Wigner functions*. Notice that the same j -value appears in the bra and ket, because each j -value generates an Irrep of $\mathcal{SO}(3)$.

The Irreps of $\mathcal{O}(3)$ are then the direct-product Reps:

	$\mathcal{SO}(3)$	$\hat{\mathcal{ISO}}(3)$
$(j+)\Gamma$	$(j)\Gamma$	$(j)\Gamma$
$(j-)\Gamma$	$(j)\Gamma$	$-(j)\Gamma$

Example 8.9

Irreps of $\mathcal{D}_2$

This is a very simple example, yet it is a good illustration of the idea of the induction of Irreps from those of the direct outer-product of constituent normal subgroups. As we have seen above

$$\mathcal{D}_2 = \{E, C_{2y}\} \otimes \{E, C_{2x}\}.$$

Each of these subgroups has the Irreps:

	$\hat{E}$	$\hat{C}_2$
$(+)\Gamma$	1	1
$(-)\Gamma$	1	-1

We immediately obtain the four one-dimensional Irreps:

	$\hat{E}$	$\hat{C}_{2x}$	$\hat{C}_{2y}$	$\hat{C}_2$
$(1)\Gamma = (+)\Gamma \otimes (+)\Gamma$	1	1	1	1
$(2)\Gamma = (+)\Gamma \otimes (-)\Gamma$	1	-1	1	-1
$(3)\Gamma = (-)\Gamma \otimes (+)\Gamma$	1	1	-1	-1
$(4)\Gamma = (-)\Gamma \otimes (-)\Gamma$	1	-1	-1	1

8.4 Semidirect product groups

Discussions of semidirect product groups may be found in references [12, 13, 14, 15, 17]. This type of product arises when we relax the subgroup invariance condition states in (i) above. More explicitly, it arises when all the elements of a group $\mathcal{G}$ can be obtained as products of the elements of its invariant subgroup $\mathcal{N} = \{N_j\}$ and another subgroup $\mathcal{Q} = \{Q_k\}$ that is *not* invariant in $\mathcal{G}$, i.e. in which $\mathcal{Q}$ does not consist of complete classes of $\mathcal{G}$. The resultant product group $\mathcal{G}$ is called a *semidirect product* group, and is written as

$$\mathcal{G} = \mathcal{N} \odot \mathcal{Q} \tag{8.27}$$

with

$$(i) \quad Q_k \mathcal{N} = \mathcal{N} Q_k \quad \forall Q_k \in \mathcal{Q}.$$

- (ii) $N_j \mathcal{Q} \neq \mathcal{Q} N_j \quad \forall N_j \in \mathcal{N}$.
- (iii) All R_i are uniquely expressed as $R_i = N_j Q_k$.

Condition (1) defines $\mathcal{N}$ as an invariant subgroup; condition (2) specifies that $\mathcal{Q}$ is not.

Example 8.10

The product group comprising the $\{E, C_3, C_3^2\}$ and $\{E, \sigma_1\}$, is a semidirect product, because the subgroup $\{E, \sigma_1\}$ does not include the operations σ_2 and σ_3 which are necessary to complete the class to which σ_1 belongs. We should also stress the significance of condition (3) by explicitly writing out the semidirect product

$$\begin{aligned} C_{3v} &= \{E, C_3, C_3^2\} \odot \{E, \sigma_1\} \\ &= \{E, C_3, C_3^2, E\sigma_1, C_3\sigma_1, C_3^2\sigma_1\} \\ &= \{E, C_3, C_3^2, \sigma_1, \sigma_3, \sigma_2\}. \end{aligned}$$

This shows that in order to uniquely identify the product operator $C_3\sigma_1$ with σ_3 we have to insist upon the ordering convention that in a semidirect product the *normal group appears first*.

We will find in Chapter 10 that semidirect products arise in a more important context when, in the process of constructing crystallographic space-groups $\mathbb{S}$, we combine crystallographic point-groups with Abelian groups of lattice translations; the latter being invariant subgroups of $\mathbb{S}$, while the former are not.

8.5 Direct inner-product groups and their representations

Discussions of direct inner-product groups may be found in references [12, 13, 14, 15, 17]. Let us consider the case of an N -electron atom, and assume for the moment that the electrons are noninteracting, classical, distinguishable particles, so that we do not have to worry about antisymmetrizing their wavefunctions. The Hamiltonian is expressed as

$$\mathcal{H} = \sum_{i=1}^N \mathcal{H}_i, \quad (8.28)$$

with each term $\mathcal{H}_i = P_i^2/2m + V(\mathbf{r}_i)$ having the symmetry group $\mathcal{O}(3)$, which we denote $\mathcal{O}^{(i)}(3)$, since it operates only on the space of the i th electron. In this case the covering symmetry group is the *direct outer-product*

$$\mathcal{G}_N^{\text{out}} = \mathcal{O}^{(1)}(3) \otimes \mathcal{O}^{(2)}(3) \otimes \cdots \otimes \mathcal{O}^{(N)}(3) \quad (8.29)$$

because each electron acts independently. However, when we turn on, say, Coulomb-type interactions $U(|\mathbf{r}_i - \mathbf{r}_j|)$, the Hamiltonian now becomes

$$\mathcal{H} = \sum_{i=1}^N \mathcal{H}_i + \frac{1}{2} \sum_{i,j} U(|\mathbf{r}_i - \mathbf{r}_j|), \quad (8.30)$$

and the covering symmetry group is restricted to those operations that leave U invariant, namely, simultaneous identical rotations of all N particles, similar to rigid-body rotations. Thus an operator in the covering group is now restricted to

$$R_k = \prod_i R_k^{(i)}, \quad R_k^{(i)} \in \mathcal{O}_i(3), \quad (8.31)$$

where the subscript k denotes a particular operation of $\mathcal{O}(3)$, and the superscript i identifies the i th electron. Such operators are identified as *inner-products* of those of the constituent groups $\mathcal{O}_i(3)$. The covering group $\mathcal{G}_N^{\text{in}}$, is called the *direct inner-product* group, comprising the restricted subset of the elements of the outer-product group $\mathcal{G}_N^{\text{out}}$, defined by (8.31). The group $\mathcal{G}_N^{\text{in}}$ is a subgroup of $\mathcal{G}_N^{\text{out}}$ that is isomorphic with the isotropy group $\mathcal{O}(3)$, since both leave angles and distances invariant.

In general, we define the direct inner-product group as

$$\mathcal{G}^{\text{in}} = \mathcal{H}^{(1)} \boxtimes \mathcal{H}^{(2)} \boxtimes \dots \boxtimes \mathcal{H}^{(N)}, \quad (8.32)$$

where each of the $\mathcal{H}^{(i)}$ is isomorphic with $\mathcal{H}$. Moreover, since an element $R_k \in \mathcal{G}^{\text{in}}$ is defined as $R_k = \prod_i H_k^{(i)}$, the direct inner-product group $\mathcal{G}^{\text{in}}$ itself is isomorphic to $\mathcal{H}$.

In order to understand the structure of the representations of inner-product groups, let us consider the case $\mathcal{G}^{\text{in}} = \mathcal{H}^{(1)} \boxtimes \mathcal{H}^{(2)}$. First, let us construct the Kronecker product Irrep generated by the irreducible basis sets $^{(\mu)}\psi_i$ and $^{(\nu)}\phi_j$ of the Irreps (μ) and (ν) of $\mathcal{H}$, respectively, namely,

$$^{(\mu \otimes \nu)}\Psi_{ij} = ^{(\mu)}\psi_i ^{(\nu)}\phi_j. \quad (8.33)$$

Since the elements of $\mathcal{G}^{\text{in}}$ are restricted to those elements of $\mathcal{G}^{\text{out}}$ that are products of identical operations of $\mathcal{H}$, we find that their representative matrices and their characters are confined to those expressed as

$$\begin{aligned} ^{(\mu \otimes \nu)}\Gamma_{ik,jl}(R) &= \left(^{(\mu)}\Delta(R) \otimes ^{(\nu)}\Delta(R) \right)_{ik,jl} = ^{(\mu)}\Delta_{ij}(R) ^{(\nu)}\Delta_{kl}(R) \\ ^{(\mu \otimes \nu)}\chi(R) &= ^{(\mu)}\chi(R) ^{(\nu)}\chi(R). \end{aligned} \quad (8.34)$$

We therefore conclude that although $^{(\mu \otimes \nu)}\Gamma$ is an Irrep of $\mathcal{G}^{\text{out}}$, it is no longer irreducible on $\mathcal{G}^{\text{in}}$. Thus the Kronecker Irrep is decomposable in terms of the Irreps of $\mathcal{G}^{\text{in}}$, which are just the Irreps of $\mathcal{H}$, namely, $^{(\mu)}\Delta$.

A key point We find that the process described here is that of forming a Kronecker product of Irreps of a *single* group and decomposing the products in terms of Irreps of the same group.

8.6 Product representations and the Clebsch–Gordan series

In this section, we explore the general process of reducing Kronecker products of Irreps. This concept of reduction of Kronecker products has far-reaching applications in simplifying the structure of physical problems as we will demonstrate in the following chapters. Further discussions can be found in references [12, 13, 14, 17, 18].

8.6.1 Reduction of Kronecker products: the Clebsch–Gordan series

The Kronecker products of Irreps play a facilitating role in many problems in physics, such as in the theory of coupled systems, the derivation of selection rules, the construction of symmetrized tensors, and in the Landau theory of phase transitions, to name a few. The decomposition of Kronecker products into Irreps of the same group is a technique frequently used in the solution of such problems. In this section we outline its mathematical basis.

The character of an operator $R \in \mathcal{G}$, in the Kronecker representation $\mu \otimes \nu$ is given in (8.23) as

$$^{(\mu \otimes \nu)}\chi(R) = ^{(\mu)}\chi(R) ^{(\nu)}\chi(R). \quad (8.35)$$

Using the character decomposition relation (4.38), we obtain

$$\begin{aligned} \langle \mu \otimes \nu | \sigma \rangle &\equiv \langle \mu \nu | \sigma \rangle = \frac{1}{g} \sum_R ^{(\mu \otimes \nu)}\chi(R) ^{(\sigma)}\chi^*(R) \\ &= \frac{1}{g} \sum_R ^{(\mu)}\chi(R) ^{(\nu)}\chi(R) ^{(\sigma)}\chi^*(R) \end{aligned} \quad (8.36)$$

or,

$$\langle \mu \nu | \sigma \rangle = \frac{1}{g} \sum_R ^{(\mu)}\chi(R) ^{(\nu)}\chi(R) ^{(\sigma)}\chi^*(R), \quad (8.37)$$

where $\langle \mu \nu | \sigma \rangle$ is the number of times that $^{(\sigma)}\Gamma$ occurs in the decomposition of the Kronecker product of $^{(\mu)}\Gamma$ and $^{(\nu)}\Gamma$. The $\langle \mu \nu | \sigma \rangle$ s are referred to as *reduction coefficients*, since they appear as coefficients in the expansion of $^{(\mu)}\Gamma \otimes ^{(\nu)}\Gamma$ into the Irreps of $\mathcal{G}$,

$$^{(\mu)}\Gamma(R) \otimes ^{(\nu)}\Gamma(R) = \sum_{\sigma}^{\oplus} \langle \mu \nu | \sigma \rangle ^{(\sigma)}\Gamma(R). \quad (8.38)$$

This expansion is called the *Clebsch–Gordan (CG) series*. Clearly, $\langle \mu \nu | \sigma \rangle = \langle \nu \mu | \sigma \rangle$, and for real Irreps it is totally symmetric with respect to the three indices. For the identity Irrep whose elements are all unity we get

$$\langle \mu \nu | 1 \rangle = \frac{1}{g} \sum_R ^{(\mu)}\chi(R) ^{(\nu)}\chi(R) = \delta_{\mu\nu}. \quad (8.39)$$

For the case of $\mu = \nu$, we show below that the CG series is separated into symmetric and antisymmetric parts:

$$\begin{aligned} \left[{}^{(\mu)}\Gamma \otimes {}^{(\mu)}\Gamma \right] &= \sum_{\sigma}^{\oplus} [\mu\mu|\sigma] {}^{(\sigma)}\Gamma, \\ \left\{ {}^{(\mu)}\Gamma \otimes {}^{(\mu)}\Gamma \right\} &= \sum_{\sigma}^{\oplus} \{\mu\mu|\sigma\} {}^{(\sigma)}\Gamma, \end{aligned} \quad (8.40)$$

where

$$\begin{aligned} [\mu\mu|\sigma] &= \frac{1}{g} \sum_R \left[{}^{(\mu)}\chi(R) \otimes {}^{(\mu)}\chi(R) \right] {}^{(\sigma)}\chi^*(R), \\ \{\mu\mu|\sigma\} &= \frac{1}{g} \sum_R \left\{ {}^{(\mu)}\chi(R) \otimes {}^{(\mu)}\chi(R) \right\} {}^{(\sigma)}\chi^*(R), \end{aligned} \quad (8.41)$$

Example 8.11

Table 8.2. *Decomposition of the Kronecker products of $\mathcal{C}_{3v}$*

$\otimes$	$(1)\Gamma$	$(2)\Gamma$	$(3)\Gamma$
$(1)\Gamma$	$(1)\Gamma$	$(2)\Gamma$	$(3)\Gamma$
$(2)\Gamma$	$(2)\Gamma$	$(1)\Gamma$	$(3)\Gamma$
$(3)\Gamma$	$(3)\Gamma$	$(3)\Gamma$	$(1)\Gamma \oplus (2)\Gamma \oplus (3)\Gamma$

Decomposition of the product representations, or Kronecker products, of $\mathcal{C}_{3v}$ are shown in Table 8.2.

8.6.2 Symmetrizing Kronecker products of the same Irrep

A special but important case arises when we take the Kronecker product of the same Irrep (μ) , namely, the representation generated by the product functions

$${}^{(\mu \otimes \mu)}\Psi_{ij} = {}^{(\mu)}\psi_i(\vec{r}) {}^{(\mu)}\phi_j(\vec{r}), \quad (8.42)$$

where, in general, $\left\{ {}^{(\mu)}\psi_i(\vec{r}) \right\}$ and $\left\{ {}^{(\mu)}\phi_j(\vec{r}) \right\}$ are two different basis sets for the same Irrep μ . We then have,

$${}^{(\mu \otimes \mu)}\Gamma_{ik,jl}(R) = {}^{(\mu)}\Gamma_{ij}(\hat{R}) {}^{(\mu)}\Gamma_{kl}(R). \quad (8.43)$$

Since

$$\begin{aligned}
 R^{(\mu \otimes \mu)} \Psi_{ij} &= \sum_{kl} (\mu \otimes \mu) \Psi_{kl}^{(\mu)} \Gamma_{ki}(R) (\mu) \Gamma_{lj}(R) \\
 &= \frac{1}{2} \sum_{kl} \left((\mu \otimes \mu) \Psi_{kl}^{(\mu)} \Gamma_{ki}(R) (\mu) \Gamma_{lj}(R) \right. \\
 &\quad \left. + (\mu \otimes \mu) \Psi_{lk}^{(\mu)} \Gamma_{li}(R) (\mu) \Gamma_{kj}(R) \right), \tag{8.44}
 \end{aligned}$$

$$\begin{aligned}
 R^{(\mu \otimes \mu)} \Psi_{ji} &= \frac{1}{2} \sum_{kl} \left((\mu \otimes \mu) \Psi_{kl}^{(\mu)} \Gamma_{kj}(R) (\mu) \Gamma_{li}(R) \right. \\
 &\quad \left. + (\mu \otimes \mu) \Psi_{lk}^{(\mu)} \Gamma_{lj}(R) (\mu) \Gamma_{ki}(R) \right), \tag{8.45}
 \end{aligned}$$

we can show that the $(\mu \otimes \mu)$ space can be split in an invariant way into a part symmetric and a part antisymmetric in the partner indices, by simply adding and subtracting (8.44) and (8.45):

$$\begin{aligned}
 R^{(\mu \otimes \mu)} \Psi_{ij} \pm (\mu \otimes \mu) \Psi_{ji} &= \sum_{kl} \left((\mu \otimes \mu) \Psi_{kl} \pm (\mu \otimes \mu) \Psi_{lk} \right) \\
 &\quad \times \frac{1}{2} \left((\mu) \Gamma_{ki}(R) (\mu) \Gamma_{lj}(R) \pm (\mu) \Gamma_{kj}(R) (\mu) \Gamma_{li}(R) \right). \tag{8.46}
 \end{aligned}$$

We now define the symmetric and antisymmetric parts by

$$\Psi_{ij}^{\pm} = \left((\mu \otimes \mu) \Psi_{ij} \pm (\mu \otimes \mu) \Psi_{ji} \right), \tag{8.47}$$

then

$$\begin{aligned}
 R^{(\mu \otimes \mu)} \Psi_{ij}^{\pm} &= \sum_{kl} (\mu \otimes \mu) \Psi_{kl}^{\pm} \frac{1}{2} \left((\mu) \Gamma_{ki}(R) (\mu) \Gamma_{lj}(R) \pm (\mu) \Gamma_{li}(R) (\mu) \Gamma_{kj}(R) \right) \\
 &= \sum_{kl} \Psi_{kl}^{\pm} (\mu \otimes \mu) \Gamma_{kl,ij}^{\pm}(R), \tag{8.48}
 \end{aligned}$$

which demonstrates that the symmetric and antisymmetric parts do not mix under a transformation. The matrices of the symmetric and antisymmetric product representations are defined as

$$\begin{aligned}
 (\mu \otimes \mu) \Gamma_{kl,ij}^{+}(R) &= \left[(\mu) \Gamma \otimes (\mu) \Gamma \right]_{kl,ij} \\
 &= \frac{1}{2} \left((\mu) \Gamma_{ki}(R) (\mu) \Gamma_{lj}(R) + (\mu) \Gamma_{kj}(R) (\mu) \Gamma_{li}(R) \right), \tag{8.49}
 \end{aligned}$$

$$\begin{aligned}
 (\mu \otimes \mu) \Gamma_{kl,ij}^{-}(R) &= \left\{ (\mu) \Gamma \otimes (\mu) \Gamma \right\}_{kl,ij} \\
 &= \frac{1}{2} \left((\mu) \Gamma_{ki}(R) (\mu) \Gamma_{lj}(R) - (\mu) \Gamma_{kj}(R) (\mu) \Gamma_{li}(R) \right). \tag{8.50}
 \end{aligned}$$

The characters of the symmetric and antisymmetric parts can be obtained by setting $(kl) = (ij)$ and taking the trace:

$$\begin{aligned}
 {}^{(\mu \otimes \mu)}\chi^+(R) &= \left[{}^{(\mu)}\chi \otimes {}^{(\mu)}\chi \right] \\
 &= \frac{1}{2} \sum_{ij} \left({}^{(\mu)}\Gamma_{ii}(R) {}^{(\mu)}\Gamma_{jj}(R) + {}^{(\mu)}\Gamma_{ij}(R) {}^{(\mu)}\Gamma_{ji}(R) \right) \\
 &= \frac{1}{2} \left(\sum_i {}^{(\mu)}\Gamma_{ii}(R) \right) \left(\sum_j {}^{(\mu)}\Gamma_{jj}(R) \right) \\
 &\quad + \frac{1}{2} \sum_i \left(\sum_j {}^{(\mu)}\Gamma_{ij}(R) {}^{(\mu)}\Gamma_{ji}(R) \right) \\
 &= \frac{1}{2} \left({}^{(\mu)}\chi^2(R) + {}^{(\mu)}\chi(R^2) \right), \tag{8.51}
 \end{aligned}$$

$$\begin{aligned}
 {}^{(\mu \otimes \mu)}\chi^-(R) &= \left\{ {}^{(\mu)}\chi \otimes {}^{(\mu)}\chi \right\} \\
 &= \frac{1}{2} \left({}^{(\mu)}\chi^2(R) - {}^{(\mu)}\chi(R^2) \right). \tag{8.52}
 \end{aligned}$$

The dimension of the symmetrized representation is $d_\mu(d_\mu + 1)/2$, while that of the anti-symmetrized representation is $d_\mu(d_\mu - 1)/2$. This can be seen directly from $\chi(E)$ in both cases. In general, both symmetric and antisymmetric representations are reducible.

Example 8.12

Consider the case of a two-dimensional Irrep Γ . From (8.24) the Kronecker product of Γ is

$$\begin{aligned}
 R \begin{bmatrix} \psi_1 \phi_1 \\ \psi_1 \phi_2 \\ \psi_2 \phi_1 \\ \psi_2 \phi_2 \end{bmatrix} &= \begin{bmatrix} \psi_1 \phi_1 & \psi_1 \phi_2 & \psi_2 \phi_1 & \psi_2 \phi_2 \end{bmatrix} \\
 &\quad \times \begin{bmatrix} \Gamma_{11}\Gamma_{11} & \Gamma_{11}\Gamma_{21} & \Gamma_{21}\Gamma_{11} & \Gamma_{21}\Gamma_{21} \\ \Gamma_{11}\Gamma_{12} & \Gamma_{11}\Gamma_{22} & \Gamma_{21}\Gamma_{12} & \Gamma_{21}\Gamma_{22} \\ \Gamma_{12}\Gamma_{11} & \Gamma_{12}\Gamma_{21} & \Gamma_{22}\Gamma_{11} & \Gamma_{22}\Gamma_{21} \\ \Gamma_{12}\Gamma_{12} & \Gamma_{12}\Gamma_{22} & \Gamma_{22}\Gamma_{12} & \Gamma_{22}\Gamma_{22} \end{bmatrix} \tag{8.53}
 \end{aligned}$$

with $\Gamma_{ij} \equiv \Gamma_{ij}(R)$. Carrying out the symmetrization (antisymmetrization) we get

$$R \begin{bmatrix} \psi_1 \phi_1 \\ (\psi_1 \phi_2 + \psi_2 \phi_1) \\ \psi_2 \phi_2 \\ (\psi_1 \phi_2 - \psi_2 \phi_1) \end{bmatrix} = \begin{bmatrix} \psi_1 \phi_1 & (\psi_1 \phi_2 + \psi_2 \phi_1) & \psi_2 \phi_2 & (\psi_1 \phi_2 - \psi_2 \phi_1) \end{bmatrix} \times \begin{bmatrix} \Gamma_{11}\Gamma_{11} & \Gamma_{11}\Gamma_{12} & \Gamma_{12}\Gamma_{12} & \\ \Gamma_{11}\Gamma_{21} & (\Gamma_{11}\Gamma_{22} + \Gamma_{12}\Gamma_{21}) & \Gamma_{12}\Gamma_{22} & \\ \Gamma_{21}\Gamma_{21} & \Gamma_{21}\Gamma_{22} & \Gamma_{22}\Gamma_{22} & \\ & & & (\Gamma_{11}\Gamma_{22} - \Gamma_{12}\Gamma_{21}) \end{bmatrix}.$$

Note that the representation has been reduced, or block diagonalized, by the symmetrization into two representations with bases: $(\psi_1 \phi_1, (\psi_1 \phi_2 + \psi_2 \phi_1), \psi_2 \phi_2)$; and $(\psi_1 \phi_2 - \psi_2 \phi_1)$. The characters of these representations are

$$\begin{aligned} [\chi(R) \otimes \chi(R)] &= \Gamma_{11}^2(R) + \Gamma_{11}(R)\Gamma_{22}(R) + \Gamma_{12}(R)\Gamma_{21}(R) + \Gamma_{22}^2(R) \\ &= \frac{1}{2} [\Gamma_{11}(R) + \Gamma_{22}(R)]^2 + \frac{1}{2} [\Gamma_{11}^2(R) + \Gamma_{12}(R)\Gamma_{21}(R) \\ &\quad + \Gamma_{12}(R)\Gamma_{21}(R) + \Gamma_{22}^2(R)] \\ &= \frac{1}{2} [\Gamma_{11}(R) + \Gamma_{22}(R)]^2 + \frac{1}{2} [\Gamma_{11}(R^2) + \Gamma_{22}(R^2)]^2 \\ &= \frac{1}{2} [\chi^2(R) + \chi(R^2)], \end{aligned}$$

and

$$\{\chi(R) \otimes \chi(R)\} = \frac{1}{2} [\chi^2(R) - \chi(R^2)],$$

in agreement with (8.51) and (8.52). Finally, we note that when $\mu = \nu$ and $\psi_i^{(\mu)} = \phi_i^{(\mu)}$ the antisymmetric representation vanishes and we obtain only the symmetric representation.

Example 8.13

Reduction of the self Kronecker product of the $\mathcal{C}_{3v}$ irreps

Table 8.3. Characters for the Kronecker products of $\mathcal{C}_{3v}$.

$\mathcal{C}_{3v}$	E	$2C_3$	$3\sigma_v$
$[(3 \otimes 3)\chi]$	3	0	1
$\{(3 \otimes 3)\chi\}$	1	1	-1

The reduction of the symmetric and antisymmetric products for $\mathcal{C}_{3v}$ leads to:

$$\begin{aligned} \left[{}^{(1)}\Gamma \otimes {}^{(1)}\Gamma \right] &= {}^{(1)}\Gamma, \quad \left\{ {}^{(1)}\Gamma \otimes {}^{(1)}\Gamma \right\} = 0, \\ \left[{}^{(2)}\Gamma \otimes {}^{(2)}\Gamma \right] &= {}^{(1)}\Gamma, \quad \left\{ {}^{(2)}\Gamma \otimes {}^{(2)}\Gamma \right\} = 0, \\ \left[{}^{(3)}\Gamma \otimes {}^{(3)}\Gamma \right] &= {}^{(1)}\Gamma \oplus {}^{(3)}\Gamma, \quad \left\{ {}^{(3)}\Gamma \otimes {}^{(3)}\Gamma \right\} = {}^{(2)}\Gamma. \end{aligned}$$

Example 8.14

Clebsch–Gordan series for $\mathcal{D}_4$ and $\mathcal{C}_{4v}$

These two groups are isomorphic, each comprising eight elements. The Kronecker products of their Irreps have the following complete set of CG series:

Table 8.4. *Decomposition of the Kronecker products of $\mathcal{C}_{4v}$.*

$\otimes$	${}^{(1)}\Gamma$	${}^{(2)}\Gamma$	${}^{(3)}\Gamma$	${}^{(4)}\Gamma$	${}^{(5)}\Gamma$
${}^{(1)}\Gamma$	${}^{(1)}\Gamma$	${}^{(2)}\Gamma$	${}^{(3)}\Gamma$	${}^{(4)}\Gamma$	${}^{(5)}\Gamma$
${}^{(2)}\Gamma$	${}^{(2)}\Gamma$	${}^{(1)}\Gamma$	${}^{(4)}\Gamma$	${}^{(3)}\Gamma$	${}^{(5)}\Gamma$
${}^{(3)}\Gamma$	${}^{(3)}\Gamma$	${}^{(4)}\Gamma$	${}^{(1)}\Gamma$	${}^{(2)}\Gamma$	${}^{(5)}\Gamma$
${}^{(4)}\Gamma$	${}^{(4)}\Gamma$	${}^{(3)}\Gamma$	${}^{(2)}\Gamma$	${}^{(1)}\Gamma$	${}^{(5)}\Gamma$
${}^{(5)}\Gamma$	${}^{(5)}\Gamma$	${}^{(5)}\Gamma$	${}^{(5)}\Gamma$	${}^{(5)}\Gamma$	${}^{(1)}\Gamma \oplus {}^{(2)}\Gamma \oplus {}^{(3)}\Gamma \oplus {}^{(4)}\Gamma$

The symmetrization of ${}^{(5)}\Gamma \otimes {}^{(5)}\Gamma$ gives

$$\begin{aligned} \left[{}^{(5)}\Gamma \otimes {}^{(5)}\Gamma \right] &= {}^{(1)}\Gamma \oplus {}^{(3)}\Gamma \oplus {}^{(4)}\Gamma, \\ \left\{ {}^{(5)}\Gamma \otimes {}^{(5)}\Gamma \right\} &= {}^{(2)}\Gamma. \end{aligned}$$

Example 8.15

Transformation tensor of a second-rank tensor

Now that we are familiar with the concept of the Kronecker or outer-product of matrices, we can explore the structure of a second, or higher, rank tensor in a rather systematic way. Furthermore, we can study its transformation with the aid of the Kronecker products of Irreps.

A second-rank tensor T can be constructed from the direct outer-product of two vectors $\bar{r} \otimes \bar{r}'$:

$$T = \begin{bmatrix} x \\ y \\ z \end{bmatrix} \begin{bmatrix} x' & y' & z' \end{bmatrix} = \begin{bmatrix} xx' & xy' & xz' \\ yx' & yy' & yz' \\ zx' & zy' & zz' \end{bmatrix}. \quad (8.54)$$

A vector $\bar{r}$ induces a three-dimensional Irrep $^{(j=1)}\Gamma^-$ of the full rotation group; for $R \in \mathcal{O}(3) = \mathcal{SO}(3) \otimes \mathcal{C}_i$

$$R \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x & y & z \end{bmatrix} {}^{(1)}\Gamma^-(R).$$

Consequently, T will transform as $\Gamma(T) = {}^{(1)}\Gamma^-(R) \otimes {}^{(1)}\Gamma^-(R)$. But, from Example 8.3 we have ${}^{(1)}\Gamma^-(R) = {}^{(1)}\Gamma(R) \otimes {}^{(-)}\Gamma(\mathcal{C}_i)$, hence, we get

$$\begin{aligned} \Gamma(T) &= {}^{(1)}\Gamma(R) \otimes {}^{(-)}\Gamma(\mathcal{C}_i) \otimes {}^{(1)}\Gamma(R) \otimes {}^{(-)}\Gamma(\mathcal{C}_i) \\ &= {}^{(1)}\Gamma(R) \otimes {}^{(+)}\Gamma(\mathcal{C}_i) \otimes {}^{(1)}\Gamma(R) \otimes {}^{(+)}\Gamma(\mathcal{C}_i) \\ &= {}^{(1)}\Gamma^+(R) \otimes {}^{(1)}\Gamma^+(R) \\ &= {}^{(0)}\Gamma(R)^+ \oplus {}^{(1)}\Gamma(R)^+ \oplus {}^{(2)}\Gamma^+(R). \end{aligned}$$

This result is familiar from quantum mechanics, where a tensor operator of rank 2 decomposes into three spherical tensor operators:

- a scalar, or spherical tensor of rank 0 ($j = 0$),
- an antisymmetric spherical tensor, transforming as $\mathbf{r} \times \mathbf{r}'$, ($j = 1$),
- a symmetric traceless spherical tensor ($j = 2$).

The spherical tensors can be separated into symmetrized and antisymmetrized components:

$$\begin{aligned} [\Gamma(T)] &= {}^{(0)}\Gamma(R)^+ \oplus {}^{(2)}\Gamma^+(R), \\ \{\Gamma(T)\} &= {}^{(1)}\Gamma(R)^+. \end{aligned}$$

8.6.3 Symmetrized p th power of an Irrep and Molien functions²

We now extend the concept of symmetrizing the square of an Irrep, delineated above, to the symmetrization of the p th tensorial product of an Irrep $^{(\mu)}\Gamma$ of a group $\mathcal{G}$. The p th power of the Irrep $^{(\mu)}\Gamma$ is denoted here by $^{(\mu)}\Gamma^p$, and its characters by $^{(\mu)}\chi^p(R_i)$. This Rep is reducible into symmetrized and antisymmetrized Reps. The invariant Irrep of $\mathcal{G}$ appears only in the reduction of the symmetrized Rep. We denote the symmetrized Rep by $[^{(\mu)}\Gamma^p]$, and its characters by $[^{(\mu)}\chi^p]$. The characters of $[^{(\mu)}\Gamma^2]$, $[^{(\mu)}\Gamma^3]$, and $[^{(\mu)}\Gamma^4]$ are

$$\begin{aligned} \chi[^{(\mu)}\Gamma^2(R)] &= \frac{1}{2} [^{(\mu)}\chi^2(R) + ^{(\mu)}\chi(R^2)], \\ \chi[^{(\mu)}\Gamma^3(R)] &= \frac{1}{6} ^{(\mu)}\chi^3(R) + \frac{1}{2} ^{(\mu)}\chi(R) ^{(\mu)}\chi(R^2) + \frac{1}{3} ^{(\mu)}\chi(R^3), \\ \chi[^{(\mu)}\Gamma^4(R)] &= \frac{1}{24} ^{(\mu)}\chi^4(R) + \frac{1}{4} ^{(\mu)}\chi^2(R) ^{(\mu)}\chi(R^2) \\ &\quad + \frac{1}{8} ^{(\mu)}\chi^2(R^2) + \frac{1}{3} ^{(\mu)}\chi(R^3) ^{(\mu)}\chi(R) + \frac{1}{4} ^{(\mu)}\chi(R^4). \end{aligned} \tag{8.55}$$

² This section is very technical and, therefore, optional.

A general expression for $\chi[\Gamma^n(R)]\chi\{\Gamma^n(R)\}$ is given by

$$\begin{aligned}\chi^{(\mu)\Gamma^n(R)} &= \sum_{\kappa_1, \dots, \kappa_n} \frac{(\mu)\chi^{\kappa_1}(R)(\mu)\chi^{\kappa_2}(R^2) \dots (\mu)\chi^{\kappa_n}(R^n)}{1^{\kappa_1} \kappa_1! 2^{\kappa_2} \kappa_2! \dots n^{\kappa_n} \kappa_n!}, \\ \chi\{(\mu)\Gamma^n(R)\} &= \sum_{\kappa_1, \dots, \kappa_n} (-1)^{(\sum_i \kappa_i) - n} \frac{(\mu)\chi^{\kappa_1}(R)(\mu)\chi^{\kappa_2}(R^2) \dots (\mu)\chi^{\kappa_n}(R^n)}{1^{\kappa_1} \kappa_1! 2^{\kappa_2} \kappa_2! \dots n^{\kappa_n} \kappa_n!}, \\ \sum_{l=1}^n l\kappa_l &= n.\end{aligned}\tag{8.56}$$

The Molien and generalized Molien functions

The reader may find discussions of *general symmetrized and antisymmetrized products of Irreps* in references [3, 19] and of *Molien functions* in references [20, 21].

We encounter many situations where it is desirable to know the frequencies of some Irrep $^{(\beta)}\Gamma(R)$ of $\mathcal{G}$ corresponding to several p th powers of the symmetrized tensorial product of Irrep $^{(\alpha)}\Gamma(R)$ of $\mathcal{G}$, namely

$$\langle \beta \mid [\alpha^p] \rangle = \frac{1}{g} \sum_{R \in \mathcal{G}} \chi_\beta(R^{-1}) \text{Tr} [^{(\alpha)}\Gamma^p(R)],\tag{8.57}$$

in the subduction of $[^{(\alpha)}\Gamma^p(R)]$ onto the Irreps of $\mathcal{G}$. We note that $\langle \beta \mid [\alpha^p] \rangle$ is also the number of linearly independent components of the tensor that transforms according to the Irrep β in the reduction of $[\alpha^p]$.

As we show below, such frequencies appear as coefficients of powers of a dummy variable in a series expansion known as the Molien series. Writing $^{(\alpha)}\Gamma(R)$ in its diagonal form, namely

$$^{(\alpha)}\Gamma(R) = \begin{pmatrix} \lambda_{\alpha 1}(R) & 0 & \dots & 0 \\ 0 & \lambda_{\alpha 2}(R) & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & \lambda_{\alpha m}(R) \end{pmatrix},$$

and noting that

$$^{(\alpha)}\Gamma(R^m) = \begin{pmatrix} \lambda_{\alpha 1}^m(R) & 0 & \dots & 0 \\ 0 & \lambda_{\alpha 2}^m(R) & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & \lambda_{\alpha m}^m(R) \end{pmatrix},$$

we obtain from (8.56)

$$\chi [^{(\alpha)}\Gamma^p(R)] = \sum_{\kappa_1 \dots \kappa_p} \prod_{l=1}^p \frac{1}{\kappa_l!} \left(\frac{\sum_i \lambda_{\alpha i}^l(R)}{l} \right)^{\kappa_l} ; \quad \sum_{l=1}^p l\kappa_l = p.\tag{8.58}$$

It can then be shown that characters of an element $R \in G$, in all the symmetrized products $[\chi_\alpha^p(R)]$ of Irrep α appear as coefficients of x^p , where x is a dummy variable, in the

expansion of

$$\frac{1}{\det [\mathbb{I} - {}^{(\alpha)}\Gamma(R)x]} = \frac{1}{\prod_{i=1}^m [1 - \lambda_{\alpha i}(R)x]} = \sum_{n=0}^{\infty} f_n(\lambda_{\alpha i}(R)) x^n, \quad (8.59)$$

where $f_n(\lambda_{\alpha i})$, a homogeneous polynomial in the $\lambda_{\alpha i}$ s of degree n , is just the expression for the character $[\chi_{\alpha}^n(R)]$ in (8.58).

Multiplying both sides of (8.57) by x^n , using (8.59), and summing over n we obtain

$$\begin{aligned} \sum_{n=0}^{\infty} \langle \beta | [\alpha^n] \rangle x^n &= \frac{1}{|G|} \sum_{R \in G} \frac{\chi_{\beta}(R^{-1})}{\det [\mathbb{I} - {}^{(\alpha)}\Gamma(R)x]} \\ &= \frac{1}{|G|} \sum_{R \in G} \frac{\chi_{\beta}(R^{-1})}{\prod_{i=1}^m [1 - \lambda_{\alpha i}(R)x]}, \end{aligned}$$

which is called the *Poincaré series* $\mathcal{M}(\beta, \alpha, x)$.

The generalized Molien function $\mathcal{M}(\beta, \alpha, x)$ The coefficient of x^p in the series expansion of $\mathcal{M}(\beta, \alpha, x)$ is the number of independent polynomials of degree p , in the p th tensorial product of Irrep α , that transform according to Irrep β , referred to as the β -covariant polynomials of degree p .

The Molien function When we consider the identity Irrep, $\chi_1(R) = 1$, $\forall R \in \mathcal{G}$, we obtain the Molien function

$$\mathcal{M}(\alpha, x) = \frac{1}{|G|} \sum_{R \in G} \frac{1}{\det [\mathbb{I} - {}^{(\alpha)}\Gamma(R)x]} = \frac{1}{|G|} \sum_{R \in G} \frac{1}{\prod_{i=1}^m [1 - \lambda_{\alpha i}(R)x]}, \quad (8.60)$$

where the coefficient of the x^k , in the series expansion of $\mathcal{M}$, is just the number of independent homogeneous polynomial invariants of degree k .

In (8.60) the evaluation of the Molien function requires knowledge of all the matrices representing the group elements in Irrep α . An alternative form of the Molien function, which needs only the Irrep characters, can be obtained by writing the general expression for $\chi[\Gamma^n(R)]$ as

$$\chi[\Gamma^n(R)] = \sum_{\kappa_1, \dots, \kappa_n} \delta_{(n, \sum l \kappa_l)} \frac{\chi^{\kappa_1}(R) \chi^{\kappa_2}(R^2) \dots \chi^{\kappa_n}(R^n)}{1^{\kappa_1} \kappa_1! 2^{\kappa_2} \kappa_2! \dots n^{\kappa_n} \kappa_n!},$$

and using the identities

$$\begin{aligned} \delta_{p,0} &= \text{Res} \frac{1}{z^{p+1}} = \frac{1}{2\pi i} \oint_C \frac{dz}{z^{p+1}} \\ \frac{1}{z^{-\sum l \kappa_l}} &= \prod_{l=1}^n z^{l \kappa_l}, \end{aligned}$$

where C is a closed contour around $z = 0$ and Res means residue, we obtain

$$\begin{aligned}
 \chi[\Gamma^n(R)] &= \frac{1}{2\pi i} \oint_C \frac{dz}{z^{n+1}} \prod_{l=1}^n \sum_{\kappa_l=0}^{\infty} \frac{z^{l\kappa_l} \chi^{\kappa_l}(R^l)}{l^{\kappa_l} \kappa_l!} \\
 &= \frac{1}{2\pi i} \oint_C \frac{dz}{z^{n+1}} \prod_{l=1}^n \sum_{\kappa_l=0}^{\infty} \frac{1}{\kappa_l!} \left(\frac{z^l \chi(R^l)}{l} \right)^{\kappa_l} \\
 &= \frac{1}{2\pi i} \oint_C \frac{dz}{z^{n+1}} \prod_{l=1}^n \exp \left[\frac{z^l \chi(R^l)}{l} \right] \\
 &= \frac{1}{n!} \frac{d^n}{dz^n} \left[\exp \left(\sum_{l=1}^{\infty} \frac{z^l \chi(R^l)}{l} \right) \right]_{z=0}
 \end{aligned} \tag{8.61}$$

which is the n th term in the Taylor expansion about $z = 0$ of the function inside the square brackets, and can write

$$\sum_{n=0}^{\infty} \chi[\Gamma^n(R)] z^n = \exp \left(\sum_{l=1}^{\infty} \frac{z^l \chi(R^l)}{l} \right). \tag{8.62}$$

8.6.4 Reduction of product basis sets: Clebsch–Gordan or Wigner coefficients

In the previous sections we defined the basis functions for the Kronecker products as products of the basis functions of their constituent Irreps. In the light of the CG series decomposition, it is appropriate to seek new corresponding basis sets. In fact, we need to find a basis set, not only for each Irrep that appears in the CG series but for as many basis sets as the number of times it appears in the CG series. Formally, this can be achieved through a unitary transformation $^{(\mu\nu)}\mathcal{M}$ that reduces the Kronecker product Rep $^{(\mu\otimes\nu)}\Gamma$ into the block-diagonal form

$$^{(\mu\nu)}\mathcal{M}^{-1} \ ^{(\mu\otimes\nu)}\Gamma \ ^{(\mu\nu)}\mathcal{M} = \begin{bmatrix} ^{(\sigma)}\Gamma^1 & & & \\ & \ddots & & \\ & & \ddots & \\ & & & ^{(\sigma)}\Gamma^{\langle\mu\nu|\sigma\rangle} & \\ & & & & \ddots \end{bmatrix}. \tag{8.63}$$

Such a transformation also defines the sought-after basis sets $\left\{ ^{(\sigma)}\Psi^s \right\}$, $s = 1, \dots, \langle\mu\nu|\sigma\rangle$ in terms of $\left\{ ^{(\mu)}\psi^{(\nu)}\phi \right\}$, as

$$^{(\sigma)}\Psi_l^s = \sum_{jk} ^{(\mu)}\psi_j^{(\nu)}\phi_k \left(\begin{array}{c|c} \mu\nu & \sigma s \\ jk & l \end{array} \right), \tag{8.64}$$

where $\left(\begin{array}{c} \mu\nu \\ jk \end{array} \middle| \begin{array}{c} \sigma s \\ l \end{array} \right)$ are the elements of $^{(\mu\nu)}\mathcal{M}$, and are called *Clebsch–Gordan coefficients* (CGC), or, sometimes, *Wigner coefficients*. The unitarity of $^{(\mu\nu)}\mathcal{M}$ implies that the basis systems are orthonormal, which allows us to invert (8.64) and obtain

$$^{(\mu)}\psi_j^{(\nu)}\phi_k = \sum_{\sigma,s,l} {}^{(\sigma)}\Psi_l^s \left(\begin{array}{c} \sigma s \\ l \end{array} \middle| \begin{array}{c} \mu\nu \\ jk \end{array} \right), \quad (8.65)$$

where

$$\left(\begin{array}{c} \sigma s \\ l \end{array} \middle| \begin{array}{c} \mu\nu \\ jk \end{array} \right) = \left(\begin{array}{c} \mu\nu \\ jk \end{array} \middle| \begin{array}{c} \sigma s \\ l \end{array} \right)^*.$$

We also find that the CGCs satisfy the relations

$$\sum_{jk} \left(\begin{array}{c} \sigma s \\ l \end{array} \middle| \begin{array}{c} \mu\nu \\ jk \end{array} \right) \left(\begin{array}{c} \mu\nu \\ jk \end{array} \middle| \begin{array}{c} \sigma' s' \\ l' \end{array} \right) = \delta_{\sigma\sigma'} \delta_{ss'} \delta_{ll'}, \quad (8.66)$$

$$\sum_{\sigma sl} \left(\begin{array}{c} \mu\nu \\ jk \end{array} \middle| \begin{array}{c} \sigma s \\ l \end{array} \right) \left(\begin{array}{c} \sigma s \\ l \end{array} \middle| \begin{array}{c} \mu\nu \\ j'k' \end{array} \right) = \delta_{jj'} \delta_{kk'}. \quad (8.67)$$

Notice that the total number of basis functions is preserved through this transformation, consequently, we have

$$d_\mu d_\nu = \sum_{\sigma} \langle \mu\nu | \sigma \rangle d_\sigma. \quad (8.68)$$

There are two possible approaches to determining the CGCs:

The projection operator method We apply the projection operator

$$^{(\sigma)}P_{ii} = \frac{d_\sigma}{g} \sum_{R \in \mathcal{G}} {}^{(\sigma)}\Gamma_{ii}(R^{-1}) \hat{R}_{\text{outer}} \quad (8.69)$$

to both sides of (8.65) to construct $^{(\sigma)}\Psi_i$, then use $^{(\sigma)}P_{ij}$ to generate the partners of $^{(\sigma)}\Psi_i$. In (8.69) $\hat{R}_{\text{outer}}$ is generated by taking the matrix outer-product

$$\hat{R}_{\text{outer}} = {}^{(\mu)}\Gamma(R) \otimes {}^{(\nu)}\Gamma(R). \quad (8.70)$$

This can be done simply in *Mathematica* with the aid of the function

```
Needs["LinearAlgebra`MatrixManipulation`"]
KroneckerProduct[a_?SquareMatrixQ, b_?SquareMatrixQ] :=
BlockMatrix[Outer[Times, a, b]];
Rmu =  $^{(\mu)}$ Γ[R];
Rnu =  $^{(\nu)}$ Γ[R];
KroneckerProduct[Rmu, Rnu] // MatrixForm
```

The construction of $^{(\sigma)}P_{ii}$ would require knowledge of the matrix Irreps $^{(\mu)}\Gamma$ and $^{(\nu)}\Gamma$, however, this is easily constructed if only the matrices corresponding to the group generators are provided! Again, once we construct the matrix $^{(\sigma)}\mathbf{P}_i$, we follow the procedure of solving the corresponding eigenvalue problem. The CGCs are just the components of eigenvectors with unity eigenvalues!

Example 8.16

**CGCs of the Kronecker product $^{(3\otimes 3)}\Gamma$ of the
two-dimensional Irrep $^{(3)}\Gamma$ of C_{3v}**

We choose the generators

$$^{(3)}\Gamma(C_3) = \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix}, \quad ^{(3)}\Gamma(\sigma_x) = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}.$$

The corresponding outer-products are

$$E_{\text{outer}} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \quad \sigma_{1\text{outer}} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

$$\sigma_{2\text{outer}} = \frac{1}{4} \begin{pmatrix} 1 & \sqrt{3} & \sqrt{3} & 3 \\ \sqrt{3} & -1 & 3 & -\sqrt{3} \\ \sqrt{3} & 3 & -1 & -\sqrt{3} \\ 3 & -\sqrt{3} & -\sqrt{3} & 1 \end{pmatrix} \quad \sigma_{3\text{outer}} = \frac{1}{4} \begin{pmatrix} 1 & -\sqrt{3} & -\sqrt{3} & 3 \\ -\sqrt{3} & -1 & 3 & \sqrt{3} \\ -\sqrt{3} & 3 & -1 & \sqrt{3} \\ 3 & \sqrt{3} & \sqrt{3} & 1 \end{pmatrix}$$

$$C_{3\text{outer}} = \frac{1}{4} \begin{pmatrix} 1 & \sqrt{3} & \sqrt{3} & 3 \\ -\sqrt{3} & 1 & -3 & \sqrt{3} \\ -\sqrt{3} & -3 & 1 & \sqrt{3} \\ 3 & -\sqrt{3} & -\sqrt{3} & 1 \end{pmatrix} \quad C_{3\text{outer}}^- = \frac{1}{4} \begin{pmatrix} 1 & -\sqrt{3} & -\sqrt{3} & 3 \\ \sqrt{3} & 1 & -3 & -\sqrt{3} \\ \sqrt{3} & -3 & 1 & -\sqrt{3} \\ 3 & \sqrt{3} & \sqrt{3} & 1 \end{pmatrix}$$

It is now very easy to construct $^{(1)}\mathbf{P}_1$ and $^{(2)}\mathbf{P}_1$

$$^{(1)}\mathbf{P}_1 = \frac{1}{2} \begin{pmatrix} 1 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 1 \end{pmatrix}, \quad ^{(2)}\mathbf{P}_1 = \frac{1}{2} \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 1 & -1 & 0 \\ 0 & -1 & 1 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}.$$

It is clear that for each there is a single eigenvector with eigenvalue 1, which when normalized is

$$^{(1)}\Psi = \frac{1}{\sqrt{2}} [1001], \quad ^{(2)}\Psi = \frac{1}{\sqrt{2}} [01 - 10].$$

As for the third Irrep, we have

$${}^{(3)}\mathbf{P}_1 = \frac{1}{2} \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \quad {}^{(3)}\mathbf{P}_2 = \frac{1}{2} \begin{pmatrix} 1 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ -1 & 0 & 0 & 1 \end{pmatrix},$$

with eigenvectors

$${}^{(1)}\Psi = \frac{1}{\sqrt{2}} [0110], \quad {}^{(2)}\Psi = \frac{1}{\sqrt{2}} [100 - 1].$$

The orthogonality method Inverting (8.63) gives

$${}^{(\mu\otimes\nu)}\Gamma = {}^{(\mu\nu)}\mathcal{M} \sum_{\sigma}^{\oplus} \langle \mu\nu | \sigma \rangle^{(\sigma)} \Gamma^{(\mu\nu)} \mathcal{M}^{-1}; \quad (8.71)$$

or, more explicitly

$$\begin{aligned} {}^{(\mu\otimes\nu)}\Gamma_{ik,jl}(R) &= {}^{(\mu)}\Gamma_{ij}(R) {}^{(\nu)}\Gamma_{kl}(R) \\ &= \sum_{\substack{\sigma s \\ rt}} \left(\begin{array}{c|c} \mu\nu & \sigma s \\ ik & r \end{array} \right) {}^{(\sigma)}\Gamma_{rt}(R) \left(\begin{array}{c|c} \sigma s & \mu\nu \\ t & jl \end{array} \right). \end{aligned} \quad (8.72)$$

Multiplying by ${}^{(\sigma)}\Gamma_{mn}^*(R)$ and summing over $R \in \mathcal{G}$, we obtain

$$\sum_s \left(\begin{array}{c|c} \mu\nu & \sigma s \\ ik & m \end{array} \right) \left(\begin{array}{c|c} \sigma s & \mu\nu \\ n & jl \end{array} \right) = \frac{d_{\sigma}}{g} \sum_{R \in \mathcal{G}} {}^{(\mu)}\Gamma_{ij}(R) {}^{(\nu)}\Gamma_{kl}(R) {}^{(\sigma)}\Gamma_{mn}^*(R). \quad (8.73)$$

In cases where $\langle \mu\nu | \sigma \rangle > 1$, the summation over s on the l.h.s. of (8.73) leaves some ambiguity in determining the corresponding CGCs.

Simply reducible groups

If all the reduction coefficients $\langle \mu\nu | \sigma \rangle$ of a group $\mathcal{G}$ assume only the values 0 or 1, the relations (8.66) and (8.67) reduce to

$$\sum_{jk} \left(\begin{array}{c|c} \sigma & \mu\nu \\ l & jk \end{array} \right) \left(\begin{array}{c|c} \mu\nu & \sigma' \\ jk & l' \end{array} \right) = \delta_{\sigma\sigma'} \delta_{ll'}, \quad (8.74)$$

$$\sum_{\sigma il} \left(\begin{array}{c|c} \mu\nu & \sigma \\ jk & l \end{array} \right) \left(\begin{array}{c|c} \sigma & \mu\nu \\ l & j'k' \end{array} \right) = \delta_{jj'} \delta_{kk'}, \quad (8.75)$$

and $\mathcal{G}$ is called a *simply reducible* group. In this case, (8.71) becomes

$${}^{(\mu\otimes\nu)}\Gamma = {}^{(\mu\nu)}\mathcal{M} \sum_{\sigma}^{\oplus} \langle \mu\nu | \sigma \rangle {}^{(\sigma)}\Gamma^{(\mu\nu)} \mathcal{M}^{-1}; \quad (8.76)$$

and since $\langle \mu\nu | \sigma \rangle$ is either 0 or 1, we drop the index s in (8.72) and (8.73) and write

$$\begin{aligned} {}^{(\mu\otimes\nu)}\Gamma_{ik,jl}(R) &= {}^{(\mu)}\Gamma_{ij}(R) {}^{(\nu)}\Gamma_{kl}(R) \\ &= \sum_{\sigma} \left(\begin{array}{c|c} \mu\nu & \sigma \\ ik & m \end{array} \right) {}^{(\sigma)}\Gamma_{mn}(R) \left(\begin{array}{c|c} \sigma & \mu\nu \\ n & jl \end{array} \right); \end{aligned} \quad (8.77)$$

$$\left(\begin{array}{c|c} \mu\nu & \sigma \\ ik & m \end{array} \right) \left(\begin{array}{c|c} \sigma & \mu\nu \\ n & jl \end{array} \right) = \frac{d_\sigma}{g} \sum_{R \in \mathcal{G}} {}^{(\mu)}\Gamma_{ij}(R) {}^{(\nu)}\Gamma_{kl}(R) {}^{(\sigma)}\Gamma_{mn}^*(R). \quad (8.78)$$

We can construct a simple scheme based on (8.73) to determine the CGCs. We first determine the CGCs with $m = n$, $i = j$, and $k = l$, which are given directly as

$$\left| \left(\begin{array}{c|c} \mu\nu & \sigma \\ ik & m \end{array} \right) \right|^2 = \frac{d_\sigma}{g} \sum_{R \in \mathcal{G}} {}^{(\mu)}\Gamma_{ii}(R) {}^{(\nu)}\Gamma_{kk}(R) {}^{(\sigma)}\Gamma_{mm}^*(R), \quad (8.79)$$

which yields at least one nonzero CGC for the σ Irrep, apart from a phase factor. Further application of (8.73) will produce the remaining CGCs, including their phase relative to the initial CGC.

Example 8.17

We consider here the Kronecker product ${}^{(3\otimes 3)}\Gamma$ of the two-dimensional Irrep ${}^{(3)}\Gamma$ of $\mathcal{C}_{3v}$:

$${}^{(3\otimes 3)}\Gamma = {}^{(1)}\Gamma \oplus {}^{(2)}\Gamma \oplus {}^{(3)}\Gamma.$$

We start with ${}^{(1)}\Gamma$, $d_1 = 1$, and using (8.79) we find

$$\begin{aligned} \left| \left(\begin{array}{c|c} 33 & 1 \\ 11 & 1 \end{array} \right) \right|^2 &= \left| \left(\begin{array}{c|c} 33 & 1 \\ 22 & 1 \end{array} \right) \right|^2 \\ &= \frac{1}{6} \left[1 + 1 + \frac{1}{4} + \frac{1}{4} + \frac{1}{4} + \frac{1}{4} \right] = \frac{1}{2}, \\ \left(\begin{array}{c|c} 33 & 1 \\ 11 & 1 \end{array} \right) \left(\begin{array}{c|c} 1 & 33 \\ 1 & 22 \end{array} \right) &= \frac{1}{6} \sum_R {}^{(3)}\Gamma_{12}^2(R) \\ &= \frac{1}{6} \left[0 + 0 + \frac{3}{4} + \frac{3}{4} + \frac{3}{4} + \frac{3}{4} \right] = \frac{1}{2}, \\ \left(\begin{array}{c|c} 33 & 1 \\ 11 & 1 \end{array} \right) \left(\begin{array}{c|c} 1 & 33 \\ 1 & 12 \end{array} \right) &= \frac{1}{6} \sum_R {}^{(3)}\Gamma_{11}^{(3)}\Gamma_{12}(R) \\ &= \frac{1}{6} \left[0 + 0 + \frac{\sqrt{3}}{4} - \frac{\sqrt{3}}{4} + \frac{\sqrt{3}}{4} - \frac{\sqrt{3}}{4} \right] = 0 \\ &= \left(\begin{array}{c|c} 33 & 1 \\ 11 & 1 \end{array} \right) \left(\begin{array}{c|c} 1 & 33 \\ 1 & 21 \end{array} \right). \end{aligned}$$

We find that the relative phases are all zero and that

$$\left(\begin{array}{c|c} 33 & 1 \\ 11 & 1 \end{array} \right) = \left(\begin{array}{c|c} 33 & 1 \\ 22 & 1 \end{array} \right) = 1/\sqrt{2},$$

and

$$\left(\begin{array}{c|c} 33 & 1 \\ 12 & 1 \end{array} \right) = \left(\begin{array}{c|c} 33 & 1 \\ 21 & 1 \end{array} \right) = 0.$$

Carrying out similar procedures for the remaining Irreps in the CG series, we obtain

$$\begin{aligned} \left(\begin{array}{c|c} 33 & 1 \\ ik & 1 \end{array} \right) &= \frac{1}{\sqrt{2}} \left(\begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array} \right), & \left(\begin{array}{c|c} 33 & 2 \\ ik & 1 \end{array} \right) &= \frac{1}{\sqrt{2}} \left(\begin{array}{cc} 0 & 1 \\ -1 & 0 \end{array} \right), \\ \left(\begin{array}{c|c} 33 & 3 \\ ik & 1 \end{array} \right) &= \frac{1}{\sqrt{2}} \left(\begin{array}{cc} 0 & 1 \\ 1 & 0 \end{array} \right), & \left(\begin{array}{c|c} 33 & 3 \\ ik & 2 \end{array} \right) &= \frac{1}{\sqrt{2}} \left(\begin{array}{cc} 1 & 0 \\ 0 & -1 \end{array} \right). \end{aligned}$$

Where the matrix forms on the r.h.s of each entry imply that if ψ_1, ψ_2 and ϕ_1, ϕ_2 are two independent basis functions belonging to $^{(3)}\Gamma$, then the basis function for, say, $^{(1)}\Gamma$ is given by

$$^{(1)}\Psi = \begin{bmatrix} \phi_1 & \phi_2 \end{bmatrix} \begin{pmatrix} 1/\sqrt{2} & 0 \\ 0 & 1/\sqrt{2} \end{pmatrix} \begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix},$$

and we obtain for $^{(3\otimes 3)}\Gamma$

$$^{(1)}\Psi = \frac{1}{\sqrt{2}}(\psi_1\phi_1 + \psi_2\phi_2), \quad ^{(2)}\Psi = \frac{1}{\sqrt{2}}(\psi_1\phi_2 - \psi_2\phi_1),$$

$$^{(3)}\Psi_1 = \frac{1}{\sqrt{2}}(\psi_1\phi_2 + \psi_2\phi_1), \quad ^{(3)}\Psi_2 = \frac{1}{\sqrt{2}}(\psi_1\phi_1 - \psi_2\phi_2),$$

apart from phase factors.

Example 8.18

CGCs for the Kronecker product $^{(5\otimes 5)}\Gamma$ of the two-dimensional Irrep $^{(5)}\Gamma$ of $\mathcal{D}_4$

The CG series

$$^{(5\otimes 5)}\Gamma = ^{(1)}\Gamma \oplus ^{(2)}\Gamma \oplus ^{(3)}\Gamma \oplus ^{(4)}\Gamma$$

comprises one-dimensional Irreps only. In order to expedite the derivation of the CGCs, we provide a list of matrices for Irrep $^{(5)}\Gamma$:

$$\begin{aligned} {}^{(5)}\Gamma(E) &= \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}, & {}^{(5)}\Gamma(C_{2x}) &= \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \\ {}^{(5)}\Gamma(C_{2y}) &= \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix}, & {}^{(5)}\Gamma(C_{2z}) &= \begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix}, \\ {}^{(5)}\Gamma(C_{4z}) &= \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix}, & {}^{(5)}\Gamma(C_{4z}^{-1}) &= \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix}, \\ {}^{(5)}\Gamma(C_{2xy}) &= \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, & {}^{(5)}\Gamma(C_{2\bar{x}\bar{y}}) &= \begin{bmatrix} 0 & -1 \\ -1 & 0 \end{bmatrix}. \end{aligned}$$

Following the procedure and notation of the previous example, we obtain

$$\begin{aligned} \left(\begin{array}{c|c} 55 & 1 \\ ik & 1 \end{array} \right) &= \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, & \left(\begin{array}{c|c} 55 & 2 \\ ik & 1 \end{array} \right) &= \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \\ \left(\begin{array}{c|c} 55 & 3 \\ ik & 1 \end{array} \right) &= \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}, & \left(\begin{array}{c|c} 55 & 4 \\ ik & 1 \end{array} \right) &= \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}. \end{aligned}$$

8.7 Computer codes

We assume that the codes for generating the multiplication table `m[[i,j]]` and the inverse elements `INL` have been written as shown in Chapter 2.

1. Generation of subgroups

```
Print["Divisors of the Group-Order = ",
      MatrixForm[ordfact=Divisors[g]]]
Print["Number of Divisors = ",Len=Length[ordfact]]
Do[t=k;nn=1;While[t!=1,t=m[[k,t]];
nn++;ord[k]=nn,{k,1,g}]
Print[MatrixForm[Array[ord,g]]]
nsub=0
group={}
Do[num[i] = 0, {i, 1, Len}]
```

```

Do[kk = ordfact[[ii]];
  Do[p[i] = 1, {i, 1, g}];
  Do[
    Switch[And[ord[i]==kk,p[i]==1],
      True, nsub++; num[ii]++; t=INL[[i]];
      Do[
        t=m[[i,t]]; Subgroup[nsub,j]=t;
        p[m[[i,t]]]=0; AppendTo[group,t],
        {j,1,ord[i]}
      ];
      Subord[nsub]=kk;
      Print["Subgroup[" , nsub, " of order ",
        in kk, " = ", group]; group={
      ], {i,2,g}
    ];
    Print["Number of Cyclic Subgroups of order ",
      kk, " = ", num[ii], {ii,2,Len}
    ]
  ]
Print["Number of Cyclic Subgroups = ", nsub]
group={}
ks=nsub
Do[
  Do[
    k=o;
    Do[
      Do[
        t=Subgroup[ii,i]; s=Subgroup[jj,j];
        u=m[[t,s]];
        Switch[FreeQ[group,u],
          True, AppendTo[group,u]; k++
        ], {j,1,Subord[jj]}
      ], {i,1,Subord[jj]}
    ]; kk=k;
  ]

```



```

Do[
  u=m[[group[[i]],group[[j]]];
  Switch[FreeQ[group,u],
    True,AppendTo[group,u];k++
    ],{i,1,kk},{j,1,kk}
  ];ls=0;
Switch[And[k≤Ordfact[[Len-1]],k≠0],
  False,ls=1,True,ls=0;
  Do[
    Switch[k==Subord[i],True,
      Do[
        Switch[MemberQ[group,Subgroup[i,1]],
          True,ls=1
          ],{1,2,k}
        ]
      ],{i,1,nsub}
    ];
  Switch[ls==0,
    True,nsub++;
    Do[
      subgroup[nsub,1]=group[[1]],{1,1,k}
    ];
    Subord[nsub]=k;
    Do[Switch[k==ordfact[[il]],
      True,num[il]++],{il,1,Len}];
    Print["Subgroup[" ,nsub,"] of order '
      k," = ",group]
    ];group={};lot={}
    ],{jj,ii+1,ks}
  ],{ii,1,ks-1}
]

```

2. Generation of left and right cosets

```

l1ot={}
r1ot={}
Do[
  Do[
    AppendTo[l1ot,Subgroup[ii,j]];
    AppendTo[r1ot,Subgroup[ii,j]],{j,1,Subord[ii]}
  ];
  nl=1;lcoset[ii,1]=1;rcoset[ii,1]=1;
  Do[
    Switch[FreeQ[l1ot,jj],
      True,nl++;lcoset[ii,nl]=jj;
      Do[
        t=m[[jj,Subgroup[ii,kk]]];
        AppendTo[l1ot,t],{kk,1,Subord[ii]}
      ]
    ],{jj,2,g}
  ];nr=1;
  Do[
    Switch[FreeQ[r1ot,jj],
      True,nr++;rcoset[ii,nr]=jj;
      Do[
        t=m[[jj,Subgroup[ii,kk]]];
        AppendTo[r1ot,t],{kk,1,Subord[ii]}
      ]
    ],{jj,2,g}
  ];l1ot={};r1ot={};
  nlc[ii]=nl;nrc[ii]=nr,{ii,1,nsub}
]
l1ot={}
r1ot={}
Do[
  Print["Left Coset Reps. of Subgroup(",i,"")"]
  Do[AppendTo[l1ot,lcoset[i,j]],{j,1,nlc[i]};

```

```

Print[l1ot];l1ot={};
Do[Print["Right Coset Reps. of Subgroup(",i'")"]
Do[AppendTo[r1ot,rcoset[i,j]],{j,1,nrcos[i]}];
Print[r1ot];r1ot={},{i,1,nsub}
]

```

3. Determination of the normal subgroups

```

Do[nsg[i] = 0, {i, 1, nsub}]
Do[
  Do[
    Switch[lcoset[i,j]==rcoset[i,j],
      False,nsg[i]=1
      ],{j,1,nlcos[i]}
    ],{i,1,nsub}
  ]
Do[
  Switch[nsg[i]==0,True,
    Print["Subgroup(",i,") is Invariant"]
    ],{i,1,nsub}
  ]

```

4. Clebsch–Gordan series

```

Do[CGS[i,j,k] = 0, {i, 1, nc}, {j, 1, nc}, {k, 1, nc}]
Do[
  Do[
    Do[
      CGS[i,j,k]+=chi[[i,1]]*chi[[j,1]]
      *chi[[k,INL[1]]],{1,1,g}
    ];CGS[i,j,k]=CGS[i,j,k]/g,{k,1,nc}
    ],{j,1,nc}
  ],{i,1,nc}
]
flag=1;

```

```

Do[
  Switch[CGS[i,j,k]≤1,False,flag=0],
  {i,1,nc},{j,1,nc},{k,1,nc}
]
Switch[flag==1,True,Print["Group is Simply Reducible"]]

```

5. Computation of Clebsch–Gordan coefficients, CGCs, for product Irreps

```

Do[
  Switch[j==k,True,
    CGC[1,j,k,kk,1,kk]=1;CGC[j,1,k,kk,kk,1]=1,
    False,CGC[1,j,k,kk,1,kk]=0;CGC[j,1,k,kk,kk,1]=0
  ],{j,1,nc},{k,1,nc},{kk,1,dim[k]}
]

```

Check for simple reducibility

```

Do[
  Do[
    Switch[CGS[i,j,k]≠0,True,
      i1=1;j1=0;CGCIN=0;
      Label[Try];j1++;
      Switch[j1>dim[j],True,i1++,j1=1];
      Do[
        CGCIN+=Γ[[i,i1,i1,m]]*Γ[[j,j1,j1,m]]
          *Γ[[k,1,1,INL[m]]],{m,1,g}
      ];CGCIN=dim[k]*CGCIN/g;
      Switch[CGFCIN==0,True,Goto[Try]];
      CGCIN=√CGCIN;
      Do[
        Do[
          CGCP=0;
          Do[
            CGCP+=Γ[[i,i1,i1,m]]

```

```

        *Γ[[j,j1,j1,m]]
        *Γ[[k,1,1,INL[m]]],
        {m,1,g}
        ];CGCP=dim[k]*CGCP/g;
        CGC[i,j,k,kk,ii,jj]=CGCP/CGCIN,
        {jj,1,dim[j]}
        ],{ii,1,dim[i]}
        ],{kk,1,dim[k]}
        ],False,
        Do[CGC[i,j,k,kk,ii,jj]=0,
        {kk,1,dim[k]},{ii,1,dim[i]},
        {jj,1,dim[j]}
        ]
        ],{k,1,nc}
        ],{i,2,nc},{j,i,nc}
    ]

```

8.8 Summary

- We write $\mathcal{H} \subseteq \mathcal{G}$ for $\mathcal{H}$ a subgroup of $\mathcal{G}$.
- The set of its conjugate subgroups, $[\mathcal{H}]_{\mathcal{G}} = \{R\mathcal{G}R^{-1}, R \in \mathcal{G}\}$, is called the conjugacy class of $\mathcal{H}$.
- The sets $R\mathcal{H}$ (or $\mathcal{H}R$) are called left (right) cosets of $\mathcal{H}$ in $\mathcal{G}$. We denote the set of cosets by $\mathcal{G} : \mathcal{H}$ ($\mathcal{H} : \mathcal{G}$).
- When it contains only $\mathcal{H}$, then $\mathcal{H} \equiv \mathcal{N}$ is an invariant subgroup of $\mathcal{G}$, namely $\mathcal{N} \triangleleft \mathcal{G}$.
- In the case of an invariant subgroup $\mathcal{N}$,

$$R\mathcal{N} = \mathcal{N}R, \quad \forall R \in \mathcal{G}.$$

There also exists a natural group law on $\mathcal{G} : \mathcal{N}$; this group is called the *quotient group* and is denoted by $\mathcal{G}/\mathcal{N}$.

- When a group $\mathcal{G}$ acts on a set of objects M , we denote by $\mathcal{G} \cdot M = \{R \cdot m, \forall R \in \mathcal{G}\}$ the *orbit* of m , i.e. the set of objects into which m is transformed.
- The set $R \cdot m = m$, $R \in \mathcal{G}$, is called the *stabilizer* of m , which is a subgroup of $\mathcal{G}$. It is usually called the little-group of m .
- The stabilizers of an orbit form the conjugacy class $[\mathcal{G}_m]_{\mathcal{G}}$.
- Two orbits with the same conjugacy class of subgroups belong to the same *orbit type*.
- A *stratum* is the union of orbits of the same type. Equivalently, two elements of M belong to the same stratum if, and only if, their stabilizers are conjugate in $\mathcal{G}$.

- The set of orbits that results from the action of $\mathcal{G}$ on M is denoted by $M|\mathcal{G}$, and the set of strata by $M||\mathcal{G}$.
- When we consider the inner automorphism of $\mathcal{G}$, which we may identify as the conjugation $RHR^{-1} = R \cdot H$, we find that the stabilizer $\mathcal{G}_H$ is the set of elements that commute with H . This set is a subgroup of $\mathcal{G}$, called the *centralizer* of H ; it is denoted by $C_{\mathcal{G}}(H)$. Moreover, the corresponding orbit $\mathcal{G} \cdot H$ is just the conjugacy class of H .
- The centralizer of the subgroup $\mathcal{H}$ is the set $RHR^{-1} = \mathcal{H}$, $R \in \mathcal{G}$. It is a subgroup called the *normalizer* of $\mathcal{H}$, and denoted by $\mathcal{N}_{\mathcal{G}}(\mathcal{H})$; it is the largest subgroup of $\mathcal{G}$ which contains $\mathcal{H}$ as an invariant subgroup. The orbit is the conjugacy class $[\mathcal{H}]_{\mathcal{G}}$ of $\mathcal{H}$ in $\mathcal{G}$. The orbit space is the set of conjugacy classes of subgroups, it is a partially ordered set.

Exercises

- 8.1 Show that if $\mathcal{H}_2 \subset \mathcal{H}_1 \subset \mathcal{G}$, and $\mathcal{H}_2 \triangleleft \mathcal{G}$ is an invariant subgroup of $\mathcal{G}$, then it is also an invariant subgroup of $\mathcal{H}_2$, i.e. $\mathcal{H}_2 \triangleleft \mathcal{H}_1$. If $\mathcal{H}_1$ is the largest invariant subgroup of $\mathcal{G}$, i.e. maximal in $\mathcal{G}$, it is called the **normalizer** of $\mathcal{H}_2$ in $\mathcal{G}$.
- 8.2 Show that the converse of Exercise 8.1 does not necessarily hold, and give an example where it is not true.
- 8.3 Prove that the number of pairs of inequivalent conjugate Irreps of a finite group is equal to the number of pairs of reciprocal classes.
- 8.4 Determine the subgroups of $\mathcal{D}_4$, and identify the invariant ones. Derive the factor groups of its invariant subgroups.
- 8.5 Determine the subgroups of the symmetric group $\mathcal{S}_4$, and identify the invariant subgroups among them. Derive the corresponding factor groups.
- 8.6 Construct the character table of $\mathcal{D}_{4h}$ from that of $\mathcal{D}_4$.
- 8.7 Generalize the previous problem for the point-groups $\mathcal{D}_{nh}$ and $\mathcal{C}_{nh}$.

8.8 Subduction of representations

Consider the vector Irrep of $\mathcal{O}(3)$, namely $^{(j=1)}\Gamma^-$.

- (i) Now select among the infinitely uncountable set of operators those that correspond to $\mathcal{C}_{4v}$, which comprise four- and two-fold rotations about the z -axis, the two reflection planes xz and yz , and the two vertical diagonal reflection planes intersecting with the xy -plane through the lines $x = y$ and $x = -y$, respectively.
- (ii) Show that this set of matrices forms a group isomorphic to $\mathcal{C}_{4v}$, i.e. they form a faithful representation of $\mathcal{C}_{4v}$.
- (iii) Decompose this representation in terms of the Irreps of $\mathcal{C}_{4v}$, and obtain the corresponding reduction coefficients $\left\langle ^{(j=1)}\Gamma^- \mid ^{(i)}\Gamma \right\rangle$.

This procedure is known as *subduction*, and will be discussed in the following chapter.

8.9 Symmetrization of a second-rank tensor

Consider a second-rank tensor associated with a three-dimensional system with $\mathcal{C}_{4v}$ symmetry. Use the fact that the $\mathcal{O}(3)$ Irrep of the tensor is given by $^{(j=1)}\Gamma^- \otimes ^{(j=1)}\Gamma^-$, and obtain its CG series in terms of the Irreps of $\mathcal{C}_{4v}$.

- 8.10 What would be the outcome of the second-rank tensor symmetrization had the symmetry of the system been $\mathcal{D}_4$ rather than $\mathcal{C}_{4v}$?

- 8.11 Repeat the symmetrization of the second-rank tensor if the symmetry of the system is $\mathcal{C}_{3v}$.
- 8.12 Consider the tetrahedral point-group $23(T)$, which contains 4-axis 3-fold operations $\{C_3^i, C_3^{-1,i}\}$, $i = 1-4$, and three 2-fold axes U^i bisecting opposite edges of the tetrahedron.
- (i) Show that it has one invariant subgroup, and determine the corresponding factor group.
 - (ii) Show that $23(T)$ can be constructed from the outer-product of the invariant subgroup with its factor group.
 - (iii) Construct its character table with the help of the above results.
- 8.13 Consider the self-direct-product of the three-dimensional Irrep T of $23(T)$, with generators

$$C_3^{xyz} = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}; \quad C_2^z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 0 & 1 \end{pmatrix}.$$

- (i) Determine the CG series.
 - (ii) Determine the CGCs.
- 8.14 Derive the steps that lead to CGCs given in Example 8.17 for the Irreps $^{(2)}\Gamma$ and $^{(3)}\Gamma$ of $\mathcal{C}_{3v}$.
- 8.15 Derive the results given in Example 8.18 for the CGCs $\left(\begin{array}{c|c} 55 & \sigma \\ ik & 1 \end{array} \right)$, $\sigma = 1, 2, 3, 4$, of $\mathcal{C}_{4v}$.

9

Induced representations

9.1 Introduction

In Chapters 2–7, we developed all the machinery necessary to generate Irreps of finite groups. We have yet to deal with the more difficult topic of infinite space-groups, where it is necessary to determine the Irreps by the process of induction, which provides a recipe for the construction of a Rep of a group $\mathcal{G}$ from a Rep of one of its subgroups $\mathcal{H}$.

In the previous chapter, we presented the concepts of subgroups, cosets, conjugate subgroups, and invariant, or normal, subgroups. Here we add to these the ideas of *inducing and subducing* Reps between a group and one of its subgroups. Then, by focusing on the case of invariant, or self-conjugate, subgroups $\mathcal{N} \triangleleft \mathcal{G}$, we introduce the concepts of conjugate Irreps, little-groups. With these tools in hand, we next develop a road map for inducing Irreps of $\mathcal{G}$. This is supported by a set of theorems, presented in the Appendix, that establish the basis for the process of inducing Irreps of $\mathcal{G}$ from Irreps of $\mathcal{N}$ and its associated little-groups. Finally, we outline the procedures for *inducing an Irrep of $\mathcal{G}$ from the Irreps of $\mathcal{N}$* , and give detailed examples to illustrate their application. For the sake of clarity, we base our discussion on point-groups, since, by now, they are quite familiar. For pedagogical reasons, we start with a brief discussion of the idea of *subduction of Reps or Irreps of a subgroup from the Irreps of its group*.

9.2 Subduced Reps and compatibility relations

Although our primary interest is in *induced* Reps, it is instructive to begin with a brief discussion of *subduced* Reps, which play an important role in establishing the validity of the Irrep induction process.

A subduced Rep of a subgroup, $\mathcal{H} \subset \mathcal{G}$ of order h , is one that is obtained by selecting from an Irrep $^{(\mu)}\mathbf{\Gamma}$ of the full group, $\mathcal{G}$, only those matrices that represent the elements $H \in \mathcal{H}$.

The subduced Rep, generally denoted by $^{(\mu)}\mathbf{\Gamma} \downarrow \mathcal{H}$, need not be one of the Irreps $^{(\sigma)}\mathbf{\Sigma}$ of $\mathcal{H}$. According to (4.38), we can expand $^{(\mu)}\mathbf{\Gamma} \downarrow \mathcal{H}$ in the form

$$^{(\mu)}\mathbf{\Gamma} \downarrow \mathcal{H} = \sum_{\sigma}^{\oplus} \left\langle ^{(\mu)}\mathbf{\Gamma} \downarrow \mathcal{H} \left| ^{(\sigma)}\mathbf{\Sigma} \right. \right\rangle ^{(\sigma)}\mathbf{\Sigma}, \quad (9.1)$$

where $\left\langle \left. {}^{(\mu)}\mathbf{\Gamma} \downarrow \mathcal{H} \right| {}^{(\sigma)}\mathbf{\Sigma} \right\rangle$ is the frequency of occurrence of ${}^{(\sigma)}\mathbf{\Sigma}$ in ${}^{(\mu)}\mathbf{\Gamma} \downarrow \mathcal{H}$, which is given, using (4.39), by

$$\left\langle \left. {}^{(\mu)}\mathbf{\Gamma} \downarrow \mathcal{H} \right| {}^{(\sigma)}\mathbf{\Sigma} \right\rangle = \frac{1}{h} \sum_{H \in \mathcal{H}} {}^{(\mu)}\chi(H) {}^{(\sigma)}\chi^*(H). \quad (9.2)$$

We use the label ${}^{(\sigma)}\mathbf{\Sigma}$ for Irreps of general subgroups $\mathcal{H}$, but reserve the label ${}^{(\alpha)}\mathbf{\Delta}$ for Irreps of normal subgroups $\mathcal{N}$.

Example 9.1

In the case of $\mathcal{C}_{3v}$, we obtain subduced Reps for the normal subgroup $\mathcal{C}_3$ by selecting the matrix representatives for $\widehat{E}$, $\widehat{C}_3^+$ and $\widehat{C}_3^-$ from the Irreps of $\mathcal{C}_{3v}$ listed in Table 9.1.

By direct inspection of Table 9.1, we find that subduction from ${}^{(1)}\mathbf{\Gamma}$ or ${}^{(2)}\mathbf{\Gamma}$ gives just one subduced Rep for $\mathcal{C}_3$, which we label ${}^{(1)}\mathbf{\Delta}$:

$$\begin{aligned} \left({}^{(1)}\mathbf{\Gamma} \downarrow \mathcal{C}_3 \right) (\widehat{E}) &= \left({}^{(2)}\mathbf{\Gamma} \downarrow \mathcal{C}_3 \right) (\widehat{E}) = {}^{(1)}\mathbf{\Delta}(\widehat{E}) = 1, \\ \left({}^{(1)}\mathbf{\Gamma} \downarrow \mathcal{C}_3 \right) (\widehat{C}_3^+) &= \left({}^{(2)}\mathbf{\Gamma} \downarrow \mathcal{C}_3 \right) (\widehat{C}_3^+) = {}^{(1)}\mathbf{\Delta}(\widehat{C}_3^+) = 1, \\ \left({}^{(1)}\mathbf{\Gamma} \downarrow \mathcal{C}_3 \right) (\widehat{C}_3^-) &= \left({}^{(2)}\mathbf{\Gamma} \downarrow \mathcal{C}_3 \right) (\widehat{C}_3^-) = {}^{(1)}\mathbf{\Delta}(\widehat{C}_3^-) = 1. \end{aligned}$$

Subduction from ${}^{(3)}\mathbf{\Gamma}$ gives us a Rep for $\mathcal{C}_3$:

$${}^{(3)}\mathbf{\Gamma} \downarrow \mathcal{C}_3(\widehat{E}) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad {}^{(3)}\mathbf{\Gamma} \downarrow \mathcal{C}_3(\widehat{C}_3^+) = \begin{pmatrix} \omega & 0 \\ 0 & \omega^* \end{pmatrix}, \quad {}^{(3)}\mathbf{\Gamma} \downarrow \mathcal{C}_3(\widehat{C}_3^-) = \begin{pmatrix} \omega^* & 0 \\ 0 & \omega \end{pmatrix}.$$

We know there are exactly three one-dimensional Irreps for $\mathcal{C}_3$, and since we have subduced two Reps from *all* the Irreps of $\mathcal{C}_{3v}$, we find that $\left({}^{(3)}\mathbf{\Gamma} \downarrow \mathcal{C}_3 \right)$ must be reducible. Indeed,

Table 9.1. *The Irreps of $\mathcal{C}_{3v}$.*

	$\widehat{E}$	$\widehat{C}_3^+$	$\widehat{C}_3^-$	$\widehat{\sigma}_1$	$\widehat{\sigma}_2$	$\widehat{\sigma}_3$
${}^{(1)}\mathbf{\Gamma}$	1	1	1	1	1	1
${}^{(2)}\mathbf{\Gamma}$	1	1	1	-1	-1	-1
${}^{(3)}\mathbf{\Gamma}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} \omega & 0 \\ 0 & \omega^* \end{pmatrix}$	$\begin{pmatrix} \omega^* & 0 \\ 0 & \omega \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & \omega^* \\ \omega & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & \omega \\ \omega^* & 0 \end{pmatrix}$

it is already diagonalized, so we obtain two Irreps from $\left({}^{(3)}\Gamma \downarrow \mathcal{C}_3\right)$, one Irrep from the set of matrix elements ${}^{(2)}\Delta = \left({}^{(3)}\Gamma \downarrow \mathcal{C}_3\right)_{11}$ and one Irrep from the set of matrix elements ${}^{(3)}\Delta = \left({}^{(3)}\Gamma \downarrow \mathcal{C}_3\right)_{22}$. Together with the Irrep ${}^{(1)}\Delta$, these give us the three Irreps for $\mathcal{C}_3$, listed in Table 9.2. We denote the subduced Irreps by Δ to conform with the convention we shall use for Irreps of normal subgroups in the remainder of this chapter.

Table 9.2. The Irreps of $\mathcal{C}_3$.

Irrep	$\hat{E}$	$\hat{C}_3^+$	$\hat{C}_3^-$
${}^{(1)}\Delta = {}^{(1)}\Gamma \downarrow \mathcal{H} = {}^{(2)}\Gamma \downarrow \mathcal{H}$	1	1	1
${}^{(2)}\Delta = \left({}^{(3)}\Gamma \downarrow \mathcal{H}\right)_{11}$	1	ω	ω^*
${}^{(3)}\Delta = \left({}^{(3)}\Gamma \downarrow \mathcal{H}\right)_{22}$	1	ω^*	ω

What we want to be able to do is carry out the inverse of this process by inducing, for example, an Irrep of $\mathcal{C}_{3v}$ from an Irrep of $\mathcal{C}_3$. Of course, for point-groups, we already know how to obtain all the Irreps, but we need to know how to obtain Irreps for space-groups. In that case, we cannot generate Irreps as we have done for point-groups. We must induce them.

9.3 Induction of group Reps from the Irreps of its subgroups

As we mentioned in the introduction, Reps of a group can be induced from Irreps of its subgroups [12, 13, 14, 15, 16, 22]. In this section we introduce new terms and definitions, develop necessary concepts, and discuss their application with the aid of examples. We also present a systematic procedure to generate induced representative matrices that is amenable to computer applications. It is based on the construction of a matrix Rep, coined the *ground Rep* by Altmann [12], which may be considered as a generalization of the regular Rep. It serves as the bridge for inducing a Rep of the full group from an Irrep of the subgroup.

9.3.1 Inducing group Reps from Irreps of subgroups

Consider a set of conjugate subgroups $\mathcal{H}^{(i)} \subset \mathcal{G}$. Let ${}^{(\sigma)}\Sigma$ be an Irrep of subgroup $\mathcal{H}^{(1)}$, with basis functions ${}^{(\sigma)}\phi_k^{\{1\}}$ that span a linear space $\mathcal{S}^{(1)}$ of dimension d_σ , such that an

operator $H1 \in \mathcal{H}^{(1)}$, gives

$$H1 {}^{(\sigma)}\phi_k^{\{1\}} = \sum_l {}^{(\sigma)}\phi_l^{\{1\}} {}^{(\sigma)}\Sigma_{ji}(H1),$$

or, $H1 \mathcal{S}^{(1)} = \mathcal{S}^{(1)}$, spanning the same space as before.

However, if we operate on the basis set ${}^{(\sigma)}\phi_k^{\{1\}}$ with an operator that is not an element of the subgroup $\mathcal{H}^{(1)}$, namely, a coset representative $R_2 \notin \mathcal{H}^{(1)}$, it does not produce a linear combination of the basis functions ${}^{(\sigma)}\phi_k^{\{1\}}$. It generates, instead, a *new* set of basis functions ${}^{(\sigma)}\phi_k^{\{2\}}$,

$$R_2 {}^{(\sigma)}\phi_k^{\{1\}} = {}^{(\sigma)}\phi_k^{\{2\}}, \quad 1 \leq k \leq d_\sigma, \quad (9.3)$$

which spans the *new* linear space $\mathcal{S}^{(2)}$.

Example 9.2

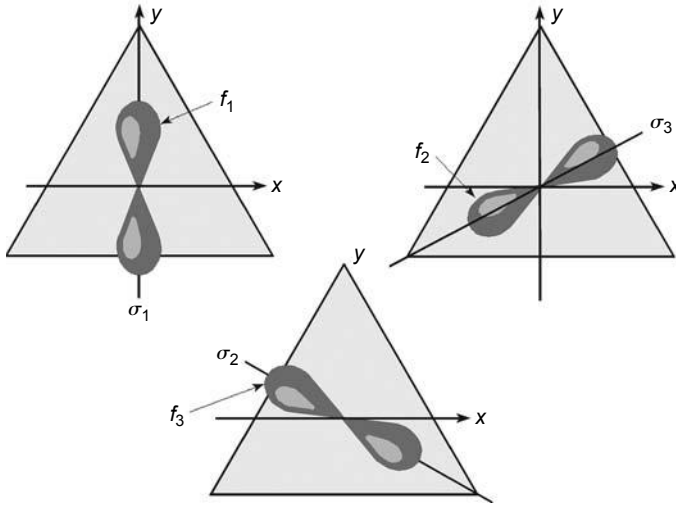


Fig. 9.1. p-orbital bases for the three conjugate subgroups $\{E, \sigma_i\}$.

Suppose we take an atomic p_y -orbital as a basis function f_1 belonging to the linear space $\mathcal{S}^{(1)}$ of an Irrep ${}^{(+)}\Gamma$ of $\mathcal{H} = \{E, \sigma_1\} \subset C_{3v}$. From Section 3.1.2 we know that operating on this p_y -orbital with the coset representatives $\hat{C}_3^+$ and $\hat{C}_3^-$ generates new basis functions as follows:

$$\begin{aligned} \hat{C}_3^+ p_y &= \frac{\sqrt{3}}{2} p_x - \frac{1}{2} p_y \equiv f_2, & \mathcal{H}^{\{2\}} &= C_3^+ \{E, \sigma_1\} C_3^- = \{E, \sigma_3\}, \\ \hat{C}_3^- p_y &= -\frac{\sqrt{3}}{2} p_x - \frac{1}{2} p_y \equiv f_3, & \mathcal{H}^{\{3\}} &= C_3^- \{E, \sigma_1\} C_3^+ = \{E, \sigma_2\}. \end{aligned}$$

The first of these new functions belongs to the space $\mathcal{S}^{(2)}$ and the second belongs to $\mathcal{S}^{(3)}$.

From Figure 9.1, or by inspection, we find that f_2 and f_3 are bases of $^{(+)}\Gamma$, for $\mathcal{H}^{\{2\}}$ and $\mathcal{H}^{\{3\}}$, respectively.

It is now possible to show that the space $\mathcal{S}^{(2)}$, defined in (9.3), is closed with respect to operations by elements of the conjugate subgroup $\mathcal{H}^{(2)} = \mathbf{R}_2 \mathcal{H}^{(1)} \mathbf{R}_2^{-1}$; for if we let $H2 = \mathbf{R}_2 H1 \mathbf{R}_2^{-1} \in \mathcal{H}^{(2)}$, then

$$\begin{aligned} H2 {}^{(\sigma)}\phi_k^{\{2\}} &= \mathbf{R}_2 H1 \mathbf{R}_2^{-1} \mathbf{R}_2 {}^{(\sigma)}\phi_k^{\{1\}} = \mathbf{R}_2 H1 {}^{(\sigma)}\phi_k^{\{1\}} \\ &= \sum_l \mathbf{R}_2 {}^{(\sigma)}\phi_l^{\{1\}} {}^{(\sigma)}\Sigma_{lk}(H1) = \sum_l {}^{(\sigma)}\phi_l^{\{2\}} {}^{(\sigma)}\Sigma_{lk}(H1) \\ &= \sum_l {}^{(\sigma)}\phi_l^{\{2\}} {}^{(\sigma)}\Sigma_{lk}(H2). \end{aligned}$$

We find that the Irrep ${}^{(\sigma)}\Sigma$ of $\mathcal{H}^{(1)}$ is also an Irrep of its conjugate subgroup $\mathcal{H}^{(2)}$ according to the mapping $H2 = \mathbf{R}_2 H1 \mathbf{R}_2^{-1}$.

In general, operating on the basis set ${}^{(\sigma)}\phi_k^{\{1\}}$ with some coset representative $\mathbf{R}_j \notin \mathcal{H}^{(1)}$, we generate a new basis function set ${}^{(\sigma)}\phi_k^{\{j\}}$,

$$\mathbf{R}_j {}^{(\sigma)}\phi_k^{\{1\}} = {}^{(\sigma)}\phi_k^{\{j\}}, \quad (9.4)$$

that spans a new linear space which we label $\mathcal{S}^{(j)}$. That is, $\mathcal{S}^{(1)}$ is mapped onto $\mathcal{S}^{(j)}$:

$$\mathbf{R}_j \mathcal{S}^{(1)} = \mathcal{S}^{(j)} \quad \text{and} \quad \mathbf{R}_j^{-1} \mathcal{S}^{(j)} = \mathcal{S}^{(1)}. \quad (9.5)$$

Operating with *all* the coset representatives on the set of basis vectors ${}^{(\sigma)}\phi_k^{\{1\}}$ will generate new sets of independent functions $\{\mathbf{R}_j {}^{(\sigma)}\phi_k^{\{1\}}\}$ that, altogether, span a linear space that is invariant under the set of operators $R \in \mathcal{G}$. From (8.6) we write $R = \mathbf{R}_j H1 \mathbf{R}_k^{-1}$, and we get, using (9.5),

$$\begin{aligned} R \mathcal{S}^{(k)} &= \mathbf{R}_j H1 \mathbf{R}_k^{-1} \mathcal{S}^{(k)} = \mathbf{R}_j H1 \mathcal{S}^{(1)} \\ &= \mathbf{R}_j \mathcal{S}^{(1)} = \mathcal{S}^{(j)}, \end{aligned} \quad (9.6)$$

where, in the last line, we used $H1 \mathcal{S}^{(1)} = \mathcal{S}^{(1)}$ since $\mathcal{S}^{(1)}$ is an invariant subspace of elements $H1$ of $\mathcal{H}^{(1)}$.

Example 9.3

Continuing from Example 9.2, we have $\mathcal{S}^{(1)}$, $\mathcal{S}^{(2)}$, and $\mathcal{S}^{(3)}$ as the linear spaces spanned by the basis functions f_1, f_2 , and f_3 , respectively. Now, for illustration purposes, let $R = C_3^-$, $R^1 = E$, $j = 2$, $k = 3$. Of course, we could not have made these choices arbitrarily. They are subject to the constraints of (8.6), which are satisfied in this case. Thus

$$\begin{aligned} \mathbf{R}_j &= \mathbf{R}_2 = C_3^+, \\ \mathbf{R}_k &= \mathbf{R}_3 = C_3^-, \\ \mathbf{R}_k^{-1} &= \mathbf{R}_3^{-1} = C_3^+. \end{aligned}$$

For this example, (9.6) becomes

$$\begin{aligned} C_3^- \mathcal{S}^{(3)} &= C_3^+ E C_3^+ \mathcal{S}^{(3)} = C_3^+ E \mathcal{S}^{(1)} \\ [2pt] &= C_3^+ \mathcal{S}^{(1)} = \mathcal{S}^{(2)}. \end{aligned}$$

Thus $C_3^- \mathcal{S}^{(3)} = \mathcal{S}^{(2)}$. Let us check this by operating with C_3^- on the basis function f_3 belonging to the space $\mathcal{S}^{(3)}$.

$$C_3^- f_3 = C_3^- \left(-\frac{\sqrt{3}}{2} p_x - \frac{1}{2} p_y \right) = -\frac{\sqrt{3}}{2} C_3^- p_x - \frac{1}{2} C_3^- p_y.$$

From the methods of Chapter 3, for function operators, we know that

$$C_3^- p_x = -\frac{1}{2} p_x + \frac{\sqrt{3}}{2} p_y,$$

$$C_3^- p_y = -\frac{\sqrt{3}}{2} p_x - \frac{1}{2} p_y.$$

Thus

$$\begin{aligned} C_3^- f_3 &= -\frac{\sqrt{3}}{2} \left(-\frac{1}{2} p_x + \frac{\sqrt{3}}{2} p_y \right) - \frac{1}{2} \left(-\frac{\sqrt{3}}{2} p_x - \frac{1}{2} p_y \right) \\ &= \frac{\sqrt{3}}{2} p_x - \frac{1}{2} p_y = f_2 \Rightarrow \mathcal{S}^{(2)}. \end{aligned}$$

Each of the linear subspaces $\mathcal{S}^{(1)}, \mathcal{S}^{(2)}, \dots, \mathcal{S}^{(g/h)}$ is a space spanned by the basis functions for one of the cosets. The union of these spaces,

$$\mathcal{S}^{(1)} \cup \mathcal{S}^{(2)} \dots \cup \mathcal{S}^{(j)} \dots \cup \mathcal{S}^{(n_h)},$$

is spanned by the full set of functions ${}^{(\sigma)}\phi_k^{\{1\}}, {}^{(\sigma)}\phi_k^{\{2\}}, \dots, {}^{(\sigma)}\phi_k^{\{g/h\}}$. This full set of functions forms a basis set for an induced Rep,

$${}^{(\text{ind})}\Gamma(R) \equiv {}^{(\sigma)}\Sigma \uparrow \mathcal{G}(R), \quad \forall R \in \mathcal{G},$$

of dimension $(g/h) \cdot d_\sigma$, where d_σ is the dimension of the Irrep ${}^{(\sigma)}\Sigma$.

Notice that we replaced $(\text{ind})\Gamma$ by the symbol $(\sigma)\Sigma \uparrow \mathcal{G}$, since this new label is more informative: it indicates that the corresponding matrices constitute a Rep of $\mathcal{G}$ induced from the Irrep $(\sigma)\Sigma$ of its subgroup $\mathcal{H}$.

This Rep is reducible, in general. A matrix representative of this Rep can be obtained with the aid of a construct called the *ground Rep*, which is reminiscent of the regular Rep and which we will develop in the following subsection.

9.3.2 The ground Rep

Let us consider the general case of a group $\mathcal{G}$, with elements R , and its subgroup $\mathcal{H}$, with elements H , and index g/h . We decompose, or partition, $\mathcal{G}$ into the set of left cosets (LCs) $\{R_{cj}\mathcal{H}\}$ of $\mathcal{H}$:

$$\mathcal{G} = \sum_{j=1}^{g/h} \mathbf{R}_j \mathcal{H}, \quad (9.7)$$

where $\mathbf{R}_j$ are the left coset representatives (LCRs), which provide the connection between the subgroup $\mathcal{H}$ and the larger group $\mathcal{G}$.

Example 9.4

In Example 8.1, we found that the subgroup $\mathcal{H} = \{E, \sigma_1\}$ of the point-group $\mathcal{C}_{3v} = \{E, C_3^+, C_3^-, \sigma_1, \sigma_2, \sigma_3\}$, which is not a normal subgroup, has three distinct left cosets, which can be generated with the coset representatives E , C_3^+ , and C_3^- . Thus we can now decompose the full group $\mathcal{C}_{3v}$ into left cosets as

$$\begin{aligned} \mathcal{C}_{3v} &= E\{E, \sigma_1\} + C_3^+\{E, \sigma_1\} + C_3^-\{E, \sigma_1\} \\ &= \{E, \sigma_1\}, \{C_3^+, \sigma_3\}, \{C_3^-, \sigma_2\}. \end{aligned}$$

When we *left-operate* on a *left-coset* by any element $R \in \mathcal{G}$, we just obtain one of the LCs of $\mathcal{H}$:

$$R\mathbf{R}_j\mathcal{H} = \mathbf{R}_k\mathcal{H}.$$

Hence, *the set of cosets is closed* under operations by group elements; they are simply permuted among themselves.

The set of left cosets forms a closed space under left operations by group elements.

We can then use the LCs, $\{\mathbf{R}_j\mathcal{H}\}$, as a basis to engender a Rep of $\mathcal{G}$ comprising a set of permutation matrices, with matrix elements defined by

$$M_{ij}(R) = \begin{cases} 1, & \text{if } \mathbf{R}_i^{-1} R \mathbf{R}_j = H \quad \text{for some } H \in \mathcal{H} \\ 0, & \text{otherwise,} \end{cases} \quad (9.8)$$

much as we did for the regular Rep. The permutation matrix, $\mathbf{M}(R)$, will have the number 1 exactly once in each row and each column. All other matrix elements will be zero. The set of permutation matrices, $\mathbf{M}(R)$, is called the **ground Rep**.

The choice of LC representatives R_{cj} is not unique but should be chosen such that

$$\mathbf{R}_j \in \mathcal{G}, \quad \mathbf{R}_j \notin \mathcal{H} \quad \text{except for } E, \quad (9.9)$$

and such that the representatives form a subgroup, if possible. We note that:

- (i) *Since a normal subgroup, $\mathcal{N}$ of order n , satisfies the relation $\mathbf{R}_i \mathcal{N} = \mathcal{N} \mathbf{R}_i$, we find that for $N \in \mathcal{N}$, $\mathbf{R}_i^{-1} N \mathbf{R}_i = N' \in \mathcal{N}$, hence, the ground Rep matrices $\mathbf{M}(N)$ are just unit matrices of dimension g/n , i.e.*

$$\mathbf{M}(N) = \mathbb{I} \left(\frac{g}{n} \times \frac{g}{n} \right). \quad (9.10)$$

- (ii) *If the subgroup $\mathcal{H}$ is chosen to be the trivial subgroup given by the identity element E , the ground Rep will be the regular Rep.*

The ground Rep

The set of permutation matrices

$$\mathbf{M}(R), \quad R \in \mathcal{G},$$

relative to the *left*-coset basis set $\{\mathbf{R}_j \mathcal{H}\}$, with matrix elements defined by (9.8), is called a *left ground Rep* of $\mathcal{G}$ by $\mathcal{H}$. $\mathbf{M}(R)$ is a $(g/h) \times (g/h)$ matrix.

Example 9.5

Ground rep of $\mathcal{C}_{3v}$ relative to $\{E, \sigma_1\}$

The subgroup $\mathcal{H} = \{E, \sigma_1\}$ of the point-group $\mathcal{C}_{3v}$ has the three distinct left cosets $\{E, \sigma_1\}, \{\sigma_2, C_3^+\}, \{\sigma_3, C_3^-\}$ with coset representatives E, C_3^+, C_3^- . Let us now operate by an F-operator on the set of basis functions consisting of the three left cosets of $\mathcal{H}$. We express, for example, the operation of $\widehat{C}_3^+$ on a row vector whose components are the

cosets. Then we have

$$\begin{aligned} \widehat{C}_3^+ (\{E, \sigma_1\}, \{C_3^+, \sigma_3\}, \{C_3^-, \sigma_2\}) &= (\{C_3^+, \sigma_3\}, \{C_3^-, \sigma_2\}, \{E, \sigma_1\}) \\ &= (\{E, \sigma_1\}, \{C_3^+, \sigma_3\}, \{C_3^-, \sigma_2\}) \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}, \end{aligned} \quad (9.11)$$

where the matrix is a permutation matrix that represents the function operator $\widehat{C}_3^+$. Proceeding in this fashion we find representatives of all the function operators of $\mathcal{C}_{3v}$ and thus generate a matrix Rep for the group $\mathcal{C}_{3v}$. The Rep will have been generated by operating on the coset basis functions.

A more systematic method, which can be implemented with a computer program, is to construct a set of matrices $\mathbf{M}(R)$ based on (9.8). We now illustrate the method, beginning with $\mathbf{M}(\sigma_1)$, as follows:

$$\begin{aligned} \mathbf{M}(\sigma_1) &\sim \begin{pmatrix} E\sigma_1 E & E\sigma_1 C_3^+ & E\sigma_1 C_3^- \\ C_3^- \sigma_1 E & C_3^- \sigma_1 C_3^+ & C_3^- \sigma_1 C_3^- \\ C_3^+ \sigma_1 E & C_3^+ \sigma_1 C_3^+ & C_3^+ \sigma_1 C_3^- \end{pmatrix} \\ &\sim \begin{pmatrix} \sigma_1 & \sigma_2 \notin \mathcal{H} & \sigma_3 \notin \mathcal{H} \\ \sigma_2 \notin \mathcal{H} & \sigma_3 \notin \mathcal{H} & \sigma_1 \\ \sigma_3 \notin \mathcal{H} & \sigma_1 & \sigma_2 \notin \mathcal{H} \end{pmatrix} \Rightarrow \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \end{aligned}$$

where, in the last step, all elements σ_1 have been replaced by 1 and all other elements have been replaced by 0, in accordance with (9.8). Rows 1, 2, and 3 of $\mathbf{M}(R)$ are labeled by the first operator in the matrix elements, namely, the inverse coset representatives E , C_3^- , and C_3^+ , respectively, in this example; and, columns 1, 2, and 3 are labeled by the last operator in the matrix elements, namely, the coset representatives E , C_3^+ , and C_3^- , respectively.

Now, suppose we wish to determine $\mathbf{M}(\sigma_2)$. We must begin anew by placing σ_2 in the center of the conjugacy relations of (9.8). Thus we get

$$\begin{aligned} \mathbf{M}(\sigma_2) &\sim \begin{pmatrix} E\sigma_2 E & E\sigma_2 C_3^+ & E\sigma_2 C_3^- \\ C_3^- \sigma_2 E & C_3^- \sigma_2 C_3^+ & C_3^- \sigma_2 C_3^- \\ C_3^+ \sigma_2 E & C_3^+ \sigma_2 C_3^+ & C_3^+ \sigma_2 C_3^- \end{pmatrix} \\ &\sim \begin{pmatrix} \sigma_2 \notin \mathcal{H} & \sigma_3 \notin \mathcal{H} & \sigma_1 \\ \sigma_3 \notin \mathcal{H} & \sigma_1 & \sigma_2 \notin \mathcal{H} \\ \sigma_1 & \sigma_2 \notin \mathcal{H} & \sigma_3 \notin \mathcal{H} \end{pmatrix} \Rightarrow \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}. \end{aligned}$$

In this way we find the ground Rep for each element of the group.

A key point For bookkeeping purposes, looking ahead, we often find it more useful to retain the actual subgroup elements H in the final matrix, so that it consists only of terms H or 0, rather than ones and zeroes. This is because we eventually wish to replace these elements by their subgroup Irrep representatives in the process of inducing Irreps of the

larger group. By retaining the actual element, it will be clear what is to replace it. Thus we introduce a *modified* ground representative given by

$$\mathbf{M}^*(\sigma_2) = \begin{pmatrix} 0 & 0 & \sigma_1 \\ 0 & \sigma_1 & 0 \\ \sigma_1 & 0 & 0 \end{pmatrix},$$

In the more general case, as we will find in Chapter 13, such a matrix might contain several different elements $H \in \mathcal{H}$. In the process of inducing a Rep, we would then replace each of these elements by their corresponding Irrep representatives.

The modified ground Rep

The set of matrices with matrix elements defined by

$$M_{ij}^*(R) = \begin{cases} H & \text{if } \mathbf{R}_i^{-1} R \mathbf{R}_j = H, \\ 0, & \text{otherwise,} \end{cases} \quad H \in \mathcal{H}, \quad (9.12)$$

is called the *modified* ground Rep of $\mathcal{G}$ by $\mathcal{H}$.

The modified ground Rep for the elements of a normal subgroup can be expressed, according to (9.12) as the direct sum

$$\mathbf{M}^*(N) = \sum_{i=1}^{g/n} \oplus \mathbf{R}_i^{-1} N \mathbf{R}_i = \sum_{i=1}^{g/n} \oplus N_i, \quad (9.13)$$

where $N_i = \mathbf{R}_i^{-1} N \mathbf{R}_i$.

Example 9.6

Ground Rep of $\mathcal{C}_{3v}$ with respect to $\mathcal{C}_3$

Following this procedure, we obtain the set of matrices that constitute the left ground Rep of $\mathcal{C}_{3v}$ relative to $\mathcal{C}_3$, as well as the corresponding modified left ground Rep. We find:

$$\begin{aligned} \mathbf{M}(E) &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, & \mathbf{M}^*(E) &= \begin{pmatrix} \hat{E} & 0 & 0 \\ 0 & \hat{E} & 0 \\ 0 & 0 & \hat{E} \end{pmatrix}, \\ \mathbf{M}(C_3^+) &= \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}, & \mathbf{M}^*(C_3^+) &= \begin{pmatrix} 0 & 0 & \hat{E} \\ \hat{E} & 0 & 0 \\ 0 & \hat{E} & 0 \end{pmatrix}, \\ \mathbf{M}(C_3^-) &= \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}, & \mathbf{M}^*(C_3^-) &= \begin{pmatrix} 0 & \hat{E} & 0 \\ 0 & 0 & \hat{E} \\ \hat{E} & 0 & 0 \end{pmatrix}, \end{aligned}$$

$$\begin{aligned}
\mathbf{M}(\sigma_1) &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, & \mathbf{M}^*(\sigma_1) &= \begin{pmatrix} \hat{\sigma}_1 & 0 & 0 \\ 0 & 0 & \hat{\sigma}_1 \\ 0 & \hat{\sigma}_1 & 0 \end{pmatrix}, \\
\mathbf{M}(\sigma_2) &= \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}, & \mathbf{M}^*(\sigma_2) &= \begin{pmatrix} 0 & 0 & \hat{\sigma}_1 \\ 0 & \hat{\sigma}_1 & 0 \\ \hat{\sigma}_1 & 0 & 0 \end{pmatrix}, \\
\mathbf{M}(\sigma_3) &= \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}, & \mathbf{M}^*(\sigma_3) &= \begin{pmatrix} 0 & \hat{\sigma}_1 & 0 \\ \hat{\sigma}_1 & 0 & 0 \\ 0 & 0 & \hat{\sigma}_1 \end{pmatrix}.
\end{aligned} \tag{9.14}$$

Each set of six matrices given by (9.14) is a faithful, but reducible, Rep of the point-group $\mathcal{C}_{3v}$. The matrices $\mathbf{M}(R_i)$ are isomorphic to the elements R_i of the corresponding multiplication table, Table 2.2. They constitute the left ground Rep of $\mathcal{C}_{3v}$ by $\{E, \sigma_1\}$.

Clearly, if the set of modified ground Rep matrices $\mathbf{M}^*$ obeys the multiplication table for the group $\mathcal{G}$, then the matrices obtained by replacing the subgroup elements in $\mathbf{M}^*$ by their subgroup matrix representatives will also be a Rep of the group $\mathcal{G}$. These supermatrices, whose elements are themselves matrices, constitute an induced Rep of $\mathcal{G}$ through $\mathcal{H}$.

Now we are at a position to write the matrix Rep ${}^{(\text{ind})}\mathbf{\Gamma}(R)$, induced from ${}^{(\sigma)}\mathbf{\Sigma}$, as

$${}^{(\text{ind})}\mathbf{\Gamma}(R) \equiv {}^{(\sigma)}\mathbf{\Sigma} \uparrow \mathcal{G}(R) = \mathbf{M}(R) \otimes {}^{(\sigma)}\mathbf{\Sigma}(H), \tag{9.15}$$

where the *meaning* of the equation is that the blocks ${}^{(\sigma)}\mathbf{\Sigma}(H)$ occur exactly once in every row and every column, where they *replace* the corresponding nonzero elements of $\mathbf{M}(R)$, namely H , which also appear exactly once in every row and every column.

A key point Equation (9.15) is deceptive. One does *not multiply* the two matrices. One *replaces* the subgroup elements $\hat{H}$ in the matrix $\mathbf{M}^*$ with the corresponding matrix representatives of ${}^{(\sigma)}\mathbf{\Sigma}(H)$.

The utility of the modified ground Rep is now clear. We know exactly where to put the blocks ${}^{(\sigma)}\mathbf{\Sigma}(H)$. They replace the corresponding elements $\hat{H}$ that occur in $\mathbf{M}^*(R)$.

Example 9.7

Consider the case of $\mathcal{H} \subset \mathcal{G}$, with index $g/h = 4$. If the modified ground Rep were

$$\mathbf{M}^*(R) = \begin{pmatrix} 0 & \hat{E} & 0 & 0 \\ \hat{\sigma}_1 & 0 & 0 & 0 \\ 0 & 0 & 0 & \hat{\sigma}_1 \\ 0 & 0 & \hat{E} & 0 \end{pmatrix},$$

then the induced Rep would be given by

$$\begin{aligned}
 {}^{(\sigma)}\Sigma \uparrow \mathcal{G}(R) &= \mathbf{M}(R) : {}^{(\sigma)}\Sigma(\widehat{H}) \\
 &= \begin{pmatrix} 0 & \widehat{E} & 0 & 0 \\ \sigma_1 & 0 & 0 & 0 \\ 0 & 0 & 0 & \sigma_1 \\ 0 & 0 & \widehat{E} & 0 \end{pmatrix} : {}^{(\sigma)}\Sigma(\widehat{H}) \\
 &= \begin{pmatrix} 0 & {}^{(\sigma)}\Sigma(\widehat{E}) & 0 & 0 \\ {}^{(\sigma)}\Sigma(\widehat{\sigma}_1) & 0 & 0 & 0 \\ 0 & 0 & 0 & {}^{(\sigma)}\Sigma(\widehat{\sigma}_1) \\ 0 & 0 & {}^{(\sigma)}\Sigma(\widehat{E}) & 0 \end{pmatrix}.
 \end{aligned}$$

Here, the zeroes represent matrices of dimension $d_\sigma \times d_\sigma$, the same as the dimension of ${}^{(\sigma)}\Sigma$, the Irreps of $\mathcal{H}$.

We will encounter supermatrices of the kind illustrated in Example 9.7 when we develop Irreps of space-groups in Chapter 11. That is, we will obtain supermatrices in which the subgroup block elements are drawn from more than one matrix representative of the subgroup, unlike what would result from using the modified ground matrices from (9.12).

The character of an induced Rep matrix ${}^{(\sigma)}\Sigma \uparrow \mathcal{G}(R)$, that is, $\chi \left(R \mid {}^{(\sigma)}\Sigma \uparrow \mathcal{G} \right)$, is just the sum of characters of submatrices ${}^{(\sigma)}\Sigma(H)$, which appear on the diagonal, whenever $\mathbf{R}_i^{-1} R \mathbf{R}_i = H \in \mathcal{H}$. Since,

$$M_{ii}(R) = \begin{cases} 1, & \text{if } \mathbf{R}_i^{-1} R \mathbf{R}_i \in \mathcal{H}, \\ 0, & \text{otherwise,} \end{cases}$$

$\chi \left(R \mid {}^{(\sigma)}\Sigma \uparrow \mathcal{G} \right)$ can be expressed as

$$\chi \left(R \mid {}^{(\sigma)}\Sigma \uparrow \mathcal{G} \right) = \sum_i M_{ii}(R) {}^{(\sigma)}\chi \left(\mathbf{R}_i^{-1} R \mathbf{R}_i = H \right). \quad (9.16)$$

In this subsection we demonstrated that an Irrep ${}^{(\sigma)}\Sigma$ of a subgroup $\mathcal{H}$ can be used to induce a Rep of ${}^{(\sigma)}\Sigma \uparrow \mathcal{G}$ of the group $\mathcal{G}$, but it may be a reducible Rep.

9.3.3 Inducing Reps of $\mathcal{C}_{3v}$ from Irreps of $\mathcal{H} = \{E, \sigma_1\}$

The subgroup $\mathcal{H} = \{E, \sigma_1\}$ has the Irreps given in Table 9.3. We can use the modified ground Rep of (9.14) and the Irreps of Table 9.3 to induce Reps of $\mathcal{C}_{3v}$. From Irrep ${}^{(+)}\Sigma$ we obtain, for example,

$$\left({}^{(+)}\Sigma \uparrow \mathcal{C}_{3v} \right) (C_3^+) = \mathbf{M}^*(C_3^+) \otimes {}^{(+)}\Sigma(E). \quad (9.17)$$

Table 9.3. The Irreps of $\mathcal{H} = \{E, \sigma_1\}$.

	E	σ_1
$(+)\Sigma$	1	1
$(-)\Sigma$	1	-1

Substituting from (9.14) and Table 9.3 and then replacing the elements E of $\mathbf{M}^*(C_3^+)$ by $(+)\Sigma(E^+)$, we obtain

$$\begin{aligned}
 \left((+)\Sigma \uparrow \mathcal{C}_{3v} \right) (C_3^+) &= \begin{pmatrix} 0 & 0 & (+)\Sigma(E) \\ (+)\Sigma(E) & 0 & 0 \\ 0 & (+)\Sigma(E) & 0 \end{pmatrix} \\
 &= \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}.
 \end{aligned} \tag{9.18}$$

In this case, the Rep $(+)\Sigma \uparrow \mathcal{C}_{3v}$ induced from $(+)\Sigma$ is identical to the ground Rep itself, because all matrix representatives of $(+)\Sigma$ are equal to unity.

We now select the Irrep $(-)\Sigma$, in which case we again get the matrix representatives of the ground Rep for the elements E, C_3^+ , and C_3^- . However, for the reflection operations we have, for example,

$$\begin{aligned}
 \left((-)\Sigma \uparrow \mathcal{C}_{3v} \right) (\sigma_3) &= \mathbf{M}^*(\sigma_3) : (-)\Sigma(\sigma_1) \\
 &= \begin{pmatrix} 0 & 0 & (-)\Sigma(\sigma_1) \\ (-)\Sigma(\sigma_1) & 0 & 0 \\ 0 & (-)\Sigma(\sigma_1) & 0 \end{pmatrix} \\
 &= \begin{pmatrix} 0 & 0 & -1 \\ -1 & 0 & 0 \\ 0 & -1 & 0 \end{pmatrix}.
 \end{aligned} \tag{9.19}$$

The complete Rep of $\mathcal{C}_{3v}$ induced from the Irrep $(-)\Sigma$ is this:

$$\begin{aligned}
 \left((-)\Sigma \uparrow \mathcal{C}_{3v} \right) (E) &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \left((-)\Sigma \uparrow \mathcal{C}_{3v} \right) (C_3^+) = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}, \\
 \left((-)\Sigma \uparrow \mathcal{C}_{3v} \right) (C_3^-) &= \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}, \quad \left((-)\Sigma \uparrow \mathcal{C}_{3v} \right) (\sigma_1) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix}, \\
 \left((-)\Sigma \uparrow \mathcal{C}_{3v} \right) (\sigma_2) &= \begin{pmatrix} 0 & 0 & -1 \\ 0 & -1 & 0 \\ -1 & 0 & 0 \end{pmatrix}, \quad \left((-)\Sigma \uparrow \mathcal{C}_{3v} \right) (\sigma_3) = \begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}.
 \end{aligned}$$

These matrix representatives obey the multiplication table for $\mathcal{C}_{3v}$. However, the Rep is reducible.

We now move on to inducing *irreducible* Reps!

9.4 Irreps induced from invariant subgroups

We focus on the case of Rep induction with respect to self-conjugate or invariant subgroups. Thus, we restrict $\mathcal{H}$ to be an invariant subgroup, $\mathcal{H} \equiv \mathcal{N}$ of order n . Then, since invariant subgroups consist of complete classes, conjugation of $\mathcal{N}$ with *any* element of the full group simply reproduces $\mathcal{N}$. The conjugate subgroups are identical to the original subgroup: $\mathcal{N}^{(j)} = \mathcal{N}$, for $1 \geq j \geq g/n$.

Example 9.8

The group $\mathcal{C}_{3v}$, with its invariant subgroup $\mathcal{N} = \mathcal{C}_3$, has conjugate subgroups $\mathcal{N}^{(j)} = \mathbf{R}_j \mathcal{N} \mathbf{R}_j^{-1}$ that are found to be identical to $\mathcal{N}$. For example, taking $\mathbf{R}_1$ to be σ_1 ,

$$\begin{aligned} \mathcal{N}^{(1)} &= \sigma_1 \{E, C_3^+, C_3^-\} \sigma_1 \\ &= \sigma_1 \{\sigma_1, \sigma_3, \sigma_2\} \\ &= \{E, C_3^-, C_3^+\} = \mathcal{N}. \end{aligned}$$

9.4.1 Conjugate Irreps of normal subgroups

Although conjugation of an invariant subgroup by an LCR $\mathbf{R}_j \notin \mathcal{N}$ simply reproduces the original invariant subgroup, it does *rearrange the order of the elements* in the subgroup. This seemingly trivial permutation of the order of the elements is important: It means that the matrix representatives of the elements will also be rearranged:

$$\Delta(N) \mapsto \Delta(\mathbf{R}_j N \mathbf{R}_j^{-1}),$$

and this new set of matrices is also a Rep, but it is not necessarily equivalent to the original one, as will soon be demonstrated. The difference, when the Irreps are inequivalent, is that the same set of matrices will correspond to different group elements in the *conjugate* Rep.

A key point An invariant subgroup is self-conjugate. It has only itself as a conjugate subgroup. However, it *may* have *inequivalent* conjugate Irreps.

Example 9.9

We know from Example 9.8 that conjugation of the elements of the subgroup $\mathcal{C}_3$ of $\mathcal{C}_{3v}$ by the coset representative σ_1 simply rearranges the subgroup elements. In particular, it interchanges C_3^+ and C_3^- . We now ask how conjugation affects the Irreps of $\mathcal{C}_3$, listed in the table below.

	E	C_3^+	C_3^-
$^{(1)}\Delta$	1	1	1
$^{(2)}\Delta$	1	ω	ω^*
$^{(3)}\Delta$	1	ω^*	ω

We define a new set of matrices formed by conjugation of the elements of the Irrep $^{(2)}\Delta$. We find that

$$\begin{aligned} {}^{(2,\sigma_1)}\Delta(E) &= {}^{(2)}\Delta(\sigma_1 E \sigma_1) = {}^{(2)}\Delta(E) = 1, \\ {}^{(2,\sigma_1)}\Delta(C_3^+) &= {}^{(2)}\Delta(\sigma_1 C_3^+ \sigma_1) = {}^{(2)}\Delta(C_3^-) = \omega^*, \\ {}^{(2,\sigma_1)}\Delta(C_3^-) &= {}^{(2)}\Delta(\sigma_1 C_3^- \sigma_1) = {}^{(2)}\Delta(C_3^+) = \omega. \end{aligned}$$

Thus the new Rep $^{(2,\sigma_1)}\Delta$ is identical to the Irrep $^{(3)}\Delta$. That is, the Irreps $^{(2)}\Delta$ and $^{(3)}\Delta$ are conjugate Irreps with respect to C_{3v} by the coset representative σ_1 .

We now develop the concept of *conjugate Irreps* with the aid of F-operator actions. We start with such action on a basis set $\{^{(\alpha)}\phi_i\}$ of Irrep $^{(\alpha)}\Delta$ of $\mathcal{N}$. For an F-operator $N \in \mathcal{N}$, we obtain

$$N^{(\alpha)}\phi_i = \sum_j {}^{(\alpha)}\phi_j {}^{(\alpha)}\Delta_{ji}(N). \quad (9.20)$$

The decomposition of $\mathcal{G}$ into *left*-cosets of $\mathcal{N}$,

$$\mathcal{G} = \sum_{k=1}^{g/n} \mathbf{R}_k \mathcal{N},$$

allows us to go a step further and consider the action of N on a new basis function, or basis vector, $(\mathbf{R}_k^{(\alpha)}\phi_i)$, where $\mathbf{R}_k$ is an LCR, $\mathbf{R}_k \notin \mathcal{N}$. We obtain

$$\begin{aligned} N(\mathbf{R}_k^{(\alpha)}\phi_i) &= (\mathbf{R}_k \mathbf{R}_k^{-1}) N(\mathbf{R}_k^{(\alpha)}\phi_i) = \mathbf{R}_k (\mathbf{R}_k^{-1} N \mathbf{R}_k)^{(\alpha)}\phi_i \\ &= \mathbf{R}_k \sum_j {}^{(\alpha)}\phi_j {}^{(\alpha)}\Delta_{ji}(\mathbf{R}_k^{-1} N \mathbf{R}_k) \\ &= \sum_j (\mathbf{R}_k^{(\alpha)}\phi_j) {}^{(\alpha)}\Delta_{ji}(N_k) \\ &= \sum_j (\mathbf{R}_k^{(\alpha)}\phi_j) {}^{(\alpha,k)}\Delta_{ji}(N), \end{aligned}$$

where N_k is an element of $\mathcal{N}$, related to N by conjugation with respect to $\mathbf{R}_k$. We write these relations in a more compact form as

$$\begin{aligned} N^{(\alpha)}\Phi &= {}^{(\alpha)}\Phi {}^{(\alpha)}\Delta(N) \\ N(\mathbf{R}_k^{(\alpha)}\Phi) &= (\mathbf{R}_k^{(\alpha)}\Phi) {}^{(\alpha,k)}\Delta(N) \\ &= {}^{(\alpha,k)}\Phi {}^{(\alpha,k)}\Delta(N). \end{aligned} \quad (9.21)$$

$^{(\alpha,k)}\Delta(N)$ is an Irrep generated through the conjugacy operation $\mathbf{R}_k^{-1} N \mathbf{R}_k$; it is called a conjugate Irrep.

Conjugate Irrep

The matrix representative of the element N in the *conjugate* Irrep $^{(\alpha,k)}\Delta$ is just the matrix representative of its conjugate element $N_k = \mathbf{R}_k^{-1} N \mathbf{R}_k$ in the original Irrep $^{(\alpha)}\Delta \equiv ^{(\alpha,1)}\Delta$.

Thus, according to this labeling convention we write

$$^{(\alpha,k)}\Delta(N) = ^{(\alpha,1)}\Delta(\mathbf{R}_k^{-1} N \mathbf{R}_k) \equiv ^{(\alpha,1)}\Delta(N_k). \quad (9.22)$$

$^{(\alpha,k)}\Delta(N)$ is said to be an Irrep of $\mathcal{N}$ conjugate to $^{(\alpha,1)}\Delta(N)$ with respect to $\mathcal{G}$. *All conjugate Irreps have the same dimension*, because the conjugations that produce these Irreps involve just a permutation of the representative matrices among the elements of $\mathcal{N}$. In all, there are g/n conjugate Irreps.

It is easily demonstrated that the matrices of a conjugate Rep satisfy the group multiplication table and thus actually *do* form a Rep of the normal subgroup $\mathcal{N}$:

$$\begin{aligned} ^{(\alpha,k)}\Delta(N) ^{(\alpha,k)}\Delta(N') &= ^{(\alpha,1)}\Delta(\mathbf{R}_k^{-1} N \mathbf{R}_k) ^{(\alpha,1)}\Delta(\mathbf{R}_k^{-1} N' \mathbf{R}_k) \\ &= ^{(\alpha,1)}\Delta(\mathbf{R}_k^{-1} N \mathbf{R}_k \mathbf{R}_k^{-1} N' \mathbf{R}_k) \\ &= ^{(\alpha,1)}\Delta(\mathbf{R}_k^{-1} N N' \mathbf{R}_k) \\ &= ^{(\alpha,k)}\Delta(N N'). \end{aligned} \quad (9.23)$$

Equivalent and inequivalent conjugate Irreps

An Irrep $^{(\alpha,k)}\Delta(N)$ conjugate to Irrep $^{(\alpha,1)}\Delta$ of $\mathcal{N}$, *may be either equivalent or inequivalent* to $^{(\alpha,1)}\Delta$. Equivalence means the Irreps differ only by a unitary transformation

$$^{(\alpha,k)}\Delta(N) = U_k^{-1} ^{(\alpha,1)}\Delta(N) U_k, \quad \forall N \in \mathcal{N}.$$

One might have thought that *all* conjugate Reps should be equivalent. They seem to be related by means of a similarity transformation, which is generally taken as a kind of equivalence relationship. The point is that although the elements $N_k = \mathbf{R}_k^{-1} N \mathbf{R}_k$ and N are in the same class *relative to the group* $\mathcal{G}$, because N has been conjugated with respect to the elements of $\mathcal{G}$, the two elements are not necessarily in the same class with respect to the normal subgroup $\mathcal{N}$. It is for this reason that conjugate Reps are not necessarily equivalent.

It is useful here to reiterate that the conjugate Rep $^{(\alpha,k)}\Delta$ consists of the same set of matrices as the original Rep $^{(\alpha,1)}\Delta$, but the matrices of the conjugate Rep are mapped

onto the group elements in a different way. This difference can result in inequivalent Reps.

Example 9.10

The elements C_3^+ and C_3^- are in the same class with respect to the full group $\mathcal{C}_{3v}$. For example,

$$\sigma_1 C_3^+ \sigma_1 = C_3^-.$$

However, when the conjugating elements are restricted to the subgroup $\mathcal{C}_3$, it is found that C_3^+ and C_3^- are in different classes. Conjugation of C_3^+ gives C_3^+ back again:

$$E C_3^+ E = C_3^+, \quad C_3^+ C_3^+ C_3^- = C_3^+, \quad C_3^- C_3^+ C_3^+ = C_3^+.$$

Similarly, conjugation of C_3^- gives C_3^- :

$$E C_3^- E = C_3^-, \quad C_3^+ C_3^- C_3^- = C_3^-, \quad C_3^- C_3^- C_3^+ = C_3^-.$$

We should have anticipated that, since the normal subgroup $\mathcal{C}_3$ is Abelian, each element is in a class by itself.

9.4.2 Group action on Irreps of normal subgroups

It is by now clear that our objective is to cast the conjugation process described above in view of *group actions* presented in Section 6.1, where, here, the set M is just the set of Irreps of the normal subgroup $\mathcal{N}$. We note here that, according to the previous section, a group action on an Irrep of $\mathcal{N}$ produces either an equivalent or inequivalent Irrep of $\mathcal{N}$, and, by definition, an equivalence amounts to producing the same Irrep. Hence we identify the orbits and stabilizers as follows:

Orbit

An *orbit* $\mathcal{O}^{(\alpha)}(\Delta)$ is the maximal set of mutually inequivalent Irreps conjugate to the Irrep $^{(\alpha)}\Delta$ of a normal subgroup $\mathcal{N}$ of $\mathcal{G}$.

$$\mathcal{O}^{(\alpha)}(\Delta) = \left\{ ^{(\alpha, \mu)}\Delta(N) \mid \forall \mu : ^{(\alpha, \mu)}\Delta(N) = ^{(\alpha)}\Delta(R_\mu^{-1} N R_\mu) \not\sim ^{(\alpha)}\Delta(N) \right\}. \quad (9.24)$$

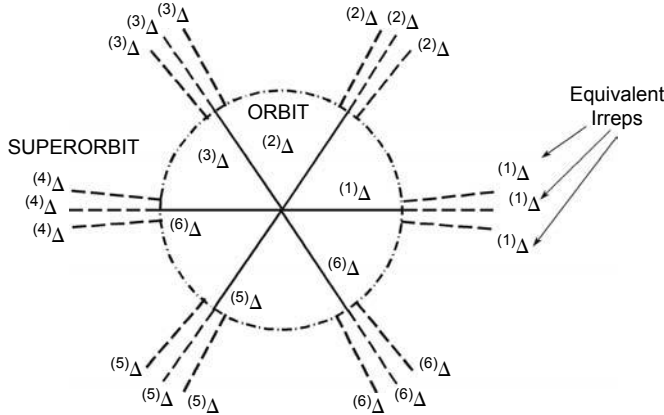


Fig. 9.2. Illustration of orbit (solid lines) and superorbit (dashed lines).

We also introduce the superorbit as:

Superorbit

The set of all equivalent and inequivalent conjugate Irreps of Δ , and is denoted by $\mathcal{O}^s$ (see Figure 9.2). A *superorbit* thus contains g/n prongs, where each conjugate Irrep $^{(\alpha,k)}\Delta$ is called a **prong** of the superorbit.

Notice that we label equivalent conjugate Irreps in the same superorbit with Roman letters, i , in $^{(\alpha,i)}\Delta$, and inequivalent conjugate Irreps with Greek letters, μ , in $^{(\alpha,\mu)}\Delta$.

Example 9.11

Orbits of $\mathcal{C}_3 \triangleleft \mathcal{C}_{3v}$

Conjugation of $^{(1)}\Delta$ with all the elements of $\mathcal{C}_{3v}$ does not yield any inequivalent Irrep. Thus we have an orbit of order one, i.e. it consists of a single prong. On the other hand, we found in Example 9.9 that conjugation of $^{(2)}\Delta$ by the group elements of $\mathcal{C}_{3v}$ yields $^{(2)}\Delta$ and $^{(3)}\Delta$. Thus these two Irreps constitute a second *orbit* of $\mathcal{C}_3$ of $\mathcal{C}_{3v}$. The orbit is of order two. *The set of all Irreps of $\mathcal{C}_3$ is partitioned into two disjoint orbits.*

We can reasonably anticipate that these two mutually inequivalent Irreps of $\mathcal{C}_3$ will induce a two-dimensional Irrep of the full group $\mathcal{C}_{3v}$. After all, we *subduced* these two subgroup Irreps from the two-dimensional Irrep of $\mathcal{C}_{3v}$ in the first section of this chapter.

Example 9.11 underscores the fact that although an orbit comprises inequivalent conjugate Irreps of $\mathcal{N}$, a single orbit may not exhaust all the Irreps of $\mathcal{N}$. In such a case, we have more than one distinct orbit, i.e. they share no conjugate Irreps.

Next, we identify the **stabilizer** of an Irrep $^{(\alpha,1)}\Delta$ of $\mathcal{N}$ as the elements of $\mathcal{G}$ that generate a set of *equivalent* Irreps $^{(\alpha,k)}\Delta \sim ^{(\alpha,1)}\Delta$ that are related by a unitary transformation, U_k ,

$$\begin{aligned} ^{(\alpha,k)}\Delta(N) &= ^{(\alpha,1)}\Delta(\mathbf{L}_k^{-1} N \mathbf{L}_k) \\ &= U_k^{-1} ^{(\alpha,1)}\Delta(N) U_k. \end{aligned} \quad (9.25)$$

It is called the *little-group of the second kind*, $\mathcal{L}_{\text{II}} \left(^{(\alpha)}\Delta \right) \subset \mathcal{G}$, or simply $\mathcal{L}_{\text{II}}^{(\alpha)}$.

Little-group of the second kind, $\mathcal{L}_{\text{II}} \left(^{(\alpha)}\Delta \right)$

All the elements of $\mathcal{G}$ that map an Irrep $^{(\alpha)}\Delta$ of the normal group $\mathcal{N}$ onto itself or an equivalent Irrep form a little-group of the second kind relative to the Irrep. Thus,

$$\begin{aligned} \mathcal{L}_{\text{II}} \left(^{(\alpha)}\Delta \right) &= \sum_{R \in \mathcal{G}} \left\{ R \equiv L \mid ^{(\alpha)}\Delta(R^{-1}NR) \sim ^{(\alpha)}\Delta(N) \right\} \\ &= \sum_{k=1}^{l_1} \mathbf{L}_k \mathcal{N} \equiv \mathcal{L}_{\text{II}}^{(\alpha)}. \end{aligned} \quad (9.26)$$

The order l_2 of $\mathcal{L}_{\text{II}}^{(\alpha)}$ satisfies the relation $n \leq l_2 = l_1 n \leq g$. The case where g/n is a prime number defines the lower or upper limit on l_2 : we set $g/l_2 = g/l_1 n = m$, an integer, then

$$l_1 m = \text{prime number}, \quad (9.27)$$

and either $m = 1$, $l_1 = g/n$ and $l_2 = g$, or $l_1 = 1$ and $l_2 = n$.

Closure under the composition law of $\mathcal{G}$ can be proved as follows: given LCRs $\mathbf{L}_i, \mathbf{L}_j$, with $\mathbf{L}_i \mathbf{L}_j = \mathbf{L}_k$, and using the definitions

$$\begin{aligned} ^{(\alpha,i)}\Delta(N) &= ^{(\alpha,1)}\Delta(\mathbf{L}_i^{-1} N \mathbf{L}_i) \sim ^{(\alpha,1)}\Delta(N), \\ ^{(\alpha,j)}\Delta(N) &= ^{(\alpha,1)}\Delta(\mathbf{L}_j^{-1} N \mathbf{L}_j) \sim ^{(\alpha,1)}\Delta(N), \end{aligned}$$

we have,

$$\begin{aligned}
 {}^{(\alpha,k)}\Delta(N) &= {}^{(\alpha,1)}\Delta(\mathbf{L}_k^{-1} N \mathbf{L}_k) = {}^{(\alpha,1)}\Delta([\mathbf{L}_i \mathbf{L}_j]^{-1} N [\mathbf{L}_i \mathbf{L}_j]) \\
 &= {}^{(\alpha,1)}\Delta(\mathbf{L}_j^{-1} \mathbf{L}_i^{-1} N \mathbf{L}_i \mathbf{L}_j) = {}^{(\alpha,j)}\Delta(\mathbf{L}_i^{-1} N \mathbf{L}_i) \\
 &= U_j^{-1} {}^{(\alpha,1)}\Delta(\mathbf{L}_i^{-1} N \mathbf{L}_i) U_j \sim U_j^{-1} {}^{(\alpha,i)}\Delta(N) U_j \\
 &= U_j^{-1} U_i^{-1} {}^{(\alpha,1)}\Delta(N) U_i U_j,
 \end{aligned}$$

where we used (9.23) in the last line. We have thus shown that if the LCRs $\mathbf{L}_i$ and $\mathbf{L}_j$ generate Irreps equivalent to ${}^{(\alpha,1)}\Delta$, so too does the LCR $\mathbf{L}_k = \mathbf{L}_i \mathbf{L}_j$.

Next, we show that *any* element $L = \mathbf{L}_i N' \in \mathbf{L}_i \mathcal{N}$ generates an Irrep equivalent to ${}^{(\alpha,1)}\Delta$

$$\begin{aligned}
 {}^{(\alpha,1)}\Delta(N'^{-1} \mathbf{L}_i^{-1} N \mathbf{L}_i N') &= {}^{(\alpha,1)}\Delta(N'^{-1}) {}^{(\alpha,1)}\Delta(\mathbf{L}_i^{-1} N \mathbf{L}_i) {}^{(\alpha,1)}\Delta(N') \\
 &\sim {}^{(\alpha,i)}\Delta(N) \sim {}^{(\alpha,1)}\Delta(N),
 \end{aligned}$$

since the matrices ${}^{(\alpha,1)}\Delta(N')$ are unitary. Thus, $\mathcal{L}_{\text{II}}^{(\alpha)}$ comprises complete LCs of $\mathcal{G}$, including $\mathcal{N}$ itself. Thus,

$$\mathcal{N} \text{ remains a normal subgroup of } \mathcal{L}_{\text{II}}^{(\alpha)} \Rightarrow \mathcal{N} \triangleleft \mathcal{L}_{\text{II}} \left({}^{(\alpha)}\Delta \right).$$

Because $\mathcal{N} \triangleleft \mathcal{L}_{\text{II}} \left({}^{(\alpha)}\Delta \right)$, we define the factor group as:

Little-group of the first kind $\mathcal{L}_{\text{I}} \left({}^{(\alpha)}\Delta \right)$

A little-group of the first kind, $\mathcal{L}_{\text{I}} \left({}^{(\alpha)}\Delta \right)$, or $\mathcal{L}_{\text{I}}^{(\alpha)}$, is the factor group

$$\mathcal{L}_{\text{I}} \left({}^{(\alpha)}\Delta \right) = \mathcal{L}_{\text{II}} \left({}^{(\alpha)}\Delta \right) / \mathcal{N} \quad (9.28)$$

relative to $\mathcal{G}$, the normal subgroup $\mathcal{N}$ and Irrep Δ . Its order is l_1 .

Notice that the little-groups are defined relative to a group, a normal subgroup, and a particular Irrep.

Example 9.12

Little-groups of $\mathcal{C}_3 \triangleleft \mathcal{C}_{3v}$

Consider the Irrep $^{(1)}\Delta$ of the subgroup $\mathcal{C}_3$.

$$\begin{array}{c|ccc} & E & C_3^+ & C_3^- \\ \hline ^{(1)}\Delta & 1 & 1 & 1 \end{array}$$

All the Irrep matrix representatives are unity. Thus, conjugation by *all* the elements of the full group $\mathcal{C}_{3v}$ maps the Irrep onto itself. In this case, the little-group of the second kind, $\mathcal{L}_{II}$, consists of all the elements of the full group $\mathcal{C}_{3v}$, relative to $\mathcal{C}_3$ and the Irrep $^{(1)}\Delta$ of the subgroup $\mathcal{C}_3$.

$$\mathcal{L}_{II} \left(^{(1)}\Delta \right) = \mathcal{C}_{3v}.$$

The corresponding little-group of the first kind is $\{E, \sigma_i\}$. Now consider the Irrep $^{(2)}\Delta$ of $\mathcal{C}_3$.

$$\begin{array}{c|ccc} & E & C_3^+ & C_3^- \\ \hline ^{(2)}\Delta & 1 & \omega^* & \omega \end{array}$$

We know from Example 9.10 that only conjugation by elements of the subgroup $\mathcal{C}_3$ itself leaves an element of $\mathcal{C}_3$ unchanged. However, conjugation by σ_1 was shown, in Example 9.9, to lead to an inequivalent conjugate Irrep. The same follows by conjugation with σ_2 or σ_3 . Thus, only the elements of the subgroup itself map the Irrep $^{(2)}\Delta$ onto itself. In this case, the little-group of the second kind, $\mathcal{L}_{II}$, consists of the elements of the subgroup $\mathcal{C}_3$, relative to $\mathcal{C}_3$ and the Irrep $^{(2)}\Delta$ of the subgroup $\mathcal{C}_3$. The same holds true for the Irrep $^{(3)}\Delta$.

$$\begin{aligned} \mathcal{L}_{II} \left(^{(2)}\Delta \right) &= \mathcal{C}_3, \\ \mathcal{L}_{II} \left(^{(3)}\Delta \right) &= \mathcal{C}_3. \end{aligned}$$

The corresponding little-group of the first kind is just the identity.

In Example 9.11, we found that for the Irrep $^{(1)}\Delta$ of $\mathcal{C}_3$, relative to $\mathcal{C}_{3v}$, *all* the elements of the full group $\mathcal{G} = \mathcal{C}_{3v}$ map the Irrep onto itself. In such a case, that is, one in which the little-group of the second kind, $\mathcal{L}_{II}$, is isomorphic with the full group $\mathcal{G}$, we only have to induce an Irrep of the isomorphic group $\mathcal{L}_{II}$. We can do this by means of the ground Rep $\mathcal{G}/\mathcal{N}$, as was demonstrated in Section 9.2. This will involve the little-group of the first kind, $\mathcal{L}_I$, to serve as the factor group. However, we should remember that $\mathcal{L}_I$ is also employed in the more general case in which the little-group $\mathcal{L}_{II}$ is *not isomorphic* to the full group $\mathcal{G}$.

Once again, the little-group is defined relative to a group, a normal subgroup, and a particular Irrep. Notice also that all the elements of $\mathcal{N}$ belong to $\mathcal{L}_{II}$.

Some properties of orbits and little-groups

- (i) The coset representative R_μ that generates the inequivalent conjugate Irrep $^{(\alpha, \mu)}\Delta$ in the orbit $\mathcal{O}({}^{(\alpha)}\Delta)$, gives rise also to the subgroup

$$\mathcal{L}_{\text{II}}^{(\alpha, \mu)} = R_\mu \mathcal{L}_{\text{II}} \left({}^{(\alpha)}\Delta \right) R_\mu^{-1}, \quad (9.29)$$

conjugate and isomorphic to $\mathcal{L}_{\text{II}}^{(\alpha)}$. Each $\mathcal{L}_{\text{II}}^{(\alpha, \mu)}$ is the little-group associated with the μ -component of the orbit $\mathcal{O}({}^{(\alpha)}\Delta)$,

$$\mathcal{L}_{\text{II}}^{(\alpha, \mu)} = \mathcal{L}_{\text{II}} \left({}^{(\alpha, \mu)}\Delta \right); \quad (9.30)$$

the proof of (9.29) is left to Exercise 9.5.

- (ii) The intersection of the conjugate little-groups of $\mathcal{L}_{\text{II}}({}^{(\alpha)}\Delta)$ is just the normal subgroup $\mathcal{N}$,

$$\mathcal{L}_{\text{II}}^{(\alpha, \mu)} \cap \mathcal{L}_{\text{II}}^{(\alpha, 1)} = \mathcal{N}. \quad (9.31)$$

- (iii) The order of an orbit is given by

$$\text{The order of the orbit } \mathcal{O} \left({}^{(\alpha)}\Delta \right), \text{ } o \left({}^{(\alpha)}\Delta \right) = \frac{g}{l_2}. \quad (9.32)$$

It is also the order of the ground Rep of $\mathcal{L}_{\text{II}}$.

- (iv) The orbits generated by two inequivalent Irreps of $\mathcal{N}$, $^{(\mu)}\Delta$ and $^{(\nu)}\Delta$, are either identical or disjoint.
- (v) All Irreps belonging to the same orbit have the same dimension.
- (vi) **Orbit/superorbit relation** Each prong of an orbit is associated with l_2/n equivalent Irreps, the index of $\mathcal{N}$ in $\mathcal{L}_{\text{II}}$. Hence, the superorbit contains l_2/n replica orbits. If we define the *orbit matrix* as

$$\mathbf{S}({}^{(\alpha)}\Delta) = \sum_{\mu=1}^{g/l_2} \oplus {}^{(\alpha, \mu)}\Delta, \quad (9.33)$$

i.e. the direct sum of all the matrices of the orbit, then we can express this relation in terms of the superorbit matrix $\mathbf{S}^s$ as

$$\begin{aligned} \mathbf{S}^s({}^{(\alpha)}\Delta) &= \sum_{i=1}^{l_2/n} \oplus S({}^{(\alpha)}\Delta) \\ &= \mathbb{I} \left(\frac{l_2}{n}, \frac{l_2}{n} \right) \otimes \mathbf{S}({}^{(\alpha)}\Delta). \end{aligned} \quad (9.34)$$

9.4.3 Establishing the road map to induction of Irreps

Now that we have identified the main ingredients for the induction process we are ready to construct the road map for the method of Irrep induction. This map will lead us from the Irreps of $\mathcal{N}$ to the Irreps of $\mathcal{L}_{\text{II}}$, and finally to the sought-after Irreps of $\mathcal{G}$. In order to construct this map we present several important theorems that guarantee the irreducibility, uniqueness, and completeness of the exhaustive set of induced Irreps. With this in hand, we finally present an outline of the induction procedures.

We use the following conventions:

- We use the symbol $\mathbf{\Gamma}$ for a Rep of group $\mathcal{G}$, and $^{(\mu)}\mathbf{\Gamma}$ for its Irreps.
- The Reps and Irreps of a general subgroup $\mathcal{H} \subset \mathcal{G}$ are denoted by $\mathbf{\Sigma}$ and $^{(\sigma)}\mathbf{\Sigma}$, respectively.
- We denote the Reps and Irreps of a normal subgroup $\mathcal{N} \triangleleft \mathcal{G}$ by $\mathbf{\Delta}$, and $^{(\alpha)}\mathbf{\Delta}$, respectively.
- The Reps and Irreps of the little-group $\mathcal{L}_{\text{II}} \left(^{(\alpha)}\mathbf{\Delta} \right)$ are designated $\mathbf{\Lambda}$ and $^{(\lambda)}\mathbf{\Lambda}$, respectively.

We provide related theorems and their proofs in the appendix, at the end of this chapter.

Conditions of irreducibility of an induced Rep $^{(\sigma)}\mathbf{\Sigma} \uparrow \mathcal{G}$

We start by considering the conditions necessary to ensure that an induced Rep $^{(\sigma)}\mathbf{\Sigma} \uparrow \mathcal{G}$ is actually an Irrep of $\mathcal{G}$. This can be established if we impose the requirement that the characters of an Irrep must satisfy the sum rule

$$\sum_{R \in \mathcal{G}} \left| \chi \left(R | ^{(\sigma)}\mathbf{\Sigma} \uparrow \mathcal{G} \right) \right|^2 = g. \quad (9.35)$$

With the aid of (9.16) we obtain for an induced Rep

$$\begin{aligned} \sum_{R \in \mathcal{G}} \left| \chi \left(R | ^{(\sigma)}\mathbf{\Sigma} \uparrow \mathcal{G} \right) \right|^2 &= \sum_i \sum_{R \in \mathcal{G}} \left| M_{ii}(R) ^{(\sigma)}\chi(\mathbf{R}_i^{-1} R \mathbf{R}_i) \right|^2 \\ &+ \sum_{i,j \neq i} \sum_{R \in \mathcal{G}} M_{ii}(R) ^{(\sigma)}\chi(\mathbf{R}_i^{-1} R \mathbf{R}_i) M_{jj}(R) ^{(\sigma)}\chi^*(\mathbf{R}_j^{-1} R \mathbf{R}_j). \end{aligned} \quad (9.36)$$

We rewrite the restriction imposed by the diagonal elements of M , namely, that the nonzero terms are those that satisfy the relation $\mathbf{R}_i^{-1} R \mathbf{R}_i = H$, as

$$R = \mathbf{R}_i H \mathbf{R}_i^{-1}, \quad (9.37)$$

and we find that by fixing i and varying $H \in \mathcal{H}$ we generate elements of the conjugate group $\mathcal{H}^{(i)}$, which is isomorphic to $\mathcal{H}$. Thus we rewrite the first sum on the r.h.s. of (9.36) as

$$\sum_i \sum_{R \in \mathcal{G}} \left| M_{ii}(R) ^{(\sigma)}\chi(\mathbf{R}_i^{-1} R \mathbf{R}_i) \right|^2 = \sum_{i=1}^{g/h} \sum_H \left| ^{(\sigma)}\chi(H) \right|^2 = \frac{g}{h} h = g, \quad (9.38)$$

where we made use of the fact that $^{(\sigma)}\Sigma$ is an Irrep of $\mathcal{H}$. Hence, the condition of irreducibility of $^{(\sigma)}\Sigma \uparrow \mathcal{G}$, according to (9.35) and (9.36), becomes

$$\sum_{i,j \neq i} \sum_{R \in \mathcal{G}} M_{ii}(R) {}^{(\sigma)}\chi(\mathbf{R}_i^{-1} R \mathbf{R}_i) M_{jj}(R) {}^{(\sigma)}\chi^*(\mathbf{R}_j^{-1} R \mathbf{R}_j) = 0. \quad (9.39)$$

The restriction imposed by $M_{ii}(R)$ and $M_{jj}(R)$ corresponds to the concurrent requirement that $R \in \mathcal{H}^{(i)}$ and $R \in \mathcal{H}^{(j)}$, or

$$R \in \mathcal{H}^{(i)} \cap \mathcal{H}^{(j)}.$$

Fixing $i = 1$, i.e. $\mathbf{R}_1 = E$, we find that $R = H \in \mathcal{H}$, and that

$$\begin{aligned} \sum_{j=2}^{g/h} \sum_{R \in \mathcal{G}} M_{11}(R) {}^{(\sigma)}\chi(\mathbf{R}_1^{-1} R \mathbf{R}_1) M_{jj}(R) {}^{(\sigma)}\chi^*(\mathbf{R}_j^{-1} R \mathbf{R}_j) \\ = \sum_{j=2}^{g/h} \sum_{H \in \mathcal{H}} {}^{(\sigma)}\chi(H) {}^{(\sigma)}\chi^*(\mathbf{R}_j^{-1} H \mathbf{R}_j). \end{aligned}$$

By fixing i at other values we arrive at identical results for the j summation by writing $\mathbf{R}_i^{-1} \mathbf{R}_j = \mathbf{R}_k$, and we obtain

$$\frac{g}{h} \sum_{k=2}^{g/h} \sum_{H \in \mathcal{H} \cap \mathcal{H}^{(k)}} {}^{(\sigma)}\chi(H) {}^{(\sigma)}\chi^*(\mathbf{R}_k^{-1} H \mathbf{R}_k) = 0, \quad (9.40)$$

where starting the summation at $k = 2$ ensures that we apply the restriction in (9.39), and thus eliminate the identity from the summation.

Condition of irreducibility for $^{(\alpha)}\Delta \uparrow \mathcal{G}$

We have shown in Section 9.4.1 that, in the case of a normal subgroup $\mathcal{N} \triangleleft \mathcal{G}$, the conjugation operation in (9.37) corresponds to the generation of an Irrep $^{(\alpha,k)}\Delta$, conjugate to $^{(\alpha)}\Delta$. Thus, with the aid of (9.22) we can rewrite the irreducibility condition (9.40) for $^{(\alpha)}\Delta \uparrow \mathcal{G}$ as

$$\frac{g}{n} \sum_{k=2}^{g/n} \sum_N {}^{(\alpha)}\chi(N) {}^{(\alpha,k)}\chi^*(N) = 0. \quad (9.41)$$

In order to satisfy (9.41), we require that for each conjugate Irrep $^{(\alpha,k)}\Delta$, the condition

$$\sum_N {}^{(\alpha)}\chi(N) {}^{(\alpha,k)}\chi^*(N) = 0 \quad (9.42)$$

must be satisfied. Since the r.h.s. of (9.42) is just a statement of the character orthogonality theorem, the l.h.s. of (9.42) then stipulates that the Irrep $^{(\alpha,k)}\Delta$ must be inequivalent to the Irrep $^{(\alpha)}\Delta$. Since (9.41) then requires that (9.42) be satisfied for all k , it demands *all*

conjugate Irreps of $^{(\alpha)}\Delta$ to be inequivalent. Hence, for the induced Irrep $^{(\alpha,k)}\Delta \uparrow \mathcal{G}$ to be irreducible, the superorbit must coincide with the orbit.

The necessary and sufficient condition for the irreducibility of $\Delta \uparrow \mathcal{G}$ is that $\Delta \uparrow \mathcal{G} \downarrow \mathcal{N}$ contains $\mathbf{S}(\Delta)$ only once,

$$\Delta \uparrow \mathcal{G} \downarrow \mathcal{N} = S(\Delta). \quad (9.43)$$

This, in turn, implies that

$$\mathcal{L}_{\Pi} \left(^{(\alpha)}\Delta \right) = \mathcal{N}, \quad (9.44)$$

and we can state, alternatively, the irreducibility condition as

The Rep $^{(\alpha)}\Delta \uparrow \mathcal{G}$ is itself irreducible if, and only if,

$$\mathcal{L}_{\Pi} \left(^{(\alpha)}\Delta \right) = \mathcal{N}.$$

However, this condition may not be satisfied for arbitrary $\mathcal{G}$, $\mathcal{N}$, and $^{(\alpha)}\Delta$. And, in general, we cannot induce directly an Irrep of $\mathcal{G}$ from Irreps of $\mathcal{N}$, since according to (9.34) we have

$$\Delta \uparrow \mathcal{G} \downarrow \mathcal{N} = \mathbb{I} \left(\frac{l_2}{n}, \frac{l_2}{n} \right) \otimes S(^{(\alpha)}\Delta). \quad (9.45)$$

Relations between Irreps of $\mathcal{G}$ and $^{(\alpha)}\Delta \uparrow \mathcal{G}$

In general, the Rep $^{(\alpha)}\Delta \uparrow \mathcal{G}$ can be decomposed onto the Irreps $^{(\mu)}\Gamma$ of $\mathcal{G}$, as

$$^{(\alpha)}\Delta \uparrow \mathcal{G} = \sum_{\mu}^{\oplus} \left\langle ^{(\alpha)}\Delta \uparrow \mathcal{G} \middle| ^{(\mu)}\Gamma \right\rangle ^{(\mu)}\Gamma. \quad (9.46)$$

If $^{(\alpha)}\Delta \uparrow \mathcal{G}$ is irreducible then $\left\langle ^{(\alpha)}\Delta \uparrow \mathcal{G} \middle| ^{(\mu)}\Gamma \right\rangle = \delta_{\mu\nu}$. With the aid of (9.45) we obtain

$$\begin{aligned} \Delta \uparrow \mathcal{G} \downarrow \mathcal{N} &= \sum_{\mu}^{\oplus} \left\langle ^{(\alpha)}\Delta \uparrow \mathcal{G} \middle| ^{(\mu)}\Gamma \right\rangle ^{(\mu)}\Gamma \downarrow \mathcal{N} \\ &= \mathbb{I} \left(\frac{l_2}{n}, \frac{l_2}{n} \right) \otimes S(^{(\alpha)}\Delta), \end{aligned} \quad (9.47)$$

which demonstrates that if $\left\langle ^{(\alpha)}\Delta \uparrow \mathcal{G} \middle| ^{(\mu)}\Gamma \right\rangle \neq 0$, then the subduction $^{(\mu)}\Gamma \downarrow \mathcal{N}$ contains, exclusively, a multiple of the orbit $\mathcal{O}(^{(\alpha)}\Delta)$.

Moreover, we can subduce the Irrep $^{(\mu)}\Gamma$ onto the Irreps $^{(\alpha)}\Delta$ as

$$^{(\mu)}\Gamma = \sum_{\nu}^{\oplus} \left\langle ^{(\mu)}\Gamma \middle| ^{(\alpha, \nu)}\Delta \right\rangle ^{(\alpha, \nu)}\Delta. \quad (9.48)$$

We can demonstrate the equality of $\left\langle ^{(\mu)}\Gamma \middle| ^{(\alpha)}\Delta \right\rangle$ and $\left\langle ^{(\mu)}\Gamma \middle| ^{(\alpha, \beta)}\Delta \right\rangle$ as follows:

$$\begin{aligned} \left\langle ^{(\mu)}\Gamma \middle| ^{(\alpha)}\Delta \right\rangle &= \frac{1}{n} \sum_N ^{(\mu)}\chi(\mathbf{R}_{\beta}^{-1} N \mathbf{R}_{\beta}) ^{(\alpha, \beta)}\chi(\mathbf{R}_{\beta}^{-1} N \mathbf{R}_{\beta}) \\ &= \frac{1}{n} \sum_N ^{(\mu)}\chi(N) ^{(\alpha, \beta)}\chi(\mathbf{R}_{\beta}^{-1} N \mathbf{R}_{\beta}) \\ &= \frac{1}{n} \sum_N ^{(\mu)}\chi(N) ^{(\alpha, \beta)}\chi(N) \\ &= \left\langle ^{(\mu)}\Gamma \middle| ^{(\alpha, \beta)}\Delta \right\rangle, \end{aligned} \quad (9.49)$$

so that all members of a given orbit occur the same number of times in the decomposition of $^{(\mu)}\Gamma$. Equation (9.49), together with Equation (9.44), demonstrates that:

An Irrep $^{(\mu)}\Gamma$ of $\mathcal{G}$ is *subduced* into a multiple direct sum of some fixed orbit matrix of its invariant subgroup $\mathcal{N}$

$$^{(\mu)}\Gamma \downarrow \mathcal{N} = \mathbf{1}(m, m) \otimes S(^{(\alpha)}\Delta). \quad (9.50)$$

We also find, using (9.47), (9.48), and the Frobenius *reciprocity theorem* (Appendix), that

$$\sum_{\mu}^{\oplus} \left| \left\langle ^{(\alpha)}\Delta \uparrow \mathcal{G} \middle| ^{(\mu)}\Gamma \right\rangle \right|^2 = \frac{l_2}{n}. \quad (9.51)$$

Induction of Irreps of $\mathcal{G}$ from allowable Irreps of the little-group $\mathcal{L}_{\Pi}$

We now demonstrate that a two-step induction procedure involving the little-groups $\mathcal{L}_{\Pi}^{(\alpha)}$ actually leads to the generation of all the Irreps $^{(\mu)}\Gamma$ of $\mathcal{G}$. This procedure is based on the selection of specific or “allowable” Irreps, from the Irreps of every $\mathcal{L}_{\Pi}^{(\alpha)}$, as candidates for the induction process.

To understand the idea of allowable Irreps, we consider some aspects related to the induction and subduction processes involving Irreps $^{(\lambda)}\Lambda$ of the little-group $\mathcal{L}_{\Pi}^{(\alpha)}$, and $^{(\alpha)}\Delta$ of $\mathcal{N}$. One of the main results of this endeavor is that not all Irreps of $\mathcal{L}_{\Pi}^{(\alpha)}$ are relevant to the process of induction of Irreps of $\mathcal{G}$. Those that are relevant are termed *allowable* or *permitted*.

Since $\mathcal{N} \triangleleft \mathcal{L}_{\Pi}^{(\alpha)}$, we infer from the definition of $\mathcal{L}_{\Pi}^{(\alpha)}$ that it is its own little-group, and that its orbit consists of only $^{(\alpha)}\Delta$. We also find that (9.47) yields

$$^{(\alpha)}\Delta \uparrow \mathcal{L}_{\Pi} (^{(\alpha)}\Delta) \downarrow \mathcal{N} \sim \sum_{i=1}^{l_2/n} {}^{\oplus} (^{(\alpha)}\Delta) = \mathbb{I} \left(\frac{l_2}{n}, \frac{l_2}{n} \right) (^{(\alpha)}\Delta). \quad (9.52)$$

Hence, we conclude that the subduction $^{(\lambda)}\Lambda \downarrow \mathcal{N}$ of an Irrep $^{(\lambda)}\Lambda$ of $\mathcal{L}_{\Pi}^{(\alpha)}$ will either contain a multiple direct sum of $^{(\alpha)}\Delta$, or not contain $^{(\alpha)}\Delta$ at all.

We identify an Irrep $^{(\lambda)}\mathbf{\Lambda}$ of $\mathcal{L}_{\text{II}} \left(^{(\alpha)}\mathbf{\Delta} \right)$ as *allowable*, if

$$\begin{aligned} ^{(\lambda)}\mathbf{\Lambda} \downarrow \mathcal{N} &\sim \sum_{i=1}^{d_{\lambda}/d_{\alpha}} \oplus ^{(\alpha)}\mathbf{\Delta} \\ &= 1 \left(\frac{d_{\lambda}}{d_{\alpha}} \times \frac{d_{\lambda}}{d_{\alpha}} \right) \otimes ^{(\alpha)}\mathbf{\Delta}, \end{aligned} \quad (9.53)$$

so that the frequency of $^{(\alpha)}\mathbf{\Delta}$ in $^{(\lambda)}\mathbf{\Lambda}$ is

$$\left\langle ^{(\lambda)}\mathbf{\Lambda} \downarrow \mathcal{N} \middle| ^{(\alpha)}\mathbf{\Delta} \right\rangle = \frac{d_{\lambda}}{d_{\alpha}}. \quad (9.54)$$

Some useful sum rules

- (i) With the aid of (9.51) we obtain the sum rule

$$\boxed{\sum_{\lambda} \left\langle ^{(\lambda)}\mathbf{\Lambda} \downarrow \mathcal{N} \middle| ^{(\alpha)}\mathbf{\Delta} \right\rangle^2 = \frac{l_2}{n}}, \quad (9.55)$$

and substituting from (9.54) we find that the dimensions of *allowable* Irreps satisfy the sum rule

$$\boxed{\sum_{\lambda} d_{\lambda}^2 = \frac{l_2}{n} d_{\alpha}^2}. \quad (9.56)$$

- (ii) We noted above that more than one orbit may emerge from the Irreps of $\mathcal{N}$, but we also noted that the orbits are disjoint. We may thus infer that the sum of the orders of all orbits associated with the normal subgroup $\mathcal{N}$ must be equal to the number of its Irreps. Since the order of an orbit is given by $o \left(^{(\alpha)}\mathbf{\Delta} \right) = g/l_2 \left(^{(\alpha)}\mathbf{\Delta} \right)$, we obtain the sum rule

$$\boxed{\sum_{\alpha}^{\text{orbits}} o \left(^{(\alpha)}\mathbf{\Delta} \right) = \sum_{\alpha}^{\text{orbits}} \frac{g}{l_2 \left(^{(\alpha)}\mathbf{\Delta} \right)} = \text{number of Irreps of } \mathcal{N}}. \quad (9.57)$$

- (iii) Irreps belonging to the orbit $\mathcal{O} \left(^{(\alpha)}\mathbf{\Delta} \right)$ have dimension d_{α} , hence, using the sum rule of Irrep dimensions we obtain

$$\sum_{\alpha}^{\text{orbits}} o \left(^{(\alpha)}\mathbf{\Delta} \right) d_{\alpha}^2 = n.$$

Since $o\left({}^{(\alpha)}\Delta\right) = g/l_2\left({}^{(\alpha)}\Delta\right)$, we obtain the sum rule

$$\sum_{\alpha}^{\text{orbits}} \frac{d_{\alpha}^2}{l_2\left({}^{(\alpha)}\Delta\right)} = \frac{n}{g}. \quad (9.58)$$

Next, we demonstrate that with the aid of allowable Irreps, ${}^{(\lambda)}\mathbf{\Lambda}$, we can generate Irreps of $\mathcal{G}$. We show that every allowable Irrep ${}^{(\lambda)}\mathbf{\Lambda}$ of a given $\mathcal{L}_{\Pi}\left({}^{(\alpha)}\Delta\right)$ induces an Irrep ${}^{(\lambda,\alpha)}\mathbf{\Gamma}$ of $\mathcal{G}$,

$${}^{(\lambda,\alpha)}\mathbf{\Gamma} \equiv {}^{(\lambda)}\mathbf{\Lambda} \uparrow \mathcal{G} \quad \text{is irreducible;} \quad (9.59)$$

that Irreps induced from different ${}^{(\lambda)}\mathbf{\Lambda}$ s are inequivalent,

$${}^{(\lambda,\alpha)}\mathbf{\Gamma} \sim^{(\mu,\nu)} \mathbf{\Gamma} \Rightarrow \mu = \lambda, \nu = \alpha; \quad (9.60)$$

and that the set of all induced Irreps is complete.

- (i) We demonstrate irreducibility by applying the irreducibility condition (9.40) with $\mathcal{H} = \mathcal{L}_{\Pi}^{(\alpha,1)}$ and $\mathcal{H}^{(k)} \equiv \mathcal{L}_{\Pi}^{(\alpha,\mu)}$, invoking property (9.31) that the intersection $\mathcal{L}_{\Pi}^{(\alpha,1)} \cap \mathcal{L}_{\Pi}^{(\alpha,\mu)}$ is just $\mathcal{N}$, and recognizing that an allowable Irrep subduces only a multiple-direct sum of an Irrep of $\mathcal{N}$. We then get

$$\frac{g}{l_2} \sum_{\mu=2}^{g/l_2} \sum_{N \in \mathcal{N}} {}^{(\alpha)}\chi(N) {}^{(\alpha)}\chi^*(\mathbf{R}_{\mu}^{-1} N \mathbf{R}_{\mu}) = 0,$$

where we made use of the fact that the definition

$${}^{(\alpha,1)}\Delta(\mathbf{R}_{\mu}^{-1} N \mathbf{R}_{\mu}) = {}^{(\alpha,\mu)}\Delta(N) \not\sim {}^{(\alpha,1)}\Delta(N)$$

implies that

$$\sum_{N \in \mathcal{N}} {}^{(\alpha)}\chi(N) {}^{(\alpha)}\chi^*(\mathbf{R}_{\mu}^{-1} N \mathbf{R}_{\mu}) = 0.$$

- (ii) We state without proof that induced Irreps are unique.
 (iii) The completeness of the set of Irreps ${}^{(\lambda,\alpha)}\mathbf{\Gamma}$ induced from Irreps of its normal subgroup Δ is expressed in terms of the dimensionality of the induced Irreps as

$$\sum_{\lambda}^{\text{allowable}} \sum_{\alpha}^{\text{orbits}} d_{\lambda,\alpha}^2 = g. \quad (9.61)$$

We prove this assertion by demonstrating that the sum rule of Irrep dimensions is satisfied. Substituting

$$d_{\lambda, \alpha} = \frac{g}{l_2} d_{\lambda} \left({}^{(\alpha)}\Delta \right) = \frac{g}{l_2} \left\langle {}^{(\lambda)}\Lambda \downarrow \mathcal{N} \left| {}^{(\alpha)}\Delta \right. \right\rangle d_{\alpha}$$

in the r.h.s. of (9.50), and using (9.41) and (9.43), we get

$$\begin{aligned} & \sum_{\lambda}^{\text{allowable}} \sum_{\alpha}^{\text{orbits}} \left(\frac{g}{l_2} \right)^2 d_{\alpha}^2 \left\langle {}^{(\lambda)}\Lambda \downarrow \mathcal{N} \left| {}^{(\alpha)}\Delta \right. \right\rangle^2 \\ &= g^2 \sum_{\alpha}^{\text{orbits}} \left(\frac{d_{\alpha}}{l_2(\alpha)} \right)^2 \sum_{\lambda}^{\text{allowable}} \left\langle {}^{(\lambda)}\Lambda \downarrow \mathcal{N} \left| {}^{(\alpha)}\Delta \right. \right\rangle^2 \\ &= g^2 \sum_{\alpha}^{\text{orbits}} \left(\frac{d_{\alpha}}{l_2(\alpha)} \right)^2 \frac{l_2}{n} \\ &= \frac{g^2}{n} \sum_{\alpha}^{\text{orbits}} \frac{d_{\alpha}^2}{l_2(\alpha)} = g. \end{aligned}$$

Example 9.13

We know from Section 9.1 that subducing a Rep of $\mathcal{C}_3$ from the Irrep ${}^{(3)}\Gamma$ of $\mathcal{C}_{3v}$ gives a reducible Rep that decomposes into the Irreps ${}^{(2)}\Delta$ and ${}^{(3)}\Delta$. We also know from Example 9.7 that ${}^{(2)}\Delta$ and ${}^{(3)}\Delta$ are conjugate Irreps of the subgroup $\mathcal{C}_3$ and thus constitute an orbit of $\mathcal{C}_3$. These two statements conform with the requirements of completeness in (9.57).

9.4.4 Irrep induction procedures based on the method of little-groups

We have labored through some tedium to get to this point. However, we now have all the tools needed for inducing Irreps from normal subgroups and little-groups. The method is outlined as follows:

- (i) Construct the Irreps, ${}^{(\alpha)}\Delta$, of a normal subgroup $\mathcal{N} \triangleleft \mathcal{G}$.
- (ii) Choose one of these Irreps, say ${}^{(\alpha,1)}\Delta$. Then determine the little-group of the second kind, $\mathcal{L}_{\text{II}} \left({}^{(\alpha,1)}\Delta \right)$, which consists of all the elements of $\mathcal{G}$ that map ${}^{(\alpha,1)}\Delta$ onto equivalent Irreps ${}^{(\alpha,i)}\Delta$.
- (iii) Determine the orbit $\mathcal{O} \left({}^{(\alpha,1)}\Delta \right)$.
- (iv) Construct the Irreps, ${}^{(\lambda)}\Lambda$, of $\mathcal{L}_{\text{II}}$: (i) Use Dixon's method, if possible; (ii) otherwise, first determine the little-group of the first kind, $\mathcal{L}_{\text{I}}$, construct its Irreps, the ground Rep relative to $\mathcal{L}_{\text{II}}$. Then, induce the Irreps of $\mathcal{L}_{\text{II}}$ using these tools.

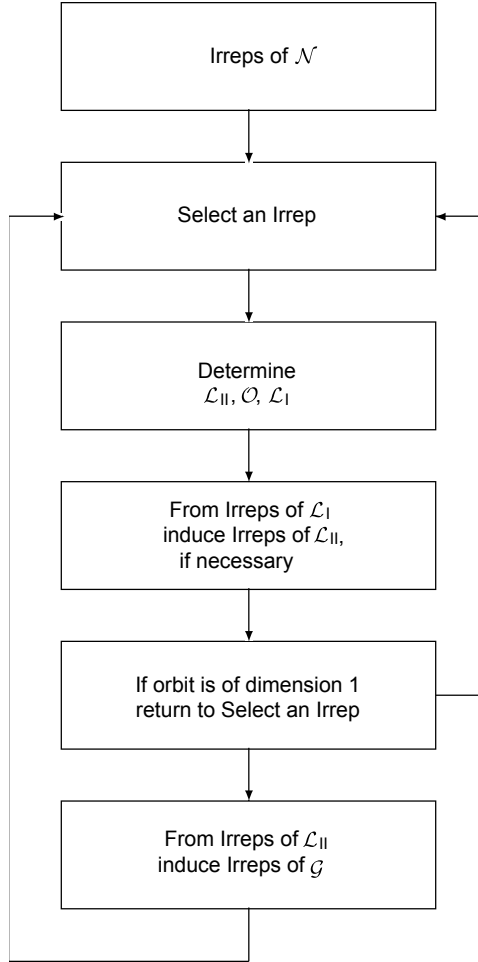


Fig. 9.3. Flow chart for inducing Irreps ($\mathcal{N} \uparrow \mathcal{G}$).

- (v) Determine the frequencies of the subduced Irreps $^{(\lambda)}\mathbf{\Lambda} \downarrow \mathcal{N}$ in the Irreps $\mathbf{\Delta}$ of $\mathcal{N}$. Use these frequencies to determine the allowable Irreps of $\mathcal{L}_{II}$. If $\mathcal{L}_{II} \left(^{(\alpha,1)}\mathbf{\Delta} \right)$ is isomorphic to $\mathcal{G}$, then its Irreps are also the Irreps of $\mathcal{G}$.
- (vi) Repeat steps (2) to (5) for other Irreps $\mathbf{\Delta}$ if they do not appear in the generated orbits, until all these Irreps are exhausted.
- (vii) Otherwise, construct the ground Rep of $\mathcal{L}_{II} \left(^{(\alpha,1)}\mathbf{\Delta} \right)$ with respect to $\mathcal{G}$, and use to induce Irreps $\mathbf{\Gamma}$ of $\mathcal{G}$ from allowable Irreps of $\mathcal{L}_{II} \left(^{(\alpha,1)}\mathbf{\Delta} \right)$. Repeat this step for every orbit.

A flow chart for inducing Irreps is given in Figure 9.3. It will be put to use in the next section.

Comments on the flow chart of Figure 9.3

- If the orbit for a particular Irrep Δ of $\mathcal{N}$ is of dimension 1, the little-group of the second kind, $\mathcal{L}_{\text{II}}$, is isomorphic to the full group $\mathcal{G}$, in which case the Irreps of $\mathcal{L}_{\text{II}}$ are *identical* to the Irreps of $\mathcal{G}$. Thus, the next step in the flow chart is superfluous for orbits of dimension 1, so one simply skips it and returns to select a new Irrep of $\mathcal{N}$ and begin anew.
- If the orbit for a particular Irrep Δ of $\mathcal{N}$ is of dimension greater than 1, it is necessary to generate the ground Rep for the little-group $\mathcal{L}_{\text{I}}$. From this one induces the Irreps of $\mathcal{G}$.

To become familiar with the procedure for inducing Irreps it is useful to work through several examples, which we present in the next section.

9.5 Examples of Irrep induction using the method of little-groups

9.5.1 Example 1: The induced Irrep for $\mathcal{C}_{3v}$

The motivation behind this example is two-fold. First, point-group $\mathcal{C}_{3v}$ is manifested in many representative physical systems, ranging from the ammonia molecule to the site-symmetry of hydrogen atoms on the (111) surface of a face-centered cubic metal. Second, it presents an opportunity to bring together the various fragments associated with this group which were given as examples at different points in this chapter.

Although this introduces a bit of repetition, it consolidates the procedure in one place, where it can be easily used for later reference. The reader might be pleased to find that much of the procedure now seems familiar, and the seemingly disparate parts fit together in a sensible way. The authors hope this is the case; for induced Reps seem to be the most difficult hurdle to overcome in understanding those aspects of group theory necessary for applications to solids.

The multiplication table for $\mathcal{C}_{3v}$ appears in Table 9.4, while that of its normal subgroup $\mathcal{C}_3$ with elements $\{E, C_3^+, C_3^-\}$ as well as its Irreps are reproduced in Tables 9.5 and 9.6, for convenience.

Table 9.4. *Multiplication table for the point-group $\mathcal{C}_{3v}$.*

	E	σ_1	σ_2	σ_3	C_3^+	C_3^-
E	E	σ_1	σ_2	σ_3	C_3^+	C_3^-
σ_1	σ_1	E	C_3^+	C_3^-	σ_2	σ_3
σ_2	σ_2	C_3^-	E	C_3^+	σ_3	σ_1
σ_3	σ_3	C_3^+	C_3^-	E	σ_1	σ_2
C_3^+	C_3^+	σ_3	σ_1	σ_2	C_3^-	E
C_3^-	C_3^-	σ_2	σ_3	σ_1	E	C_3^+

Table 9.5. *Multiplication table for the subgroup $\mathcal{C}_3$.*

	E	C_3^+	C_3^-
E	E	C_3^+	C_3^-
C_3^+	C_3^+	C_3^-	E
C_3^-	C_3^-	E	C_3^+

Table 9.6. *The Irreps of $\mathcal{C}_3$.*

	E	C_3^+	C_3^-
$^{(1)}\Delta$	1	1	1
$^{(2)}\Delta$	1	ω	ω^*
$^{(3)}\Delta$	1	ω^*	ω

Table 9.7. *The conjugate elements of $\mathcal{C}_3$ for all elements of $\mathcal{C}_{3v}$.*

	E	C_3^+	C_3^-	σ_1	σ_2	σ_3
E	E	E	E	E	E	E
C_3^+	C_3^+	C_3^+	C_3^+	C_3^-	C_3^-	C_3^-
C_3^-	C_3^-	C_3^-	C_3^-	C_3^+	C_3^+	C_3^+

We begin by finding, for each element $R \in \mathcal{C}_{3v}$, all the conjugates $R^{-1}NR$ for each element $N \in \mathcal{C}_3$. These conjugate elements are listed in Table 9.7, where the columns are labeled by the elements of $\mathcal{C}_{3v}$ and the rows are labeled by the elements of the normal subgroup $\mathcal{C}_3$. For example, with the help of Table 9.4 the conjugates of $\{E, C_3^+, C_3^-\}$ by σ_2 of the full group $\mathcal{C}_{3v}$ are found to be $\{E, C_3^-, C_3^+\}$. They are listed in the column labeled σ_2 in Table 9.7. Table 9.7 will be useful in constructing Table 9.8.

The first row of the Table 9.8, labeled E , contains the three one-dimensional Irreps of $\mathcal{C}_3$ taken from Table 9.6. These are the conjugate Irreps of $\mathcal{C}_3$ obtained by conjugation with E and its inverse. Of course, conjugation by E changes nothing. Not surprisingly, conjugation by the remaining elements of $\mathcal{C}_3$, namely, C_3^+ and C_3^- also changes nothing: The first three rows of Table 9.8 are identical.

We illustrate the procedure for obtaining the remaining conjugate Irreps using σ_2 as the conjugating element. We consider the effect of conjugation on Irrep $^{(2)}\Delta$.

The matrix representatives of $\{E, C_3^+, C_3^-\}$ for Irrep $^{(2)}\Delta$ are taken from Table 9.6. Now, to obtain the matrix representatives listed in Table 9.8 for the row labeled σ_2 and the major column labeled Irrep $^{(2)}\Delta$, we replace the matrix representatives of the minor columns, labeled E, C_3^+ and C_3^- , in the row labeled σ_2 , by the matrix representatives of the corresponding conjugates $\{E, C_3^-, C_3^+\}$ from $^{(2)}\Delta$ in Table 9.6. Care in maintaining the correct ordering is essential in order to have the correct correspondences.

Table 9.8. The conjugate Irreps of $\mathcal{C}_3$.

	⁽¹⁾ Δ			⁽²⁾ Δ			⁽³⁾ Δ		
	E	C_3^+	C_3^-	E	C_3^+	C_3^-	E	C_3^+	C_3^-
E	1	1	1	1	ω	ω^*	1	ω^*	ω
C_3^+	1	1	1	1	ω	ω^*	1	ω^*	ω
C_3^-	1	1	1	1	ω	ω^*	1	ω^*	ω
σ_1	1	1	1	1	ω^*	ω	1	ω	ω^*
σ_2	1	1	1	1	ω^*	ω	1	ω	ω^*
σ_3	1	1	1	1	ω^*	ω	1	ω	ω^*

The matrix representatives of the conjugates $\{E, C_3^-, C_3^+\}$ for the Irrep $^{(2)}\Delta$ are listed in Table 9.6 as $1, \omega^*, \omega$, respectively. We assign these matrix representatives, in the same order, to the row labeled by σ_2 and the column labeled by Irrep $^{(2)}\Delta$. We find that the Irrep generated by the conjugation is identical to $^{(3)}\Delta$. Thus we have generated a distinct and *inequivalent* Irrep, namely the conjugate Irrep to $^{(2)}\Delta$ by σ_2 , which is the Irrep $^{(3)}\Delta$ of $\mathcal{C}_3$.

Discussion of Table 9.8

The six rows of Table 9.8 give the sets of all conjugate Irreps of $\mathcal{C}_3$. The second row, for instance, consists of the three Irreps $^{(1)}\Delta$, $^{(2)}\Delta$, $^{(3)}\Delta$ that are conjugate by the element C_3^+ of the full group $\mathcal{C}_{3v}$. We see that Irrep $^{(1)}\Delta$ is self-conjugate with respect to all group operations.

By contrast, we find for Irrep $^{(2)}\Delta$ by σ_1 is $^{(3)}\Delta$ that:

- The first three rows of the table contain equivalent Irreps. They are actually *identical* to the original Irreps given in Table 9.6. No unitary transformation is required to show the equivalence. The second set of three rows contains mutually equivalent conjugate Irreps, which are distinct from and inequivalent to the original Irrep.
- When all redundant Irreps are removed, leaving only mutually inequivalent conjugate Irreps, we are left with the *orbits* listed in Table 9.9.
- The row labeled $\mathcal{L}_{II}$ designates the little-group of the second kind for each Irrep. When Irreps conjugate to $^{(1)}\Delta$ are formed, we find that *all* of the elements of the full group $\mathcal{C}_{3v}$ map the Irrep $^{(1)}\Delta$ onto itself. Thus for this Irrep, the little-group $\mathcal{L}_{II}$ consists of the full group $\mathcal{C}_{3v}$. On the other hand, for Irreps $^{(2)}\Delta$ and $^{(3)}\Delta$, only the elements of the normal subgroup $\mathcal{C}_3$ map an Irrep onto itself. Thus here the little-group $\mathcal{L}_{II}$ is just $\mathcal{C}_3$.
- The row labeled $\mathcal{L}_I$ lists the distinct cosets that make up the elements of the little-group $\mathcal{L}_I$ relative to the Irrep designated by the column heading.
- The next row lists the values of g/l_2 , the index of the little-group $\mathcal{L}_{II}$ in the big-group $\mathcal{C}_{3v}$. For Irrep $^{(1)}\Delta$, the little-group $\mathcal{L}_{II}$ and the big-group are identical and the index g/l_2 is 1. For Irreps $^{(2)}\Delta$ and $^{(3)}\Delta$, the little-group consists of the three elements of $\mathcal{C}_3$ and the index is 2.
- The last row gives l_2/n , the index of the normal group in the little-group. Here $\mathcal{N} = \mathcal{C}_3$.

Table 9.9. Summary of conjugations of $\mathcal{C}_3$.

	$^{(1)}\Delta$	$^{(2)}\Delta$	$^{(3)}\Delta$
orbits	$^{(1)}\Delta$	$^{(2)}\Delta, ^{(3)}\Delta$	$^{(3)}\Delta, ^{(2)}\Delta$
$\mathcal{L}_{\text{II}}$	$\mathcal{C}_{3v}$	$\mathcal{C}_3$	$\mathcal{C}_3$
$\mathcal{L}_I$	$\{\mathcal{C}_3, \sigma_1\mathcal{C}_3\}$	E	E
g/l_2	1	2	2
l_2/n	2	1	1

Inducing the Irreps of $\mathcal{C}_{3v}$

We begin by selecting the identity Irrep $^{(1)}\Delta$. We know, from Table 9.9, that the little-group $\mathcal{L}_{\text{II}}$ with respect to $\mathcal{C}_{3v}$ is $\mathcal{C}_{3v}$ itself. Thus the little-group $\mathcal{L}_I$ relative to $^{(1)}\Delta$ is

$$\mathcal{L}_I = \frac{\mathcal{L}_{\text{II}}}{\mathcal{C}_3} = \frac{\mathcal{C}_{3v}}{\mathcal{C}_3}.$$

This little-group has as its group elements the distinct cosets

$$\begin{aligned} E\{E, C_3^+, C_3^-\} &= EC_3 = \{E, C_3^+, C_3^-\}, \\ \sigma_1\{E, C_3^+, C_3^-\} &= \sigma_1\mathcal{C}_3 = \{\sigma_1, \sigma_2, \sigma_3\}. \end{aligned} \quad (9.62)$$

With just two elements and two classes, there are only two one-dimensional Irreps of $\mathcal{L}_I$ relative to $^{(1)}\Delta$. They are given in Table 9.10.

The orbit of $^{(1)}\Delta$ is of dimension 1, so the induced Rep for $\mathcal{C}_{3v}$ will also be one-dimensional, as well as isomorphic with $\mathcal{L}_{\text{II}}$. Thus, starting with the Irrep $^{(+)}\mathbf{A}$ of $\mathcal{L}_I$ we induce the first Irrep of $\mathcal{L}_{\text{II}}$ by assigning to every element of the coset $\mathcal{C}_3$ the matrix representative +1, and to every element of the coset $\sigma_1\mathcal{C}_3$ the matrix representative +1. Now, since $\mathcal{L}_{\text{II}} = \mathcal{C}_{3v}$, relative to $^{(1)}\Delta$, this gives the Irrep $^{(1)}\mathbf{\Gamma}$ of $\mathcal{C}_{3v}$ in Table 9.11, which is just the identical Irrep again.

We induce another Irrep of $\mathcal{C}_{3v}$ by using the Irrep $^{(-)}\mathbf{A}$ and assigning to every element of the coset $\mathcal{C}_3$ the matrix representative +1, and to every element of the coset $\sigma_1\mathcal{C}_3$ the matrix representative -1. This gives the Irrep $^{(2)}\mathbf{\Gamma}$ of $\mathcal{C}_{3v}$ in Table 9.11.

We have obtained all that we can from $^{(1)}\Delta$ of $\mathcal{C}_3$, so we move on to the Irrep $^{(2)}\Delta$, which has a conjugate Irrep $^{(3)}\Delta$. These two inequivalent mutually conjugate Irreps form an orbit which induces a two-dimensional Irrep of $\mathcal{C}_{3v}$. Inducing two-dimensional Irreps requires the use of the ground Rep. The Irreps of the little-group, $\mathcal{L}_{\text{II}} = \mathcal{C}_3$ are already known, so we just need to determine the ground Rep of $\mathcal{G} = \mathcal{C}_{3v}$ by $\mathcal{C}_3$.

Table 9.10. The Irreps of $\mathcal{L}_1 = \mathcal{C}_{3v}$.

	EC_3	$\sigma_1 C_3$
$(+)\mathbf{\Lambda}$	1	1
$(-)\mathbf{\Lambda}$	1	-1

Table 9.11. Irreps of $\mathcal{C}_{3v}$.

	E	C_3^+	C_3^-	σ_1	σ_2	σ_3
$(1)\mathbf{\Gamma}$	1	1	1	1	1	1
$(2)\mathbf{\Gamma}$	1	1	1	-1	-1	-1

The full group $\mathcal{C}_{3v}$ can be expanded in left cosets as before:

$$\mathcal{C}_{3v} = E\{E, C_3^+, C_3^-\} + \sigma_1\{E, C_3^+, C_3^-\},$$

where E and σ_1 are the coset representatives. A typical modified ground representative is found as follows:

$$\mathbf{M}^*(C_3^+) \sim \begin{pmatrix} EC_3^+ E & EC_3^+ \sigma_1 \\ \sigma_1 C_3^+ E & \sigma_1 C_3^+ \sigma_1 \end{pmatrix} = \begin{pmatrix} C_3^+ & \sigma_3 \neq N \\ \sigma_2 \neq N & C_3^- \end{pmatrix} \Rightarrow \begin{pmatrix} C_3^+ & 0 \\ 0 & C_3^- \end{pmatrix}.$$

Continuing in this fashion, we obtain the complete set of modified ground representatives

$$\begin{aligned} \mathbf{M}^*(E) &= \begin{pmatrix} E & 0 \\ 0 & E \end{pmatrix}, & \mathbf{M}^*(C_3^+) &= \begin{pmatrix} C_3^+ & 0 \\ 0 & C_3^- \end{pmatrix}, \\ \mathbf{M}^*(C_3^-) &= \begin{pmatrix} C_3^- & 0 \\ 0 & C_3^+ \end{pmatrix}, & \mathbf{M}^*(\sigma_1) &= \begin{pmatrix} 0 & E \\ E & 0 \end{pmatrix}, \\ \mathbf{M}^*(\sigma_2) &= \begin{pmatrix} 0 & C_3^- \\ C_3^+ & 0 \end{pmatrix}, & \mathbf{M}^*(\sigma_3) &= \begin{pmatrix} 0 & C_3^+ \\ C_3^- & 0 \end{pmatrix}. \end{aligned} \quad (9.63)$$

We now have all we need to induce the remaining Irrep $(3)\mathbf{\Gamma}$ of $\mathcal{C}_{3v}$, which we can express as

$$(3)\mathbf{\Gamma}(R) = \sum_{N \in \mathcal{C}_3} \mathbf{M}^*(R) (2)\mathbf{\Delta}(N). \quad (9.64)$$

Now we replace the elements of $\mathcal{C}_3$ in the ground representatives by the appropriate matrix representatives of $^{(2)}\Delta$. For example,

$$\begin{aligned}
 {}^{(3)}\Gamma(\sigma_2) &= \sum_{N \in \mathcal{C}_3} \mathbf{M}^*(\sigma_2) {}^{(2)}\Delta(N) \\
 &= \sum_{N \in \mathcal{C}_3} \begin{pmatrix} 0 & C_3^- \\ C_3^+ & 0 \end{pmatrix} \Delta(N) \\
 &= \begin{pmatrix} 0 & {}^{(2)}\Delta(C_3^-) \\ {}^{(2)}\Delta(C_3^+) & 0 \end{pmatrix} = \begin{pmatrix} 0 & \omega^* \\ \omega & 0 \end{pmatrix}.
 \end{aligned} \tag{9.65}$$

Continuing the process, we would find the two-dimensional Irrep of $\mathcal{C}_{3v}$ to be exactly the same Irrep as ${}^{(3)}\Gamma$ listed in Table 9.1. We have *induced* the Irreps of $\mathcal{C}_{3v}$!

9.5.2 Example 2: induced Irreps for $\mathcal{C}_{4v}$

It is instructive to repeat the process of inducing Irreps using the somewhat larger point-group $\mathcal{C}_{4v}$, which is, for example, characteristic of all (100) surfaces of a cubic crystalline structure.

The symmetry operations of $\mathcal{C}_{4v}$ are shown in Figure 9.4, and their multiplication table given in Table 9.12. $\mathcal{C}_{4v}$ has five and three normal subgroups of orders 2 and 4, respectively. It can only be constructed as a semidirect product since the intersections among all its normal subgroups contain more than just E !

The Irreps of the normal subgroup $\mathcal{C}_4 = \{E, C_2, C_4^+, C_4^-\}$ are listed in Table 9.13.

The distinct cosets for $\mathcal{C}_{4v}$ are

$$E\mathcal{C}_4 = \{E, C_2, C_4^+, C_4^-\}, \quad \sigma_v^1\mathcal{C}_4 = \{\sigma_v^1, \sigma_v^2, \sigma_d^1, \sigma_d^2\}. \tag{9.66}$$

The factor group $\mathcal{C}_{4v}/\mathcal{C}_4$ is isomorphic with $\mathcal{C}_s$, its one-dimensional Irreps are given in Table 9.14.

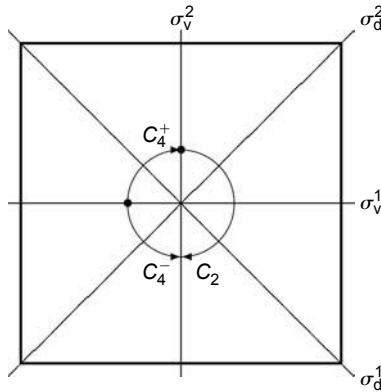


Fig. 9.4. Symmetry operations of $\mathcal{C}_{4v}$.

Table 9.12. *Multiplication table for the point-group $\mathcal{C}_{4v}$.*

	E	C_2	C_4^+	C_4^-	σ_v^1	σ_v^2	σ_d^1	σ_d^2
E	E	C_2	C_4^+	C_4^-	σ_v^1	σ_v^2	σ_d^1	σ_d^2
C_2	C_2	E	C_4^-	C_4^+	σ_v^2	σ_v^1	σ_d^2	σ_d^1
C_4^+	C_4^+	C_4^-	C_2	E	σ_d^1	σ_d^2	σ_v^1	σ_v^2
C_4^-	C_4^-	C_4^+	E	C_2	σ_d^2	σ_d^1	σ_v^2	σ_v^1
σ_v^1	σ_v^1	σ_v^2	σ_d^2	σ_d^1	E	C_2	C_4^-	C_4^+
σ_v^2	σ_v^2	σ_v^1	σ_d^1	σ_d^2	C_2	E	C_4^+	C_4^-
σ_d^1	σ_d^1	σ_d^2	σ_v^1	σ_v^2	C_4^+	C_4^-	E	C_2
σ_d^2	σ_d^2	σ_d^1	σ_v^2	σ_v^1	C_4^-	C_4^+	C_2	E

Table 9.13. *Irreps of $\mathcal{C}_4$.*

	E	C_2	C_4^+	C_4^-
$^{(1)}\Delta$	1	1	1	1
$^{(2)}\Delta$	1	1	-1	-1
$^{(3)}\Delta$	1	-1	i	$-i$
$^{(4)}\Delta$	1	-1	$-i$	i

Table 9.14. *The Irreps of $\mathcal{L}_1 = \mathcal{C}_{4v}/\mathcal{C}_4$.*

	EC_4	$\sigma_v^1 C_4$
$^{(+)}\Lambda$	1	1
$^{(-)}\Lambda$	1	-1

Table 9.15. *The conjugate elements of $\mathcal{C}_4$ for all elements of $\mathcal{C}_{4v}$.*

	E	C_2	C_4^+	C_4^-	σ_v^1	σ_v^2	σ_d^1	σ_d^2
E	E	E	E	E	E	E	E	E
C_2	C_2	C_2	C_2	C_2	C_2	C_2	C_2	C_2
C_4^+	C_4^+	C_4^+	C_4^+	C_4^+	C_4^-	C_4^-	C_4^-	C_4^-
C_4^-	C_4^-	C_4^-	C_4^-	C_4^-	C_4^+	C_4^+	C_4^+	C_4^+

We now obtain the conjugations $R^{-1}NR$, $\forall R \in \mathcal{C}_{4v}$, for each element $N \in \mathcal{C}_4$. These conjugate elements are listed in Table 9.15, where the columns are labeled by the elements of $\mathcal{C}_{4v}$ and the rows are labeled by the elements of the normal subgroup $\mathcal{C}_4$. We observe that conjugations by the elements of the normal subgroup $\mathcal{C}_4$ change nothing, while those effected by the σ s interchange the elements C_4^+ and C_4^- .

Next, we construct the conjugate Irreps for each Irrep of $\mathcal{C}_4$ listed in Table 9.13, using all elements $R \in \mathcal{C}_{4v}$, which we list in Table 9.16. Following the results of Table 9.15, we find that the first four rows of Table 9.16 are identical copies of the original four Irreps of $\mathcal{C}_4$ listed in Table 9.13, while the remaining rows reflect the action of interchanging C_4^+ and C_4^- under conjugation.

C_4^+ and C_4^- have the same matrix representatives in both Irreps $^{(1)}\Delta$ and $^{(2)}\Delta$, so the interchange of C_4^+ and C_4^- has no effect. Conjugation changes nothing, so all the rows of $^{(1)}\Delta$ and $^{(2)}\Delta$ in Table 9.16 are identical. Both Irreps have $\mathcal{L}_{II} = \mathcal{C}_{4v}$, and $\mathcal{L}_I = \mathcal{C}_{4v}/\mathcal{C}_4$.

On the other hand, the representatives of C_4^+ and C_4^- in the Irreps $^{(3)}\Delta$ and $^{(4)}\Delta$ are of opposite sign, so conjugation by σ interchanges the matrix representatives for these Irreps, leading to the interchange of i and $-i$ in the rows of Table 9.16 labeled by a σ . Both Irreps have $\mathcal{L}_{II} = \mathcal{C}_4$.

We are now ready to induce the Irreps for $\mathcal{C}_{4v}$. For one-dimensional ground Reps, the induction rule for one-dimensional Irreps can be simply expressed, for an element R ,

Table 9.16. *The conjugate Irreps of $\mathcal{C}_4$.*

	$^{(1)}\Delta$				$^{(2)}\Delta$				$^{(3)}\Delta$				$^{(4)}\Delta$			
	E	C_2	C_4^+	C_4^-	E	C_2	C_4^+	C_4^-	E	C_2	C_4^+	C_4^-	E	C_2	C_4^+	C_4^-
E	1	1	1	1	1	1	-1	-1	1	-1	i	$-i$	1	-1	$-i$	i
C_2	1	1	1	1	1	1	-1	-1	1	-1	i	$-i$	1	-1	$-i$	i
C_4^+	1	1	1	1	1	1	-1	-1	1	-1	i	$-i$	1	-1	$-i$	i
C_4^-	1	1	1	1	1	1	-1	-1	1	-1	i	$-i$	1	-1	$-i$	i
σ_v^1	1	1	1	1	1	1	-1	-1	1	-1	$-i$	i	1	-1	i	$-i$
σ_v^2	1	1	1	1	1	1	-1	-1	1	-1	$-i$	i	1	-1	i	$-i$
σ_d^1	1	1	1	1	1	1	-1	-1	1	-1	$-i$	i	1	-1	i	$-i$
σ_d^2	1	1	1	1	1	1	-1	-1	1	-1	$-i$	i	1	-1	i	$-i$

Table 9.17. *Summary of conjugation results of $\mathcal{C}_4$.*

	$^{(1)}\Delta$	$^{(2)}\Delta$	$^{(3)}\Delta$	$^{(4)}\Delta$
orbits	$^{(1)}\Delta$	$^{(2)}\Delta$	$^{(3)}\Delta, ^{(4)}\Delta$	$^{(4)}\Delta, ^{(3)}\Delta$
$\mathcal{L}_{II}$	$\mathcal{C}_{4v}$	$\mathcal{C}_{4v}$	$\mathcal{C}_4$	$\mathcal{C}_4$
$\mathcal{L}_I$	$\{\mathcal{C}_4, \sigma_v^1 \mathcal{C}_4\}$	$\{\mathcal{C}_4, \sigma_v^1 \mathcal{C}_4\}$	E	E
g/l_2	1	1	2	2
l_2/n	2	2	1	1

belonging to coset $R_j\mathcal{C}_4$, i.e. $R = R_jN_k$, $N_k \in \mathcal{C}_4$, as

$$^{(i,l)}\mathbf{\Gamma}(R) = {}^{(i)}\mathbf{\Lambda}(R_j\mathcal{C}_4)^{(l)}\mathbf{\Delta}(N_k). \quad (9.67)$$

- (i) **Inductions** $^{(1)}\mathbf{\Delta} \uparrow \mathcal{C}_{4v}$ We start by inducing Irreps of $\mathcal{C}_{4v}$ based on the $^{(\pm)}\mathbf{\Lambda}$ Irreps of the little-group $\mathcal{L}_I(^{(1)}\mathbf{\Delta})$ of Table 9.14. For $^{(+)}\mathbf{\Lambda}$, we assign +1 as the matrix representative for every element of the coset $EN = \mathcal{C}_4 = \{E, C_2, C_4^+, C_4^-\}$ and also for every element of the coset $\sigma_v^1\mathcal{N} = \sigma_1\mathcal{C}_4 = \{\sigma_v^1, \sigma_v^2, \sigma_d^2, \sigma_d^1\}$. This gives us the Irrep $^{(+,1)}\mathbf{\Gamma}$, labeled $^{(1)}\mathbf{\Gamma}$ in Table 9.18. We have mapped the matrix representatives of the *cosets*, which are the elements of the little-group $\mathcal{L}_I$ with Irrep $^{(+)}\mathbf{\Lambda}$, onto the matrix representatives of *elements of the cosets*.

Repeating the process, this time with Irrep $^{(-)}\mathbf{\Lambda}$, we assign +1 as the representative for every element of the coset $EN = \mathcal{C}_4 = \{E, C_2, C_4^+, C_4^-\}$, as before, but we assign -1 as the representative for every element of the coset $\sigma_v^1\mathcal{N} = \sigma_v^1\mathcal{C}_4 = \{\sigma_v^1, \sigma_v^2, \sigma_d^2, \sigma_d^1\}$. This gives the Irrep $^{(-,1)}\mathbf{\Gamma}$, labeled $^{(2)}\mathbf{\Gamma}$ in Table 9.18.

We have exhausted what can be done with induced Irreps based on $^{(1)}\mathbf{\Delta}$ of the subgroup $\mathcal{C}_4$.

- (ii) **Inductions** $^{(2)}\mathbf{\Delta} \uparrow \mathcal{C}_{4v}$ We start with the Irrep $^{(+)}\mathbf{\Lambda}$ of Table 9.13, which has +1 for its representatives. We still follow the rule (9.67), since the ground Rep is of dimension 1. Thus, we take the representatives from $^{(2)}\mathbf{\Delta}$ and multiply by +1 for every element of the coset $\{E, C_2, C_4^+, C_4^-\}$. Then we repeat the process for this Irrep by taking as a representative for each element of the coset $\{\sigma_v^1, \sigma_v^2, \sigma_d^2, \sigma_d^1\}$ the product of +1 and, for each *element* in the coset, the representative of the *corresponding element* in the coset $\{E, C_2, C_4^+, C_4^-\}$. This gives us the Irrep $^{(+,2)}\mathbf{\Gamma}$, labeled $^{(3)}\mathbf{\Gamma}$ in Table 9.18.

Staying with Irrep $^{(2)}\mathbf{\Delta}$ of $\mathcal{C}_4$, we now take the Irrep $^{(-)}\mathbf{\Lambda}$ of Table 9.14, which has +1 for the representative of the coset EC_4 and -1 for the representative of the coset $\sigma_1\mathcal{C}_4$. Thus, we take the representatives from $^{(2)}\mathbf{\Delta}$ and multiply by +1 for every element of the coset $\{E, C_2, C_4^+, C_4^-\}$. Then we repeat the process for this Irrep by taking as a representative for each element of the coset $\{\sigma_v^1, \sigma_v^2, \sigma_d^2, \sigma_d^1\}$ the product of -1 and, for each *element* in the coset, the representative of the *corresponding element* in the coset $\{E, C_2, C_4^+, C_4^-\}$. The bookkeeping requires some care to ensure that one correctly maps corresponding elements. This gives us the Irrep $^{(-,2)}\mathbf{\Gamma}$, labeled $^{(4)}\mathbf{\Gamma}$ in Table 9.18.

We have now found all the one-dimensional Irreps of $\mathcal{C}_{4v}$. Since the group $\mathcal{C}_{4v}$ has five classes, and thus five Irreps, we know we need to induce one more Irrep.

Table 9.18. *The one-dimensional induced Irreps for $\mathcal{C}_{4v}$.*

	E	C_2	C_4^+	C_4^-	σ_v^1	σ_v^2	σ_d^1	σ_d^2
$^{(1)}\mathbf{\Gamma}$	1	1	1	1	1	1	1	1
$^{(2)}\mathbf{\Gamma}$	1	1	1	1	-1	-1	-1	-1
$^{(3)}\mathbf{\Gamma}$	1	1	-1	-1	1	1	-1	-1
$^{(4)}\mathbf{\Gamma}$	1	1	-1	-1	-1	-1	1	1

We also know it must be two-dimensional in order to satisfy the requirement that $\sum_{\alpha}^{(\alpha)} d^2 = 8$, where 8 is the number of elements in the group.

- (iii) **Inductions** $^{(3,4)}\Delta \uparrow \mathcal{C}_{4v}$ The two-dimensional Irrep is found by inducing, from $^{(3)}\Delta$ and $^{(4)}\Delta$, the two inequivalent conjugate Reps that form an orbit of dimension 2 and thus induce a two-dimensional Irrep of $\mathcal{C}_{4v}$. As before, we use the recipe of the modified ground Rep, which has conjugation built into the method, and which gives us

$$\begin{aligned}
 \mathbf{M}^*(E) &= \begin{pmatrix} E & 0 \\ 0 & E \end{pmatrix}, & \mathbf{M}^*(C_2) &= \begin{pmatrix} C_2 & 0 \\ 0 & C_2 \end{pmatrix}, \\
 \mathbf{M}^*(C_4^+) &= \begin{pmatrix} C_4^+ & 0 \\ 0 & C_4^- \end{pmatrix}, & \mathbf{M}^*(C_4^-) &= \begin{pmatrix} C_4^- & 0 \\ 0 & C_4^+ \end{pmatrix}, \\
 \mathbf{M}^*(\sigma_v^1) &= \begin{pmatrix} 0 & E \\ E & 0 \end{pmatrix}, & \mathbf{M}^*(\sigma_v^2) &= \begin{pmatrix} 0 & C_2 \\ C_2 & 0 \end{pmatrix}, \\
 \mathbf{M}^*(\sigma_d^1) &= \begin{pmatrix} 0 & C_4^+ \\ C_4^- & 0 \end{pmatrix}, & \mathbf{M}^*(\sigma_d^2) &= \begin{pmatrix} 0 & C_4^- \\ C_4^+ & 0 \end{pmatrix}.
 \end{aligned} \tag{9.68}$$

One now finds the induced two-dimensional Irrep by replacing the matrix elements of $\mathbf{M}^*$ by the corresponding representative $^{(3)}\Delta(N)$. This procedure give us the two-dimensional Irrep of Table 9.19.

Table 9.19. *The two-dimensional induced Irrep $^{(5)}\Gamma$ for $\mathcal{C}_{4v}$.*

$^{(5)}\Gamma(E)$	$= \begin{pmatrix} ^{(3)}\Delta(E) & 0 \\ 0 & ^{(3)}\Delta(E) \end{pmatrix}$	$= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$
$^{(5)}\Gamma(C_2)$	$= \begin{pmatrix} ^{(3)}\Delta(C_2) & 0 \\ 0 & ^{(3)}\Delta(C_2) \end{pmatrix}$	$= \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$
$^{(5)}\Gamma(C_4^+)$	$= \begin{pmatrix} ^{(3)}\Delta(C_4^+) & 0 \\ 0 & ^{(3)}\Delta(C_4^-) \end{pmatrix}$	$= \begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix}$
$^{(5)}\Gamma(C_4^-)$	$= \begin{pmatrix} ^{(3)}\Delta(C_4^-) & 0 \\ 0 & ^{(3)}\Delta(C_4^+) \end{pmatrix}$	$= \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix}$
$^{(5)}\Gamma(\sigma_v^1)$	$= \begin{pmatrix} 0 & ^{(3)}\Delta(E) \\ ^{(3)}\Delta(E) & 0 \end{pmatrix}$	$= \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$
$^{(5)}\Gamma(\sigma_v^2)$	$= \begin{pmatrix} 0 & ^{(3)}\Delta(C_2) \\ ^{(3)}\Delta(C_2) & 0 \end{pmatrix}$	$= \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$
$^{(5)}\Gamma(\sigma_d^1)$	$= \begin{pmatrix} 0 & ^{(3)}\Delta(C_4^+) \\ ^{(3)}\Delta(C_4^-) & 0 \end{pmatrix}$	$= \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix}$
$^{(5)}\Gamma(\sigma_d^2)$	$= \begin{pmatrix} 0 & ^{(3)}\Delta(C_4^-) \\ ^{(3)}\Delta(C_4^+) & 0 \end{pmatrix}$	$= \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$

A key point With a slightly different approach, we could have, for example, arrived at the result

$${}^{(5)}\Gamma(C_4^+) = \begin{pmatrix} {}^{(3)}\Delta(C_4^+) & 0 \\ 0 & {}^{(4)}\Delta(C_4^+) \end{pmatrix}$$

rather than

$${}^{(5)}\Gamma(C_4^+) = \begin{pmatrix} {}^{(3)}\Delta(C_4^+) & 0 \\ 0 & {}^{(3)}\Delta(C_4^-) \end{pmatrix},$$

as given in Table 9.19. The former makes it explicitly clear that induction depends on *both* conjugate Irreps of Δ . It emphasizes the role of conjugate Irreps, but it loses some of its appeal with the necessity to be more careful in the bookkeeping as to which element is from which conjugate Irrep. The approach we have taken leaves no ambiguity in the process.

Appendix Frobenius reciprocity theorem and other useful theorems

The following theorems and their proofs are adopted from reference [12]. We start with theorems relating frequencies of Reps of a group and its subgroups. The most important among them is the *reciprocity theorem* of Frobenius. This is a very powerful theorem since it relates the frequency in the group to that in the subgroup.

Theorem 1: Frequency for induced Reps *The frequency of the invariant Irrep ${}^{(1)}\Gamma$ of $\mathcal{G}$ in the induced Rep $\Sigma \uparrow \mathcal{G}$ equals that of the invariant Irrep ${}^{(1)}\Sigma$ of $\mathcal{H}$ in Σ :*

$$\left\langle \Sigma \uparrow \mathcal{G} \middle| {}^{(1)}\Gamma \right\rangle = \left\langle \Sigma \middle| {}^{(1)}\Sigma \right\rangle. \quad (9.69)$$

Proof

$$\begin{aligned} \left\langle \Sigma \uparrow \mathcal{G} \middle| {}^{(1)}\Gamma \right\rangle &= \frac{1}{g} \sum_R \chi(R | \Sigma \uparrow \mathcal{G}) \\ &= \frac{1}{g} \sum_R \sum_{i=1}^{g/h} \chi(\mathbf{R}_i^{-1} R \mathbf{R}_i | \Sigma), \quad \mathbf{R}_i^{-1} R \mathbf{R}_i \in \mathcal{H} \end{aligned}$$

We now rewrite the restriction on the sum, $\mathbf{R}_i^{-1} R \mathbf{R}_i \in \mathcal{H}$, as

$$R = \mathbf{R}_i H \mathbf{R}_i^{-1},$$

so that, if we fix i , every $H \in \mathcal{H}$ will contribute a nonzero term to the sum, and we get

$$\begin{aligned} \left\langle \Sigma \uparrow \mathcal{G} \middle| {}^{(1)}\Gamma \right\rangle &= \frac{1}{g} \sum_{i=1}^{g/h} \sum_H \chi(\mathbf{R}_i^{-1} \mathbf{R}_i H \mathbf{R}_i^{-1} | \Sigma) \\ &= \frac{1}{g} \frac{g}{h} \sum_H \chi(H | \Sigma) = \left\langle \Sigma \middle| {}^{(1)}\Sigma \right\rangle. \end{aligned}$$

Theorem 2: The equivalence theorem *The inner product of a Rep Γ of $\mathcal{G}$ with a Rep of $\mathcal{G}$ induced from a Rep Σ of its subgroup $\mathcal{H}$, is equivalent to a Rep of $\mathcal{G}$ induced from the inner product of Σ and the subduced Rep $\Gamma \downarrow \mathcal{H}$:*

$$\Gamma \boxtimes (\Sigma \uparrow \mathcal{G}) \sim [(\Gamma \downarrow \mathcal{H}) \boxtimes \Sigma] \uparrow \mathcal{G}$$

or,

$$\chi(R|\Gamma \boxtimes (\Sigma \uparrow \mathcal{G})) = \chi(R|\{\Gamma \downarrow \mathcal{H} \boxtimes \Sigma\} \uparrow \mathcal{G}). \quad (9.70)$$

Proof Using (9.31) and (9.16) we write the l.h.s. of (9.56) as

$$\begin{aligned} \chi(R|\Gamma \boxtimes (\Sigma \uparrow \mathcal{G})) &= \chi(R|\Gamma) \chi(R|\Sigma \uparrow \mathcal{G}) \\ &= \chi(R|\Gamma) \sum_i' \chi(\mathbf{R}_i^{-1} R \mathbf{R}_i|\Sigma), \end{aligned}$$

and we also use

$$\chi(H|\{\Gamma \downarrow \mathcal{H}\} \boxtimes \Sigma) = \chi(H|\Sigma) \chi(H|\Gamma \downarrow \mathcal{H})$$

to write the r.h.s. as

$$\begin{aligned} \chi(R|[\Gamma \downarrow \mathcal{H} \boxtimes \Sigma] \uparrow \mathcal{G}) &= \sum_i' \chi(\mathbf{R}_i^{-1} R \mathbf{R}_i|[\Gamma \downarrow \mathcal{H}] \boxtimes \Sigma) \\ &= \sum_i' \chi(\mathbf{R}_i^{-1} R \mathbf{R}_i|[\Gamma \downarrow \mathcal{H}]) \chi(\mathbf{R}_i^{-1} R \mathbf{R}_i|\Sigma). \end{aligned}$$

Since the prime expresses the restriction $\mathbf{R}_i^{-1} R \mathbf{R}_i = H_R^i \in \mathcal{H}$, and the subduction confines the Γ Rep matrices to those of $H \in \mathcal{H}$, we write

$$\chi(R|[\Gamma \downarrow \mathcal{H} \boxtimes \Sigma] \uparrow \mathcal{G}) = \sum_i' \chi(\mathbf{R}_i^{-1} R \mathbf{R}_i|\Gamma) \chi(\mathbf{R}_i^{-1} R \mathbf{R}_i|\Sigma),$$

and since $\mathbf{R}_i^{-1} R \mathbf{R}_i$ is in the same class of $\mathcal{G}$ as R , then

$$\chi(\mathbf{R}_i^{-1} R \mathbf{R}_i|\Gamma) = \chi(R|\Gamma),$$

and we obtain

$$\chi(R|[\Gamma \downarrow \mathcal{H} \boxtimes \Sigma] \uparrow \mathcal{G}) = \chi(R|\Gamma) \sum_i' \chi(R_i^{-1} R R_i|\Sigma).$$

Theorem 3: *The frequency of an Irrep $^{(\mu)}\Gamma$ in a Rep Γ is equal to the frequency of the invariant Irrep in the inner product of $^{(\mu)}\Gamma$ and the conjugate Rep Γ^* .*

$$\begin{aligned} \left\langle \Gamma \middle| ^{(\mu)}\Gamma \right\rangle &= \left\langle ^{(\mu)}\Gamma^* \boxtimes \Gamma \middle| ^{(1)}\Gamma \right\rangle \\ &= \left\langle ^{(\mu)}\Gamma \boxtimes \Gamma^* \middle| ^{(1)}\Gamma \right\rangle. \end{aligned} \quad (9.71)$$

Proof

$$\begin{aligned} \left\langle ^{(\mu)}\Gamma^* \boxtimes \Gamma \middle| ^{(1)}\Gamma \right\rangle &= \frac{1}{g} \sum_R ^{(1)}\chi^*(R) \chi(R| ^{(\mu)}\Gamma^* \boxtimes \Gamma) \\ &= \frac{1}{g} \sum_R ^{(\mu)}\chi^*(R) \chi(R) \\ &= \left\langle \Gamma \middle| ^{(\mu)}\Gamma \right\rangle, \end{aligned}$$

since $^{(1)}\chi^*(R) = 1, \forall R$.

Theorem 4: Frobenius reciprocity theorem

$$\left\langle \left(^{(\sigma)}\Sigma \uparrow \mathcal{G} \right) \middle| ^{(\mu)}\Gamma \right\rangle = \left\langle \left(^{(\mu)}\Gamma \downarrow \mathcal{H} \right) \middle| ^{(\sigma)}\Sigma \right\rangle. \quad (9.72)$$

The frequency of $^{(\mu)}\Gamma$ in the induced Rep $\left(^{(\sigma)}\Sigma \uparrow \mathcal{G} \right)$ is equal to the frequency of $^{(\sigma)}\Sigma$ in the subduced Rep $\left(^{(\mu)}\Gamma \downarrow \mathcal{H} \right)$.

Proof Using (9.57), then (9.56), we obtain

$$\begin{aligned} \left\langle ^{(\sigma)}\Sigma \uparrow \mathcal{G} \middle| ^{(\mu)}\Gamma \right\rangle &= \left\langle ^{(\mu)}\Gamma^* \boxtimes \left(^{(\alpha)}\Sigma \uparrow \mathcal{G} \right) \middle| ^{(1)}\Gamma \right\rangle \\ &= \left\langle \left[\left(^{(\mu)}\Gamma^* \downarrow \mathcal{H} \right) \boxtimes ^{(\sigma)}\Sigma \right] \uparrow \mathcal{G} \middle| ^{(1)}\Gamma \right\rangle, \end{aligned}$$

and since the Rep

$$\left({}^{(\mu)}\Gamma^* \downarrow \mathcal{H} \right) \boxtimes {}^{(\sigma)}\Sigma \equiv {}^{(\alpha)}\Sigma \boxtimes \left({}^{(\mu)}\Gamma^* \downarrow \mathcal{H} \right)$$

is a Rep of $\mathcal{H}$, the corresponding invariant Irrep is just ${}^{(1)}\Sigma$; then according to (9.55) we get

$$\left\langle {}^{(\alpha)}\Sigma \uparrow \mathcal{G} \left| {}^{(\mu)}\Gamma \right. \right\rangle = \left\langle {}^{(\alpha)}\Sigma \boxtimes \left({}^{(\mu)}\Gamma^* \downarrow \mathcal{H} \right) \left| {}^{(1)}\Sigma \right. \right\rangle.$$

Using (9.57) in reverse we finally get

$$\left\langle {}^{(\alpha)}\Sigma \uparrow \mathcal{G} \left| {}^{(\mu)}\Gamma \right. \right\rangle = \left\langle {}^{(\mu)}\Gamma \downarrow \mathcal{H} \left| {}^{(\alpha)}\Sigma \right. \right\rangle.$$

Theorem 5: Transitivity of induction and subduction

Given $\mathcal{M} \subset \mathcal{H} \subset \mathcal{G}$, then

$$(\mathbf{\Omega} \uparrow \mathcal{H}) \uparrow \mathcal{G} \sim (\mathbf{\Omega} \uparrow \mathcal{G}), \quad (9.73)$$

$$(\mathbf{\Omega} \downarrow \mathcal{H}) \downarrow \mathcal{G} \sim (\mathbf{\Omega} \downarrow \mathcal{G}), \quad (9.74)$$

where $\mathbf{\Omega}$ is an Irrep of $\mathcal{M}$.

Proof We show that

$$\left\langle \mathbf{\Omega} \uparrow \mathcal{H} \uparrow \mathcal{G} \left| {}^{(\mu)}\Gamma \right. \right\rangle = \left\langle \mathbf{\Omega} \uparrow \mathcal{G} \left| {}^{(\mu)}\Gamma \right. \right\rangle.$$

$$\begin{aligned} \left\langle \mathbf{\Omega} \uparrow \mathcal{G} \left| {}^{(\mu)}\Gamma \right. \right\rangle &= \left\langle {}^{(\mu)}\Gamma^* \boxtimes (\mathbf{\Omega} \uparrow \mathcal{G}) \left| {}^{(1)}\Gamma \right. \right\rangle \\ &= \left\langle \left[\left({}^{(\mu)}\Gamma^* \downarrow \mathcal{M} \right) \boxtimes \mathbf{\Omega} \right] \uparrow \mathcal{G} \left| {}^{(1)}\Gamma \right. \right\rangle \\ &= \left\langle \left({}^{(\mu)}\Gamma^* \downarrow \mathcal{M} \right) \boxtimes \mathbf{\Omega} \left| {}^{(1)} \left[\left({}^{(\mu)}\Gamma \downarrow \mathcal{M} \right) \boxtimes \mathbf{\Omega} \right] \right. \right\rangle \\ &= \left\langle \left({}^{(\mu)}\Gamma^* \downarrow \mathcal{M} \right) \boxtimes \mathbf{\Omega} \left| {}^{(1)}\mathbf{\Omega} \right. \right\rangle. \end{aligned}$$

$$\begin{aligned} \left\langle (\mathbf{\Omega} \uparrow \mathcal{H}) \uparrow \mathcal{G} \left| {}^{(\mu)}\Gamma \right. \right\rangle &= \left\langle {}^{(\mu)}\Gamma^* \boxtimes [(\mathbf{\Omega} \uparrow \mathcal{H}) \uparrow \mathcal{G}] \left| {}^{(1)}\Gamma \right. \right\rangle \\ &= \left\langle \left[\left({}^{(\mu)}\Gamma^* \downarrow \mathcal{H} \right) \boxtimes (\mathbf{\Omega} \uparrow \mathcal{H}) \right] \uparrow \mathcal{G} \left| {}^{(1)}\Gamma \right. \right\rangle \end{aligned}$$

since $\left({}^{(\mu)}\Gamma^* \downarrow \mathcal{H} \right) \boxtimes (\Omega \uparrow \mathcal{H})$ is a Rep of $\mathcal{H}$, the corresponding invariant Irrep is just ${}^{(1)}\Sigma$, and according to (9.55) we have

$$\begin{aligned} \left\langle (\Omega \uparrow \mathcal{H}) \uparrow \mathcal{G} \left| {}^{(\mu)}\Gamma \right. \right\rangle &= \left\langle \left({}^{(\mu)}\Gamma^* \downarrow \mathcal{H} \right) \boxtimes (\Omega \uparrow \mathcal{H}) \left| {}^{(1)}\Sigma \right. \right\rangle \\ &= \left\langle \left[\left({}^{(\mu)}\Gamma^* \downarrow \mathcal{H} \right) \downarrow \mathcal{M} \boxtimes \Omega \right] \uparrow \mathcal{H} \left| {}^{(1)}\Sigma \right. \right\rangle \\ &= \left\langle \left[\left({}^{(\mu)}\Gamma^* \downarrow \mathcal{M} \right) \boxtimes \Omega \right] \uparrow \mathcal{H} \left| {}^{(1)}\Sigma \right. \right\rangle \\ &= \left\langle \left({}^{(\mu)}\Gamma^* \downarrow \mathcal{M} \right) \boxtimes \Omega \left| {}^{(1)}\Omega \right. \right\rangle. \end{aligned}$$

Exercises

- 9.1 Show explicitly that the set of matrices $\mathbf{M}^*$ in (9.12) obeys the group multiplication table for $\mathcal{C}_{3v}$.
- 9.2 Carry out all the steps to assure yourself that the results of (9.33) are correct. Show explicitly that the set of matrices obeys the group multiplication table for $\mathcal{C}_{4v}$.
- 9.3 Prove (9.30).
- 9.4 Consider the symmetric group $\mathcal{S}_4$ of order 24; it has five classes and two normal subgroups, as was determined in Exercise 4.5. Use the normal subgroup isomorphic to $\mathcal{T}$ to induce Irreps of $\mathcal{S}_4$.
- 9.5 Consider the isomorphic point-groups $\mathcal{C}_{2nv}$ and $\mathcal{D}_{2n}$.
 - (i) Show that their order is $4n$.
 - (ii) Show that $\mathcal{D}_4$ and $\mathcal{D}_6$ have five and seven classes.
 - (iii) Generalize these results by showing that for an arbitrary n there correspond $n + 3$ classes and hence $n + 3$ Irreps.
 - (iv) Describe the nature of the different classes.
 - (v) Show that the Irrep dimension sum-rule uniquely determines the dimensionality of the Irreps.
 - (vi) Determine the invariant subgroup of either $\mathcal{C}_{2nv}$ or $\mathcal{D}_{2n}$.
 - (vii) Use this normal subgroup and its factor group to construct the group Irreps.
- 9.6 Consider the $\mathcal{C}_{(2n+1)v}$ and $\mathcal{D}_{2n+1}$ type point-groups.
 - (i) Show that their order is $4n + 2$.
 - (ii) Show that they have $n + 2$ classes.
 - (iii) Describe the nature of the different classes.
 - (iv) Show that the Irrep dimension sum-rule uniquely determines the dimensionality of the Irreps.

- (v) Determine the invariant subgroup of either $\mathcal{C}_{2nv}$ or $\mathcal{D}_{2n}$.
 - (vi) Use this normal subgroup and its factor group to construct the group Irreps.
- 9.7 The proper cubic point-group $432 (\mathcal{O})$ contains the tetrahedral point-group $23 (\mathcal{T})$ as a normal subgroup. From the four Irreps of 23 , derived in Exercise 8.12, construct the Irreps of 432 .
- 9.8 Use the Irreps of the normal subgroup $\mathcal{C}_4 \triangleleft \mathcal{D}_4$ to induce the latter's Irreps.

10

Crystallographic symmetry and space-groups

10.1 Euclidean space

Rotations in isotropic Euclidean spaces of dimension $n > 1$ constitute a continuous, infinitely uncountable, set which includes all arbitrary infinitesimal rotation operations. Moreover, under the binary composition law that the sequential application of two rotation operations is equivalent to a distinct rotation operation, this continuous set constitutes a group. The essential features of this continuous group belong to a large class of continuous groups known as *Lie groups*. Although these groups play an important role in field theoretical methods in condensed matter physics, they are outside the scope of this book, and will be the subject of a future monograph. Here, we confine ourselves to presenting a detailed description of the rotation group, its representations, and its extension to the full Euclidean group.

10.1.1 Rotations and angular momentum

Rotations in three-dimensional Euclidean space

A rotation operation in n -dimensional Euclidean space (real space $\mathfrak{R}^{(n)}$) is specified by assigning to it an axis whose direction is defined by the unit vector, $\hat{\phi}$, and a magnitude of the angle of rotation, ϕ ; it is written in the form $R(\phi)$ or $R(\hat{\phi}, \phi)$. The binary composition law for rotations in this space has the general form

$$R(\phi_i) R(\phi_j) = R(\phi_k). \quad (10.1)$$

The identity operation involves a *zero* angle rotation, in general modulo 2π , $E \equiv R(\mathbf{0})$. We denote this group by $\mathcal{R}(n)$.

We will now establish some important matrix representative groups that are faithful to the rotation group in n dimensions by considering coordinate transformations associated with $\mathcal{R}(n)$.

The special orthogonal group in n dimensions A vector $\mathbf{x}$ in an n -dimensional Euclidean space can be expressed as $\mathbf{x}_{\mathbf{K}} = (x_1, x_2, \dots, x_n)$ with respect to a frame of reference $\mathbf{K}$. It may also be described within the frame $\mathbf{K}'$ sharing the same origin but

rotated by an angle ϕ about the direction $\hat{\phi}$, as

$$\mathbf{x}_{\mathbf{K}'} = (x'_1, x'_2, \dots, x'_n), \quad \text{with} \quad x'_i = \sum_{j=1}^n R_{ij} x_j,$$

or, in matrix form: as $\mathbf{x}' = \mathbf{R} \mathbf{x}$. (10.2)

Since such rotations leave the vector norm unchanged we have

$$\widetilde{(R \mathbf{x})} \cdot (R \mathbf{x}) = \tilde{\mathbf{x}} \tilde{R} R \mathbf{x} = |\mathbf{x}|^2,$$

where $\tilde{\mathbf{x}}$ denotes a transpose of matrix $\mathbf{x}$; in component form it is written as

$$\sum_{i=1}^n x'_i x'_i = \sum_{j=1}^n \sum_{k=1}^3 \left(\sum_{i=1}^n R_{ij} R_{ik} \right) x_j x_k = \sum_{j=1}^n \sum_{k=1}^n \delta_{jk} x_j x_k.$$

One thus obtains the condition

$$\sum_{i=1}^n (\tilde{R})_{ji} R_{ik} = \delta_{jk}, \quad (10.3)$$

i.e. $\mathbf{R}$ must be a real, orthogonal matrix, that is, a unitary matrix for which all the elements are real:

$$\tilde{\mathbf{R}} \mathbf{R} = \mathbf{R} \tilde{\mathbf{R}} = \mathbb{I}. \quad (10.4)$$

Equations (10.2) and (10.3) represent $n(n+1)/2$ independent equations; (10.3) also implies that

$$(\det \mathbf{R})^2 = 1, \quad \text{or} \quad \det \mathbf{R} = \pm 1.$$

The $n \times n$ R matrices with $+1$ value correspond to proper rotations and form a group, $SO(n)$, the *special orthogonal group in n real dimensions*:

$$SO(n) = \{ R : \mathfrak{R}^{(n)} \rightarrow \mathfrak{R}^{(n)} \text{ linear} \mid \det R = 1, \tilde{R}R = \mathbb{I} \}. \quad (10.5)$$

The $SO(n)$ group is a faithful Irrep of the rotation group in n dimensions. Although each of these matrices has n^2 components, (2) represents $n(n+1)/2$ independent equations relating these components; thus, each matrix can be expressed in terms of only $n(n-1)/2$ independent parameters.

The $n \times n$ R matrices with -1 value correspond to improper rotations; these together with the proper rotations form a group known as the *orthogonal group in n real dimensions*:

$$O(n) = \{ R : \mathfrak{R}^{(n)} \rightarrow \mathfrak{R}^{(n)} \text{ linear} \mid \det R = \pm 1, \tilde{R}R = \mathbb{I} \}. \quad (10.6)$$

We will consider spaces of dimensionality $n > 3$ when we study quasi-crystals and incommensurate systems. Here, we focus on spaces with $n \leq 3$.

- (i) **$SO(2)$ and $U(1)$** First, we consider the case of $\mathcal{R}(2)$, i.e. the group of rotations in two dimensions. This group comprises all rotations about a single fixed axis which we take to be the 3-axis. It is an Abelian group, since

$$R(\phi_i) R(\phi_j) = R(\phi_j) R(\phi_i) = R(\phi_i + \phi_j).$$

Hence, all its Irreps are one-dimensional. The $SO(2)$ matrices are given by

$$\mathbf{x}' = R(\phi) \mathbf{x} = \begin{pmatrix} \cos \phi & -\sin \phi \\ \sin \phi & \cos \phi \end{pmatrix} \mathbf{x}, \quad (10.7)$$

where $\mathbf{x} \equiv (x_1, x_2)$. Notice that all the elements of $SO(2)$ are defined in terms of a single real parameter ϕ .

The set of 2×2 orthogonal matrices, $SO(2)$, can be viewed as a faithful representation of the abstract group of two-dimensional rotations. However, it is reducible over the field of complex numbers. To demonstrate this reduction, we apply the transformation

$\begin{pmatrix} 1 & i \\ 1 & -i \end{pmatrix}$ to (10.7), and obtain

$$\begin{pmatrix} x'_1 + i x'_2 \\ x'_1 - i x'_2 \end{pmatrix} = \begin{pmatrix} e^{-i\phi} & 0 \\ 0 & e^{i\phi} \end{pmatrix} \begin{pmatrix} x_1 + i x_2 \\ x_1 - i x_2 \end{pmatrix}, \quad (10.8)$$

which reduces the 2×2 unitary matrix representation of $SO(2)$ to two faithful 1×1 unitary Irreps, $e^{i\phi}$ and $e^{-i\phi}$, of $\mathcal{R}(2)$. Each of these two representations is designated as $U(1)$, the group of unitary 1×1 matrices.

(ii) **$SO(3)$** Next, we consider an operation in $SO(3)$ involving rotation by an angle ϕ about a direction $\hat{\phi}$, $R(\phi)$.

Its action on a vector $\mathbf{x}$ can be expressed with the help of the three mutually orthogonal vectors: $\hat{\phi}$, $\hat{\phi} \times \mathbf{x}$, $\hat{\phi} \times (\hat{\phi} \times \mathbf{x})$, shown in Figure 10.1, as

$$\mathbf{x}' = R(\phi) \mathbf{x} = (\hat{\phi} \cdot \mathbf{x}) \hat{\phi} - (\hat{\phi} \times \mathbf{x}) \sin \phi - \hat{\phi} \times (\hat{\phi} \times \mathbf{x}) \cos \phi. \quad (10.9)$$

The first term shows that the projection of $\mathbf{x}$ onto $\hat{\phi}$ is invariant, while the two remaining terms represent the rotation in a plane perpendicular to $\hat{\phi}$. Making use of the identity $\mathbf{a} \times (\mathbf{b} \times \mathbf{c}) = \mathbf{b} (\mathbf{c} \cdot \mathbf{a}) - \mathbf{c} (\mathbf{a} \cdot \mathbf{b})$, (10.9) becomes

$$\mathbf{x}' = \mathbf{x} \cos \phi - \hat{\phi} \times \mathbf{x} \sin \phi + (1 - \cos \phi) (\hat{\phi} \cdot \mathbf{x}) \hat{\phi}, \quad (10.10)$$

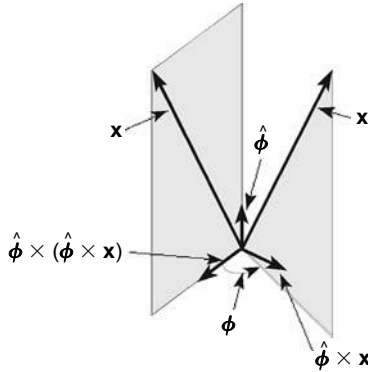


Fig. 10.1. Orthogonal vectors: $\hat{\phi}$, $\hat{\phi} \times \mathbf{x}$, $\hat{\phi} \times (\hat{\phi} \times \mathbf{x})$.

and, squaring the components of the three mutually orthogonal vectors of (10.9),

$$\begin{aligned}
 (\mathbf{x}')^2 &= (\hat{\phi} \cdot \mathbf{x})^2 + (\hat{\phi} \times \mathbf{x})^2 \sin^2 \phi + (\hat{\phi} \times (\hat{\phi} \times \mathbf{x}))^2 \cos^2 \phi \\
 &= |\mathbf{x}|^2 \left[\cos^2 \phi + \sin^2 \phi \sin^2 \phi + \sin^2 \phi \cos^2 \phi \right] \\
 &= |\mathbf{x}|^2.
 \end{aligned} \tag{10.11}$$

Infinitesimal rotations and their generators We are working with continuous groups and need to describe infinitesimal rotations. We obtain the following expression for an infinitesimal rotation by setting $\phi = \epsilon \ll 1$ in (10.10), expanding the trigonometric functions to terms of order ϵ , and expressing $\hat{\phi} \times \mathbf{x}$ in matrix form:

$$\begin{aligned}
 \mathbf{x}' &= \mathbf{x} - (\hat{\phi} \times \mathbf{x}) \epsilon + O(\epsilon^2) \\
 &= \mathbf{x} - \epsilon \left[(\phi_2 x_3 - \phi_3 x_2) \hat{\mathbf{x}}_1 + (\phi_3 x_1 - \phi_1 x_3) \hat{\mathbf{x}}_2 \right. \\
 &\quad \left. + (\phi_1 x_2 - \phi_2 x_1) \hat{\mathbf{x}}_3 \right] + O(\epsilon^2) \\
 &= \mathbf{x} - \epsilon \begin{pmatrix} 0 & -\phi_3 & \phi_2 \\ \phi_3 & 0 & -\phi_1 \\ -\phi_2 & \phi_1 & 0 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} + O(\epsilon^2) \\
 &= \mathbf{x} - \epsilon \left[\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix} \phi_1 + \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{pmatrix} \phi_2 \right. \\
 &\quad \left. + \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \phi_3 \right] \mathbf{x} + O(\epsilon^2).
 \end{aligned} \tag{10.12}$$

Denoting the last three matrices by

$$\frac{i}{\hbar} J_1 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}, \quad \frac{i}{\hbar} J_2 = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{pmatrix}, \quad \frac{i}{\hbar} J_3 = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \tag{10.13}$$

with $\mathbf{J} = (J_1, J_2, J_3)$ we write, anticipating that $\mathbf{J}$ will become the angular momentum operator,

$$\mathbf{x}' = \left[\mathbb{I} - \frac{i}{\hbar} \epsilon \hat{\phi} \cdot \mathbf{J} \right] \mathbf{x} + O(\epsilon^2). \tag{10.14}$$

A close examination of (10.7) and (10.13) shows that an infinitesimal transformation in $SO(2)$ can be written as

$$\mathbf{x}' = \left[\mathbb{I} - \frac{i}{\hbar} \epsilon J_3 \right] \mathbf{x} + O(\epsilon^2).$$

We can obtain an expression for a *finite* rotation ϕ in terms of $\mathbf{J}$ by executing a sequence of n *infinitesimal* operations, each involving an angle $\epsilon = \phi/n$, such that

$$\mathbf{x}' = R(\phi) \mathbf{x} = \lim_{n \rightarrow \infty} \left(\mathbb{I} - i \frac{\phi}{n} \hat{\phi} \cdot \mathbf{J} \right)^n \mathbf{x} = \exp(-i\phi \cdot \mathbf{J}) \mathbf{x}, \quad (10.15)$$

where we henceforth set $\hbar = 1$; we obtain

$$R(\phi) = \exp(-i\phi \cdot \mathbf{J}). \quad (10.16)$$

Thus, for example, using the fact that $J_1^2 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$, we get

$$\begin{aligned} R(\hat{\mathbf{x}}, \phi) &= \mathbb{I} - iJ_1\phi - \frac{J_1^2\phi^2}{2} - \dots \\ &= \mathbb{I} - \left[\frac{1}{2!} \phi^2 - \frac{1}{4!} \phi^4 + \dots \right] \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \\ &\quad - i \left[\phi - \frac{1}{3!} \phi^3 + \dots \right] \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix} \\ &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \phi & \sin \phi \\ 0 & -\sin \phi & \cos \phi \end{pmatrix}, \end{aligned} \quad (10.17)$$

similarly, we get

$$R(\hat{\mathbf{y}}, \phi) = \begin{pmatrix} \cos \phi & 0 & \sin \phi \\ 0 & 1 & 0 \\ -\sin \phi & 0 & \cos \phi \end{pmatrix}. \quad (10.18)$$

The three components of $\mathbf{J}$ are called the generators of $SO(3)$. We will show in the next subsection that we can identify $\mathbf{J}$ with the angular momentum operator, just as the symbol indicates!

Infinitesimal rotations and their commutators Let us now consider infinitesimal rotations about the x - and y -axes, and check their commutator. We get, from

(10.15) and (10.17),

$$\begin{aligned}
 R(\hat{\mathbf{x}}, \delta\phi) &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 - \frac{\delta\phi^2}{2} & -\delta\phi \\ 0 & \delta\phi & 1 - \frac{\delta\phi^2}{2} \end{pmatrix}, & R(\hat{\mathbf{y}}, \delta\phi) &= \begin{pmatrix} 1 - \frac{\delta\phi^2}{2} & 0 & \delta\phi \\ 0 & 1 & 0 \\ -\delta\phi & 0 & 1 - \frac{\delta\phi^2}{2} \end{pmatrix}, \\
 R(\hat{\mathbf{x}}, \delta\phi) R(\hat{\mathbf{y}}, \delta\phi) &= \begin{pmatrix} 1 - \frac{\delta\phi^2}{2} & 0 & \delta\phi \\ \delta\phi^2 & 1 - \frac{\delta\phi^2}{2} & -\delta\phi \\ -\delta\phi & \delta\phi & 1 - \delta\phi^2 \end{pmatrix}, \\
 R(\hat{\mathbf{y}}, \delta\phi) R(\hat{\mathbf{x}}, \delta\phi) &= \begin{pmatrix} 1 - \frac{\delta\phi^2}{2} & \delta\phi^2 & \delta\phi \\ 0 & 1 - \frac{\delta\phi^2}{2} & -\delta\phi \\ -\delta\phi & \delta\phi & 1 - \delta\phi^2 \end{pmatrix},
 \end{aligned} \tag{10.19}$$

so that the commutator is

$$\begin{aligned}
 [R(\hat{\mathbf{x}}, \delta\phi), R(\hat{\mathbf{y}}, \delta\phi)] &= R(\hat{\mathbf{x}}, \delta\phi)R(\hat{\mathbf{y}}, \delta\phi) - R(\hat{\mathbf{y}}, \delta\phi)R(\hat{\mathbf{x}}, \delta\phi) \\
 &= \begin{pmatrix} 0 & -\delta\phi^2 & 0 \\ \delta\phi^2 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \\
 &= R(\hat{\mathbf{z}}, \delta\phi^2) - \mathbb{I}.
 \end{aligned} \tag{10.20}$$

If we now substitute for the $R(\delta\phi)$ s from the expansion of (10.19) and retain up to quadratic terms in $\delta\phi$, we obtain

$$\begin{aligned}
 &\left(1 - iJ_x\delta\phi - \frac{J_x^2\delta\phi^2}{2}\right) \left(1 - iJ_y\delta\phi - \frac{J_y^2\delta\phi^2}{2}\right) \\
 &\quad - \left(1 - iJ_y\delta\phi - \frac{J_y^2\delta\phi^2}{2}\right) \left(1 - iJ_x\delta\phi - \frac{J_x^2\delta\phi^2}{2}\right) = 1 - iJ_z\delta\phi^2 - 1.
 \end{aligned} \tag{10.21}$$

The lowest order terms that survive on the l.h.s. are of order $\delta\phi^2$. Thus, retaining only terms of order $\delta\phi^2$ on the l.h.s., we get for the commutator $[J_x, J_y]$,

$$[J_x, J_y] = J_x J_y - J_y J_x = i J_z. \tag{10.22}$$

Repeating these steps for other combinations of the principal rotation axes we obtain, using the Levi-Civita ε_{ijk} notation, the relations

$$[J_i, J_j] = i \varepsilon_{ijk} J_k, \tag{10.23}$$

called the *fundamental commutation relations of angular momentum*.

Eigenvalues and eigenfunctions of the angular momentum We find that the operator $\mathbf{J}^2 = J_1^2 + J_2^2 + J_3^2$ commutes with all the J_i , namely,

$$[\mathbf{J}^2, J_i] = 0, \quad i = 1, 2, 3. \quad (10.24)$$

According to (10.17), $\mathbf{J}^2$ commutes with all the rotation operators $R(\phi)$, and according to Schur's lemma, it is represented by a scalar in any irreducible space. Since the J_i s do not mutually commute, we choose J_3 as a commuting partner of $\mathbf{J}^2$, and thus they share the same eigenfunctions. Thus, we write

$$\mathbf{J}^2 \Psi_{\ell, m} = \ell \Psi_{\ell, m}, \quad (10.25)$$

$$J_3 \Psi_{\ell, m} = m \Psi_{\ell, m}. \quad (10.26)$$

We introduce the *ladder operators*

$$J_{\pm} = J_1 \pm i J_2, \quad (10.27)$$

$$[J_+, J_-] = 2J_3, \quad (10.28)$$

$$[J_3, J_{\pm}] = \pm 2J_{\pm}, \quad (10.29)$$

$$[\mathbf{J}^2, J_{\pm}] = 0. \quad (10.30)$$

Next, we operate on the function $J_{\pm} \Psi_{\ell, m}$ by J_3

$$J_3 J_{\pm} \Psi_{\ell, m} = (J_{\pm} J_3 \pm J_{\pm}) \Psi_{\ell, m} = (m \pm 1) J_{\pm} \Psi_{\ell, m}, \quad (10.31)$$

$$\mathbf{J}^2 J_{\pm} \Psi_{\ell, m} = J_{\pm} \mathbf{J}^2 \Psi_{\ell, m} = \ell J_{\pm} \Psi_{\ell, m}, \quad (10.32)$$

and we conclude that

$$J_{\pm} \Psi_{\ell, m} = \Psi_{\ell, m \pm 1}. \quad (10.33)$$

Thus we establish the existence of degenerate subspaces of $\mathbf{J}^2$, each comprising several eigenfunctions with different values of m , but having the same eigenvalue of ℓ . We establish the relation between ℓ and its corresponding m s with the aid of the relation

$$\mathbf{J}^2 - J_3^2 = J_+ J_- + J_- J_+ = J_+ J_+^{\dagger} + J_+^{\dagger} J_+, \quad (10.34)$$

where $J_+^{\dagger}$ is the Hermitian adjoint of J_+ , and we thus conclude that $J_+ J_+^{\dagger}$ must have a non-negative expectation value, or that

$$\langle \Psi_{\ell, m} | \mathbf{J}^2 - J_3^2 | \Psi_{\ell, m} \rangle \geq 0.$$

This sets an upper limit on $|m| \leq M$, which we can express as

$$J_{\pm} \Psi_{\ell, \pm M} = 0 \Rightarrow J_{\mp} J_{\pm} \Psi_{\ell, \pm M} = 0.$$

We use (10.28) and (10.34) to write

$$J_- J_+ \Psi_{\ell, M} = (\mathbf{J}^2 - J_3^2 - J_z) \Psi_{\ell, M} = (\ell - M^2 - M) \Psi_{\ell, M} = 0,$$

and we obtain

$$\ell = M(M+1) \equiv j(j+1), \quad (10.35)$$

where we set $M = j$. We modify (10.25) and (10.26) to read

$$\begin{aligned}\mathbf{J}^2 \Psi_{j,m} &= j(j+1) \Psi_{j,m}, \\ J_3 \Psi_{j,m} &= m \Psi_{j,m}, \quad -j \leq m \leq j.\end{aligned}$$

Matrix elements Writing $\Psi_{j,m}$ in ket form $|j, m\rangle$ we obtain

$$\begin{aligned}\langle j, m' | \mathbf{J}^2 | j, m \rangle &= j(j+1) \delta_{jj'} \delta_{mm'}, \\ \langle j, m' | J_3 | j, m \rangle &= m \delta_{jj'} \delta_{mm'}, \\ \langle j, m | J_- J_+ | j, m \rangle &= \langle j, m | J_+^\dagger J_+ | j, m \rangle = j(j+1) - m^2 - m \\ &= j(j+1) - m(m+1) \\ &= (j-m)(j+m+1).\end{aligned}\tag{10.36}$$

Similarly, we obtain

$$\langle j, m | J_+ J_- | j, m \rangle = \langle j, m | J_-^\dagger J_- | j, m \rangle = (j+m)(j-m+1),$$

and we arrive at

$$\langle j', m' | J_\pm | j, m \rangle = \sqrt{(j \mp m)(j \pm m + 1)} \delta_{j'j} \delta_{mm \pm 1}.\tag{10.37}$$

With the matrix elements of the angular momentum operators at hand, we now proceed to determine the Irrep matrices for $\mathcal{O}(3)$, using (10.16), together with the relation

$$\mathbf{J}^2 R(\phi) |j, m\rangle = R(\phi) \mathbf{J}^2 |j, m\rangle = j(j+1) R(\phi) \mathbf{J}^2 |j, m\rangle,$$

and obtain

$${}^{(j)}\Gamma_{mm'}(R(\phi)) = \langle j, m' | \exp(-i\phi \cdot \mathbf{J}) | j, m \rangle,\tag{10.38}$$

which are referred to as the *Wigner functions*. ${}^{(j)}\Gamma$ is a $(2j+1) \times (2j+1)$ Irrep of $\mathcal{O}(3)$.

10.1.2 The Euclidean group in n -dimensional space: $\mathcal{E}(n)$

The Euclidean group in n -dimensional space is the covering group of operations that leave the distance between any two points in the space invariant. As we have shown above, the group $U(n)$ satisfies this condition; however, we also find that rigid translations also leave the distance between two points unchanged.

In order to formulate the combined effect of translations and rotations in that space, we introduce a Cartesian frame of reference $\mathbf{K}$, with orthonormal axes $\hat{\mathbf{n}}_i$, $i = 1, \dots, n$. We first define the operations $T(\mathbf{a})$ of the translation group $\mathcal{T}_n$, with $\mathbf{a} = \sum_{i=1}^n a^i \hat{\mathbf{n}}_i$,

$$T(\mathbf{a}) \mathbf{r} = \mathbf{r} + \mathbf{a}.\tag{10.39}$$

The action of the F-operator on a function $f(\mathbf{r})$ is defined as

$$\hat{T}(\mathbf{a}) f(\mathbf{r}) = f(\mathbf{r} - \mathbf{a}).\tag{10.40}$$

The combined roto-translational operation is then defined as

$$(R | T(\mathbf{a})) = T(\mathbf{a}) R, \quad (10.41)$$

and we write

$$(R | T(\mathbf{a})) \mathbf{r} = R \mathbf{r} + \mathbf{a}, \quad (10.42)$$

or

$$x'_i = \sum_{j=1}^n R_{ij} x_j + a_i. \quad (10.43)$$

We may obtain the corresponding binary composition law by considering the following sequential application of two operators,

$$\begin{aligned} (R_2 | T(\mathbf{a}_2)) (R_1 | T(\mathbf{a}_1)) \mathbf{r} &= (R_2 | T(\mathbf{a}_2)) (R_1 \mathbf{r} + \mathbf{a}_1) \\ &= R_2 R_1 \mathbf{r} + R_2 \mathbf{a}_1 + \mathbf{a}_2 \\ &= (R_2 R_1 | R_2 \mathbf{a}_1 + T(\mathbf{a}_2)) \mathbf{r}, \end{aligned}$$

and hence we define the composition law as

$$(R_2 | T(\mathbf{a}_2)) (R_1 | T(\mathbf{a}_1)) = (R_2 R_1 | R_2 \mathbf{a}_1 + T(\mathbf{a}_2)). \quad (10.44)$$

Next, (10.44) allows us to define the inverse operation, namely, using the fact

$$(R | T(\mathbf{a}))^{-1} (R | T(\mathbf{a})) = (R' | T(\mathbf{a}')) (R | T(\mathbf{a})) = (E | T(\mathbf{0})), \quad (10.45)$$

we find that $R' R = E$, and $R' \mathbf{a} + \mathbf{a}' = \mathbf{0}$, hence we obtain

$$(R | T(\mathbf{a}))^{-1} = (R^{-1} | T(-R^{-1} \mathbf{a})). \quad (10.46)$$

Finally, we consider the effect of conjugation with respect to an arbitrary operation $(R' | T(\mathbf{a}'))$. Using (10.44) and (10.46) we obtain

$$(R' | T(\mathbf{a}')) (R | T(\mathbf{a})) (R' | T(\mathbf{a}'))^{-1} = (R' R R'^{-1} | T(\mathbf{a}' + R' \mathbf{a} - R' R R'^{-1} \mathbf{a}')).$$

(10.47)

When we apply the conjugation (10.47) to a pure translation operation, we determine the classes of $\mathcal{T}_n$ in $\mathcal{E}(3)$, namely

$$(R' | T(\mathbf{a}')) (E | T(\mathbf{a})) (R' | T(\mathbf{a}'))^{-1} = (E | T(R' \mathbf{a})), \quad (10.48)$$

which shows that translations of the same distance belong to the same class, since $|R' \mathbf{a}| = |\mathbf{a}|$.

Example 10.0 $\mathcal{E}(2)$

The elements of the Euclidean group in two dimensions can be expressed, according to (10.41), by augmenting the 2×2 matrices of $SO(2)$ in the form

$$(R | T(\mathbf{a}_1, \mathbf{a}_2)) = \begin{bmatrix} \cos \theta & -\sin \theta & a_1 \\ \sin \theta & \cos \theta & a_2 \\ 0 & 0 & 1 \end{bmatrix}. \quad (10.49)$$

The infinitesimal generators are then expressed as

$$J_\theta = \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \quad J_1 = \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \quad J_2 = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{bmatrix}, \quad (10.50)$$

satisfying the commutators

$$[J_\theta, J_1] = J_2, \quad [J_\theta, J_2] = -J_1, \quad [J_1, J_2] = 0. \quad (10.51)$$

10.2 Crystallography

In the rest of this chapter and following chapters, we will focus on special subgroups of $\mathcal{E}(n)$, the *crystallographic space-groups*. Space-groups are associated with the symmetry of idealized crystals, envisioned as perfect lattices of infinite extent. They consist of small identical unit cells of atoms assembled together in a regular array that exhibits perfect translational symmetry. Such idealized crystals present the advantage that their mathematical description can be simplified with the aid of periodic boundary conditions, so that, in a single stroke, we avoid unwieldy surface effects, and confine the analysis to only a finite region of the crystal, the single unit, or primitive, cell.

The complete classification of the symmetries of periodic crystals, in three and lower dimensions, was carried out in the nineteenth and early twentieth centuries by Bravais [23], Fedorov [24], Schoenflies [25], Bieberbach [26], and others. It presents a unique framework for determining and describing the structures of materials with diffraction patterns consisting of Bragg peaks. The classification has been organized into 32 crystallographic point-groups (10 in two dimensions), which specify the symmetry of translationally invariant macroscopic features of crystals, the *crystal habit*, responses to external perturbations, etc. This classification also covers the description of the 14 Bravais lattices and 230 space-groups in three dimensions (5 and 17 in two dimensions), and relies heavily on periodicity, as specified by the real-space lattices which describe the microscopic translational symmetries of crystalline materials [13, 14, 17, 22, 27, 28, 29, 30].

In this chapter we expound upon the outstanding features of lattices and crystals in n dimensions, and describe the various ways of classifying them. Some of the classification methods presented are useful in classifying crystalline systems in dimensions higher than three, where visual aids are absent. These higher dimension spaces play a major role in the theoretical framework of incommensurate and quasi-crystalline systems, discussed in Chapter 18. In the present chapter, however, we confine our discussion to crystalline systems in two- and three-dimensions.

10.3 The perfect crystal

A mathematical framework for describing the symmetry of crystals begins with the geometric concept of a space lattice, called a *Bravais lattice*, after Auguste Bravais who in 1850 [23] correctly enumerated the complete set of 14 such lattices in three dimensions. It is a periodic array of points whose positions are defined by a set of lattice vectors that span the Euclidean space over which the lattice is defined. Thus, for an n -dimensional lattice, ${}^n\mathcal{L}$, we express a general *primitive* lattice vector ${}^n\mathbf{t}_m$ as

$${}^n\mathbf{t}_m = \sum_{i=1}^n m_i \mathbf{a}_i, \quad \forall m = \{m_1, m_2, \dots, m_n\} \in {}^n\mathbb{Z}, \quad (10.52)$$

where $\mathbf{a}_1, \mathbf{a}_2, \dots, \mathbf{a}_n$ constitute a *primitive* basis set of translation vectors, and $m \equiv \{m_1, m_2, \dots, m_n\}$ is a set of integers that defines the primitive lattice vector ${}^n\mathbf{t}_m$ in terms of the primitive basis vectors. It is obvious that a displacement of a Bravais lattice by any of its defining vectors will leave it invariant. We thus discern the translational symmetry of Bravais lattices. The operation of addition manifest in (10.52) establishes the set $\mathbb{T}(n) = \{{}^n\mathbf{t}_m\}$ as an Abelian group. It also establishes the isomorphism $\mathbb{T}(n) \sim {}^n\mathbb{Z}$. For simplicity we will often omit the superscript n on ${}^n\mathbf{t}_m$; its presence will be implicit.

In addition to translation symmetry, ${}^n\mathcal{L}$ possesses roto/reflection or *point-group* symmetries. Point-group symmetry implies operations about a single point in space that remains unchanged. The set of such operations (represented by orthogonal matrices) that leaves the lattice ${}^n\mathcal{L}$ invariant forms the *crystallographic point-group* of the lattice. It is a subgroup of $\mathcal{O}(n)$.

The combination of translation and point-group symmetries constitutes the space-group of the Bravais lattice. As such, a space-group is considered as an *extension* of the translation group $\mathbb{T}(n)$ by the point-group. We will also demonstrate, shortly, that a space-group symmetry can be associated with some type of a perfect crystal. We will begin with a discussion of the lattice translation groups, and then consider the restrictions they impose on allowable point-group operations.

10.3.1 The translation group

The set of primitive lattice vectors $\{\mathbf{t}_m\}$, defining a Bravais lattice, is countably infinite. It can be thought of as the set of covering operations of a Bravais lattice and, as such, constitutes the translation group of the lattice. We interpret the translation operators in the *active* sense as described in Chapter 1. However, in this chapter, we are concerned

primarily with operations on functions, as a step in the process of generating irreducible representations of space-groups.

Translation F-operators, $\hat{\mathbf{t}}$ and $\hat{\mathbf{a}}$, are defined such that

$$\begin{aligned}\hat{\mathbf{t}}_m \psi(\mathbf{r}) &= \psi(\mathbf{r} - \mathbf{t}_m), \\ \hat{\mathbf{a}}_i \psi(\mathbf{r}) &= \psi(\mathbf{r} - \mathbf{a}_i).\end{aligned}\tag{10.53}$$

The translation F-operators obey the group multiplication rule

$$\begin{aligned}\hat{\mathbf{t}}_i \hat{\mathbf{t}}_j \psi(\mathbf{r}) &= \psi(\mathbf{r} - \mathbf{t}_i - \mathbf{t}_j) = \hat{\mathbf{t}}_j \hat{\mathbf{t}}_i \psi(\mathbf{r}) \\ &= \hat{\mathbf{t}}_k \psi(\mathbf{r}),\end{aligned}\tag{10.54}$$

which demonstrates that the operators are *Abelian*; hence, the *Irreps of the translation group are one-dimensional*.

The lattice translation group $\mathbb{T}(n)$ is a discrete Abelian subgroup of $\mathcal{T}_n$, the continuous translation group in n -dimensional Euclidean space. It comprises the infinitely countable set of translation operators ${}^n\hat{\mathbf{t}}$. Moreover, its construction may be viewed as the *direct product* of n one-dimensional isomorphic translation groups, namely,

$$\mathbb{T}(n) = \prod_{i=1}^n \mathbb{T}^{(i)}(1),$$

or,

$$\boxed{{}^n\hat{\mathbf{t}}_m = \prod_{i=1}^n \hat{\mathbf{a}}_i^{m_i}},\tag{10.55}$$

where $m = (m_1, \dots, m_n)$, and $\hat{\mathbf{a}}_i^{m_i} \in \mathbb{T}^{(i)}(1)$ is the primitive translation vector $\hat{\mathbf{a}}_i$ raised to the power m_i , i.e. applied m_i times. Since there is a finite number of primitive translation vectors $\mathbf{a}_i$, $\mathbb{T}$ is said to be a *finitely generate free Abelian group*.

Each one-dimensional translation group, $\mathbb{T}(1)$, is also of infinite countable order. We are concerned in this and the following chapters with lattices in three and two dimensions.

10.3.2 The Holohedry group and classification of Bravais lattices

In addition to translation symmetry, a Bravais lattice possesses rotation and reflection symmetries. However, the translational symmetry restricts its rotational invariance to a small number of compatible rotation or reflection operations. The set of such point operations that leaves the lattice invariant form a group called its *holohedry* [14, 22, 31].

The geometric holohedry

When the operations of the lattice holohedry are represented by orthogonal matrices, it is called a *geometric holohedry*, $\mathbb{P}_B \in \mathcal{O}(n)$, with

$$\mathbb{P}_B {}^n\mathcal{L} = {}^n\mathcal{L}.\tag{10.56}$$

When a lattice ${}^n\mathcal{L}$ with geometric (g-) holohedry $\mathbb{P}_B$ is operated on by any $R \in \mathcal{O}(n)$ it transforms into an equivalent lattice, ${}^n\mathcal{L}_{\text{equiv}} = R {}^n\mathcal{L}$ with a g-holohedry $\mathbb{P}_B^{\text{equiv}}$. We then have

$$\mathbb{P}_B^{\text{equiv}} {}^n\mathcal{L}_{\text{equiv}} = {}^n\mathcal{L}_{\text{equiv}} \Rightarrow R^{-1} \mathbb{P}_B^{\text{equiv}} R {}^n\mathcal{L} = {}^n\mathcal{L}. \quad (10.57)$$

The two g-holohedries are conjugate groups with respect to $\mathcal{O}(n)$, i.e. they are related by a conjugacy operation in $\mathcal{O}(n)$; the corresponding lattices are said to be *geometrically equivalent*. Therefore, in classifying g-holohedries we have to distinguish among conjugacy classes in $\mathcal{O}(n)$, and not among equivalent g-holohedry groups within a given class. Bieberbach showed that the number of geometrically equivalent classes is finite for any n -dimensional space [26]. Each conjugacy class contains an infinite number of *geometrically equivalent* lattices! These conjugacy classes of g-holohedries are referred to as *lattice systems*.

Two lattices belong to the same lattice system if their g-holohedries are geometrically equivalent.

As we demonstrated in Section 2.3, the structure of lattices restricts rotational symmetry to a few allowable angles: $\pi, \pi/2, \pi/3$, and $\pi/6$.

Another requirement of a Bravais lattice is that space inversion is a symmetry operation, since if $\mathbf{t}$ defines a lattice point, $-\mathbf{t}$ must also define another lattice point. Consequently, each holohedry group contains $\mathfrak{I}$.

These restrictions result in limiting the number of allowed g-holohedry classes.

In 3D there are just seven possible g-holohedry classes, or lattice systems, that cover all 3D Bravais lattices, namely,

$$\mathbb{C}_i, \mathbb{C}_{2h}, \mathbb{D}_{2h}, \mathbb{D}_{4h}, \mathbb{D}_{3d}, \mathbb{D}_{6h}, \text{ and } \mathbb{O}_h.$$

A hierarchical arrangement of these g-holohedries is shown in Figure 10.2, and the corresponding primitive bases are defined in Table 10.1. The different notations, in current use, for the elements of the point-group 432 are given in Table 10.2.

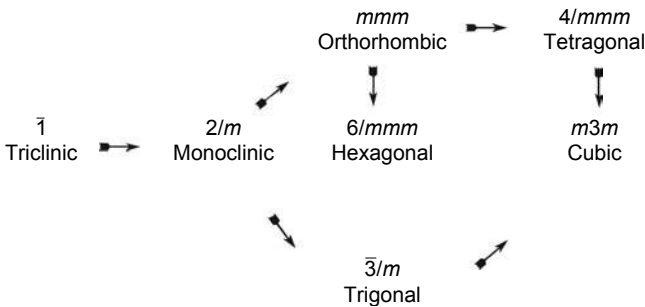


Fig. 10.2. Diagram of the hierarchy of 3D g-holohedries.

Table 10.1. *The seven three-dimensional lattice systems; vectors and angles are defined in Figure 10.3.*

Lattice system	International short symbol	Schoenflies symbol	Lattice vectors
Triclinic	$\bar{1}$	$\mathbb{C}_i$	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$
Monoclinic	$2/m$	$\mathbb{C}_{2h}$	$a \neq b \neq c$ $\alpha = \beta = 90^\circ \neq \gamma$ or $\alpha = \gamma = 90^\circ \neq \beta$
Orthorhombic	mmm	$\mathbb{D}_{2h}$	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$
Tetragonal	$4/mmm$	$\mathbb{D}_{4h}$	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$
Trigonal	$\bar{3}m$	$\mathbb{D}_{3d}$	$a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$
Hexagonal	$6/mmm$	$\mathbb{D}_{6h}$	$a = b \neq c$ $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$
Cubic	$m\bar{3}m$	$\mathbb{O}_h$	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$

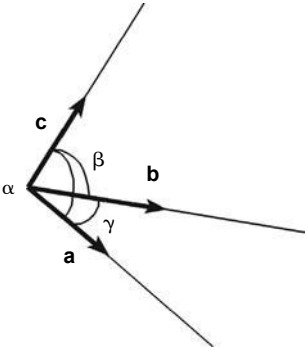


Fig. 10.3. Specification of lattice vectors and angles presented in Table 10.1.

In 2D there are five g-holohedry classes, or lattice systems, with respect to $\mathcal{O}(2)$: when the 2D space that contains the lattice is considered single-sided, or monohedral, as we find on the surfaces of crystalline systems or the lattice of a monolayered crystal supported on a substrate, we identify the holohedry as $(\mathbb{C}_2)$, $(\mathbb{C}_{2v})$, $\mathbb{C}_{3v}$, $\mathbb{C}_{4v}$, $\mathbb{C}_{6v}$. On the other hand, for the case of two-sided or dihedral systems, such as membranes, the g-holohedry groups are $\mathbb{D}_{1h}$, $\mathbb{D}_{2h}$, $\mathbb{D}_{3h}$, $\mathbb{D}_{4h}$, $\mathbb{D}_{6h}$.

10.3.3 Lattice metric, arithmetic holohedries, and Bravais classes

We can refine the system of classifying lattices and space-groups by introducing two new crystallographic concepts: [22, 31, 32, 33] the representation of point-group operations by integer matrices, engendered by the primitive lattice basis, and the concept of the lattice metric and its invariance. These concepts provide deep insight into the physical significance of crystal symmetries and provide the machinery for studying crystallography in dimensions higher than three. Although the discussion of these and other concepts is generalized for an n -dimensional Euclidean space, our interest in this chapter will involve two- and three-dimensional lattice systems.

Since our lattices are constructed in a Euclidean space, where vector scalar products are conserved, we define the metric for a lattice in n -dimensional space with primitive basis vectors, $\mathbf{A} = \{\mathbf{a}_1, \mathbf{a}_2, \dots, \mathbf{a}_n\}$, as the real symmetric matrix $\mathbf{g}$:

$$g_{ij} = \mathbf{a}_i \cdot \mathbf{a}_j, \quad \text{or} \quad \mathbf{g} = \mathbf{A}^T : \mathbf{A},$$

and the primitive cell volume $\mathbb{V}$ can be expressed as

$$\mathbb{V}^2 = \det \mathbf{g}. \quad (10.58)$$

Next, we apply a point-group operation $R \in \mathcal{O}(n)$ on $\mathcal{L}$ and transform it to $\mathcal{L}'$ with basis vectors

$$\mathbf{a}'_i = \sum_k R_{ik} \mathbf{a}_k, \Rightarrow \mathbf{g}' = \mathbf{R}^T \mathbf{g} \mathbf{R}, \quad (10.59)$$

where $\mathbf{R} \equiv \{R_{ik}\}$ is an $n \times n$ matrix representation engendered by $\mathbf{A}$, i.e. $\mathbf{R} \in GL(n, \mathbb{R})$ the general linear group of real $n \times n$ matrices.

Now, suppose that the operation R is an element of the holohedry which leaves the lattice $\mathcal{L}$ invariant, i.e.

$$R\mathcal{L} = \mathcal{L},$$

then the new basis vectors $\mathbf{a}'$ must belong to the set of lattice vectors defining $\mathcal{L}$; accordingly, an integer relationship exists between the new and old primitive lattice vectors, namely,

$$\mathbf{a}'_i = \sum_j m_{ij} \mathbf{a}_j;$$

where $m_{ij} \in \mathbb{Z}$, in which case the matrix representation $\mathbf{M}(R)$ engendered by R has integer elements,

$$\mathbf{a}'_i = \sum_j m_{ij}(R) \mathbf{a}_j, \Rightarrow \mathbf{g}' = \mathbf{M}^T(R) \mathbf{g} \mathbf{M}(R). \quad (10.60)$$

Since the metric is a property of the lattice and not the particular basis vectors chosen, it should be independent of the transformation $\mathbf{M}$, and we have the condition

$$\mathbf{g} = \mathbf{M}^T \mathbf{g} \mathbf{M}. \quad (10.61)$$

Moreover, the primitive cell volume should be invariant under such transformation, and we require that

$$\det \mathbf{g} = \det \mathbf{M} \det \mathbf{g} \det \mathbf{M}^T \Rightarrow \det \mathbf{M} = \pm 1. \quad (10.62)$$

Equations (10.61) and (10.62) ensure that the transformation $\mathbf{M}$ is unimodular. It belongs to the general linear group of $n \times n$ integer matrices,

$$\mathbf{M} \in GL(n, \mathbb{Z}).$$

Thus, the set of $\mathbf{M}$ matrices that satisfy (10.61) and (10.62) for a particular lattice form a subgroup of $GL(n, \mathbb{Z})$. This group provides a faithful representation of the holohedry and is referred to as the *arithmetic holohedry* $\mathbb{A}_B$.

Definition We define an arithmetic (a-) holohedry $\mathbb{A}_B$ of a lattice with metric tensor $\mathbf{g}$ as the group of invertible integer matrices $\mathbf{M}(R)$, such that

$$\mathbf{M}(R)^T \mathbf{g} \mathbf{M}(R) = \mathbf{g}.$$

Following the same scenario adopted for the g-holohedry, we obtain equivalent a-holohedry as conjugate subgroups with respect to the covering group $GL(n, \mathbb{Z})$, as

$$\mathbb{A}'_B = \mathbf{N}^T \mathbb{A}_B \mathbf{N}, \quad \mathbf{N} \in GL(n, \mathbb{Z}). \quad (10.63)$$

An equivalence- or conjugacy-class of these subgroups is identified as a *Bravais class*.

Two lattices belong to the same Bravais class if their a-holohedries are equivalent.

We should note that a g-holohedry, or lattice system, may comprise several Bravais classes. This is because a symmetry operation $R \in \mathbb{P}_B \subset \mathcal{O}(n)$ may be represented in different primitive bases by integral matrices which need not be conjugate in the more restrictive $GL(n, \mathbb{Z})$.

Thus, we find that conjugacy in $GL(n, \mathbb{Z})$ is a stricter condition than conjugacy in $\mathcal{O}(n)$.

To demonstrate this property we consider an orthonormal coordinate basis set, $\hat{\mathbf{e}}_i$, in the Euclidean space $\mathbb{R}^n$, such that $\hat{\mathbf{e}}_i \cdot \hat{\mathbf{e}}_j = \delta_{ij}$. We express the primitive basis $\mathbf{a}_i$, generating lattice $\mathcal{L}$, in terms of the coordinate basis as

$$\mathbf{a}_i = \sum_j c_{ij} \hat{\mathbf{e}}_j, \quad \text{or} \quad \mathbf{A} = \mathbf{C} \mathbf{E}, \quad (10.64)$$

where $\mathbf{C} \in GL(n, \mathbb{R})$. Now, the action of an operator R on the space $\mathbb{R}^n$ gives

$$\mathbf{A}' = \mathbf{M}(R) \mathbf{A} = \mathbf{C} R^{-1} \mathbf{E} = \mathbf{C} R^{-1} \mathbf{C}^{-1} \mathbf{A}, \quad (10.65)$$

which establishes the relation

$$\mathbf{M}(R) = \mathbf{C} R^{-1} \mathbf{C}^{-1} \quad (10.66)$$

between the g- and a-holohedries of a given lattice $\mathcal{L}$ in the form

$$\mathbb{A}_B(\mathcal{L}) = \mathbf{C}(\mathcal{L}) \mathbb{P}_B \mathbf{C}^{-1}(\mathcal{L}). \quad (10.67)$$

Thus, if several lattices belong to the same g-holohedry, i.e. crystal system, they still have distinct component-matrices $\mathbf{C}(\mathcal{L})$ and, hence, may belong to a-holohedries, which may not be equivalent, i.e. cannot be conjugated under the operations of $GL(n, \mathbb{Z})$. We then conclude that:

A lattice system may contain several Bravais classes. Because two arithmetically equivalent point-groups are also geometrically equivalent, each lattice system consists of whole Bravais classes.

Example 10.1

The two-dimensional $2mm$ lattice system

This system has the holohedry class E , C_2 , σ_x , σ_y , and contains two Bravais classes:

(a) $\mathbf{a}_1 = (a, 0)$, $\mathbf{a}_2 = (0, b)$; a P-mesh with a-holohedry

$$E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad C_2 = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \sigma_x = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

(b) $\mathbf{a}'_1 = \frac{1}{2}(a, b)$, $\mathbf{a}'_2 = \frac{1}{2}(-a, b)$; a C-mesh with a-holohedry

$$E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad C_2 = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}.$$

The two a-holohedries are inequivalent, since there is no element of $GL(2, \mathbb{Z})$ that transforms one into the other. Hence, the lattices belong to different Bravais classes. However,

lattice (b) can be obtained from lattice (a) by the unitary transformation

$$\begin{pmatrix} \mathbf{a}'_1 \\ \mathbf{a}'_2 \end{pmatrix} = \mathbf{S} \begin{pmatrix} \mathbf{a}_1 \\ \mathbf{a}_2 \end{pmatrix}$$

$$\mathbf{S} = \frac{1}{2} \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}.$$

Notice that the unit cell of the C-mesh is a P-mesh containing two lattice points, which is also the value of $[\det \mathbf{S}]^{-1}$.

Centering and the standard (conventional) lattice

The transformation $\mathbf{S}$ in the above example is a typical representative of the centering process mentioned earlier: The unprimed basis vectors represent the simplest possible rectangular lattice (primitive or p-rectangular), while the primed basis involves the introduction of an extra lattice point at the center of the p-rectangular mesh. The resulting mesh is referred to as a centered or c-mesh, while the process of introducing the extra lattice points is referred to as *centering*.

Example 10.2

The simplest lattice in the cubic system is denoted by P, for primitive; its basis consists of three vectors (100), (010), (001).

One centered version in this system is the body-centered cubic, denoted by I, which is obtained with the centering vector $(1/2, 1/2, 1/2)$, and has the basis set

$$(1/2, 1/2, -1/2), (1/2, -1/2, 1/2), (-1/2, 1/2, 1/2).$$

The cubic holohedry is isomorphic with the point-group O_h , with the g-holohedry representatives of its generators

$$C_{4z} = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad C_{3xyz} = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}, \quad \mathfrak{I} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}.$$

The representative I a-holohedry matrices of these generators are

$$C_{4z} = \begin{pmatrix} 1 & 1 & 1 \\ 0 & 0 & -1 \\ -1 & 0 & 0 \end{pmatrix}, \quad C_{3xyz} = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}, \quad \mathfrak{I} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}.$$

We notice that the g-holohedry representative matrix of C_{4z} reflects the nature of the 90° rotation about the z -axis, namely, $\begin{matrix} -x \rightarrow y \\ y \rightarrow x \end{matrix}$, and, by contrast, the corresponding a-holohedry matrix does not.

Table 10.3. *Centering matrices and indices of 3D Bravais classes.*

Bravais class	Centering matrix	Index
P	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	1
I	$\frac{1}{2} \begin{pmatrix} -1 & 1 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{pmatrix}$	2
A, B, C	$\frac{1}{2} \begin{pmatrix} 0 & 0 & 2 \\ -1 & 1 & 0 \\ 1 & 1 & 0 \end{pmatrix}, \frac{1}{2} \begin{pmatrix} -1 & 1 & 0 \\ 0 & 0 & 2 \\ 1 & 1 & 0 \end{pmatrix}, \frac{1}{2} \begin{pmatrix} -1 & 1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix}$	2
F	$\frac{1}{2} \begin{pmatrix} 1 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 1 \end{pmatrix}$	4

In general, the matrices of a lattice a-holohedry do not clearly show the character of the transformation they represent. In many cases, this becomes clearer if the a-holohedry of a sublattice basis is chosen, where, if possible, the symmetry elements are represented by orthogonal matrices. The desired lattice is obtained from the sublattice basis by the addition of vectors in the unit cell of the latter. Again, this is the centering process. The chosen sublattice is called *standard* or *conventional*, and its basis a *standard basis*. In this scenario, the a-holohedry matrices $\mathbf{M}_s$, centering vectors, and nonprimitive translations are given with respect to the conveniently chosen standard basis. The standard lattices are usually the primitive ones. Retrieval of the centered basis, a-holohedry $\mathbf{M}$, etc. is effected with the aid of the rational matrix transformation $\mathbf{S}$, which is called a *centering matrix*:

$$\mathbf{M} = \mathbf{S} \mathbf{M}_s \mathbf{S}^{-1}, \quad \mathbf{X} = \mathbf{S} \mathbf{X}_s. \quad (10.68)$$

For orthogonal primitive lattices, these centering matrices coincide with the $\mathbf{C}(\mathcal{L})$ s.

Thus, in each lattice system, a *conventional* or *standard lattice* is chosen, whereby the a-holohedry of every other lattice belonging to the system, or family, can be obtained from that of the standard lattice by a centering *rational matrix* $\mathbf{S}$.

The determinant of $\mathbf{S}^{-1}$ is the number of lattice points inside the *standard*, or unit, cell. This number is called the *index of the centered lattice in the standard lattice*.

A basis for the standard lattice is a *standard basis*. Centerings are given by the basis transformation from a standard basis for the family to a primitive basis of the Bravais class. Conventionally the basis transformation is given by a lower case letter for 2D and an upper case letter for 3D.

*Example 10.3***The three-dimensional cubic holohedry ($m\bar{3}m$)**

There are three Bravais classes: P, I, and F. The reason for choosing P as the conventional lattice is to make the point-group matrices orthogonal, with each row and each column having precisely one nonzero entry. Both I- and F-lattices have a sublattice of the $m\bar{3}mP$ Bravais class. Bases for the two lattices are obtained from the conventional basis by rational basis transformations with determinant $1/2$ and $1/4$ (indices 2 and 4), respectively:

$$\frac{1}{2} \begin{pmatrix} -1 & 1 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{pmatrix}; \quad \frac{1}{2} \begin{pmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix}.$$

The centering may be given by the basis transformation, or by the lattice vectors inside the conventional unit cell. For the examples, these are: $0, 0, 0$; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ and $0, 0, 0$; $\frac{1}{2}, \frac{1}{2}, 0$; $0, \frac{1}{2}, \frac{1}{2}$. The index of the I-lattice is two, that of the F-lattice is four.

There are four possible arrangements that are shared by every space dimension:

- (i) Index 1 lattice indicated by P, for primitive.
- (ii) Index 2 lattice indicated by I (I, German for Innenzentrierung): where, in addition to the origin, it contains the center of the standard unit cell.
- (iii) Index 3 lattice indicated by R: has three lattice translations along the diagonals of the unit cell.
- (iv) Index 4 lattice indicated by F: has a lattice translation in the middle of each pair of the standard basis vectors.

There is only one centered lattice in 2D, the c-rectangular mesh discussed in Example 10.1; all the remaining Bravais classes in 2D are primitive. The Bravais classes in 3D together with their centering matrices and indices are given in Table 10.3.

10.3.4 Lattice systems and Bravais classes in two and three dimensions

Equation (10.67) shows that the g-holohedry group $\mathbb{P}_B \subset O(n)$ is related to the a-holohedry $\mathbb{A}_B \subset GL(n, \mathbb{Z})$ by a similarity transformation that preserves the matrix trace. Because $\mathbb{A}_B$ matrices have integer entries, the traces of $\mathbb{P}_B$ matrices must be integers [22, 31].

In 2D isometry rotations of $O(2)$ have traces $2 \cos \theta$, which can have integer values only for 1-, 2-, 3-, 4-, or 6-fold rotations, so that the possible g-holohedries are 1, 2, 3, 4, 6, m , $2mm$, $3m$, $4mm$, and $6mm$. However, the fact that each holohedry has to contain the inversion operation, which is a 2-fold rotation in 2D, limits the allowable holohedries in 2D to six: 2, 4, 6, $2mm$, $4mm$, and $6mm$. Yet we find that the groups 4 and 6 cannot describe the full symmetry of a lattice, and we are left with four 2D lattice systems: 2, $2mm$, $4mm$, and $6mm$.

Since C_2 is the center of $GL(2, \mathbb{Z})$, i.e. it is in a class by itself, the subgroup C_2 is self-conjugate, and has a unique Bravais class, $2p$. In Example 10.1 we showed that the system $2mm$ contains the two inequivalent Bravais classes pmm and cm ; this inequivalence arises from the different representations of the two reflections in both holohedries, namely,

$$2mmp \Rightarrow \pm \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad 2mmc \Rightarrow \pm \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.$$

However, when $a = b$ they reduce to a single Bravais class $p4mm$, corresponding to the system $4mm$. This can be shown to be also true for the system $6mm$ which has the unique Bravais class $p6mm$.

Thus, in 2D we define the arithmetic generators, or elements:

$$\begin{aligned} p1 &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} & p2 &= \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} & pm &= \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} & cm &= \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \\ p4 &= \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} & p3 &= \begin{pmatrix} 0 & -1 \\ 1 & -1 \end{pmatrix} & p6 &= \begin{pmatrix} 1 & -1 \\ 1 & 0 \end{pmatrix} \end{aligned} \quad (10.69)$$

The pm and $p4$ operations require an orthogonal basis, i.e. with angle of $\pi/2$ between basis vectors, while $p3$ and $p6$ require $2\pi/3$; no basis restriction is imposed by cm . Moreover, except for pm the two vectors must have the same norm.

A Bravais lattice in 2D is usually referred to as a *net* or a *mesh*; we have five distinct nets, or 2D Bravais lattices, four primitive and one centered rectangular, shown in Figure 10.4.

In 3D, the condition that the trace $1 + 2\cos\theta$ must be an integer leads to the same allowable rotations as in 2D, and gives rise to 32 g-classes, out of which only 11 contain

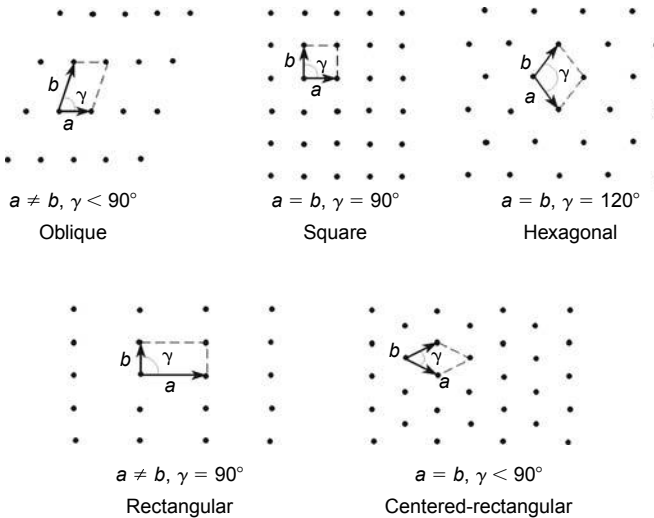


Fig. 10.4. The five two-dimensional Bravais lattices.

inversion. It can be shown that four of these, $4/m$, $\bar{3}$, $6/m$, and $m\bar{3}$, fail to describe a lattice; we thus end up with the seven 3D lattice systems.

At the outset, it seems reasonable to associate one Bravais lattice with each of the seven 3D g-holohedry groups listed above, and thus infer a total of seven 3D Bravais lattices, as listed in Table 10.1.

However, we find that two of these seven lattices, hexagonal and trigonal, are actually equivalent, thus reducing the number to six. Yet we find that, in the case of the g-holohedries C_{2h} , D_{2h} , D_{4h} , and O_h , it is possible to generate eight additional inequivalent Bravais lattices through centering of the constituent standard or unit cells of the original six Bravais lattices. This yields a total of 14 Bravais lattices in 3D.

The original six Bravais systems are designated as primitive (P), and the remaining eight are identified as body-centered (I), face-centered (F), and *one* face-centered (A, B, or C) depending on the location of the centered face. The 3D Bravais lattices are shown in Figures 10.5 to 10.9.

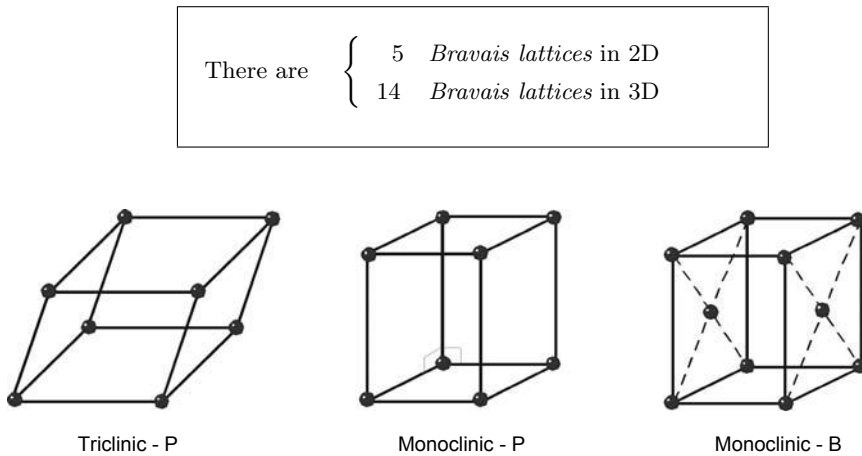


Fig. 10.5. The 3D triclinic and monoclinic Bravais lattices.

The designations, P, I, etc. also define the different *Bravais classes*, which are determined as follows:

- (i) The triclinic system, $\bar{1}$, has only one representation $\pm\bar{1}$; and hence one Bravais class $\bar{1}P$.
- (ii) The monoclinic system, $2/m$, has one reflection, so it contains two inequivalent integer representations $2/mP$ and $2/mC$.
- (iii) The orthorhombic system, mmm , has a primitive lattice with a-holohedry $mmmP$, and has three other Bravais classes:
 - (a) Centering with vector $(1/2, 1/2, 1/2)$ defines the Bravais class $mmmI$,
 - (b) Centering the three faces produces the Bravais class $mmmF$,
 - (c) Centering only one face, similar to the 2D rectangular case, gives the Bravais class $mmmC$.

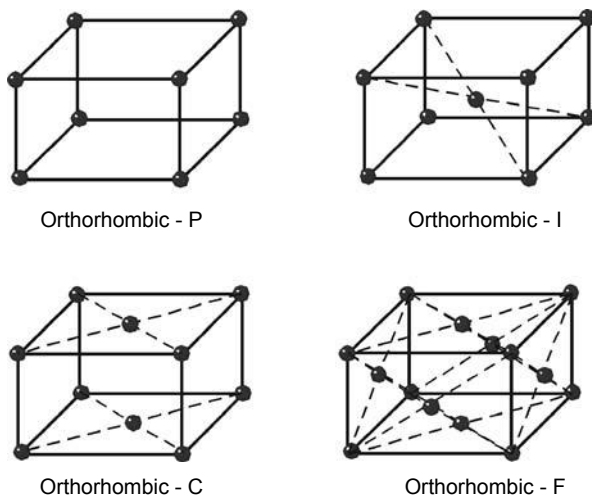


Fig. 10.6. The 3D orthorhombic Bravais lattices.

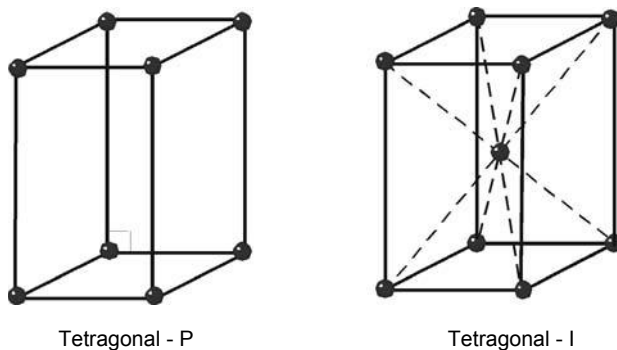


Fig. 10.7. The 3D tetragonal Bravais lattices.

The lattices $Fmmm$ and $Immm$ are dual of each other.

- (iv) The tetragonal system, $4/mmm$, can be regarded as a limit of the orthorhombic case with $a = b$, and like the 2D case the Bravais classes $4/mmmP$ and $4/mmmC$ become equivalent, and so do the Bravais classes $4/mmmI$ and $4/mmmF$. Thus, we have two inequivalent Bravais classes designated $4/mmmP$ and $4/mmmI$.
- (v) In the cubic case the $I-F$ equivalence no longer holds because the equivalence of the a-holohedries does not extend from $4/mmm$ to the larger group $m\bar{3}m$. Thus, the cubic system has three Bravais classes: $m\bar{3}mP$, $m\bar{3}mI$, $m\bar{3}mF$.
- (vi) The rhombohedral system, $\bar{3}m$, has one Bravais class $\bar{3}mR$.
- (vii) The hexagonal system, $6/mmm$, has one Bravais class $6/mmmP$.

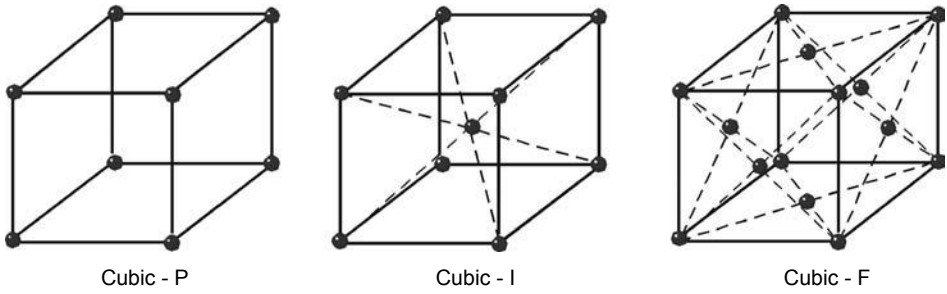


Fig. 10.8. The 3D cubic Bravais lattices.

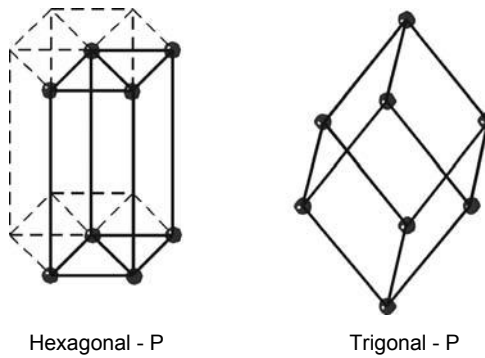


Fig. 10.9. The 3D hexagonal and trigonal Bravais lattices.

The 19 arithmetic generators listed below are needed to produce the a-holohedries of the standard lattices:

$$\begin{aligned}
 E(1) &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & \mathfrak{I}(2) &= \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} & \sigma_z(3) &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \\
 C_{2z}(4) &= \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & C_{2x}(5) &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} & \sigma_y(6) &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \\
 \sigma_x(7) &= \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & C_{4z}(8) &= \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} & U_{xy}(9) &= \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \\
 S_{4z}(10) &= \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} & C_{3z}(11) &= \begin{pmatrix} -1 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} & C'_2(12) &= \begin{pmatrix} 1 & 1 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}
 \end{aligned}$$

$$S_6(13) = \begin{pmatrix} 1 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$
$$C_{6z}^{-1}(16) = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$
$$C_{3xyz}^{-1}(18) = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}$$

$$\sigma_{\bar{x}y}(14) = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$
$$C_{2x}(17) = \begin{pmatrix} 0 & 1 & 0 \\ -1 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$
$$C_{3xyz}(19) = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$$

$$C_{6z}(15) = \begin{pmatrix} 1 & 1 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$(10.70)$$

Table 10.4. *Lattice systems, Bravais classes, and metric tensors in 3D*

Bravais class	P	I	A, B, C, or R*	F
Lattice system	Metric tensor			
Triclinic	$\begin{pmatrix} a & d & e \\ d & b & f \\ e & f & c \end{pmatrix}$	—	—	—
Monoclinic	$\begin{pmatrix} a & d & 0 \\ d & b & 0 \\ 0 & 0 & c \end{pmatrix}$	$\frac{1}{4} \begin{pmatrix} \alpha & \gamma & \delta \\ \gamma & \alpha & \eta \\ \delta & \eta & \beta \end{pmatrix}$	—	—
Orthorhombic	$\begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{pmatrix}$	$\frac{1}{4} \begin{pmatrix} \alpha & \beta & \gamma \\ \beta & \alpha & \delta \\ \gamma & \delta & \alpha \end{pmatrix}$	$\frac{1}{4} \begin{pmatrix} \alpha & \gamma & 0 \\ \gamma & \alpha & 0 \\ 0 & 0 & \beta \end{pmatrix}$	$\frac{1}{4} \begin{pmatrix} \alpha & a & b \\ a & \beta & c \\ b & c & \gamma \end{pmatrix}$
Tetragonal	$\begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & c \end{pmatrix}$	$\frac{1}{4} \begin{pmatrix} \alpha & \beta & \gamma \\ \beta & \alpha & \gamma \\ \gamma & \gamma & \alpha \end{pmatrix}$	—	—
Trigonal	—	—	$\begin{pmatrix} a & b & b \\ b & a & b \\ b & b & a \end{pmatrix}^*$	—
Hexagonal	$\begin{pmatrix} a & a/2 & 0 \\ a/2 & a & 0 \\ 0 & 0 & c \end{pmatrix}$	—	—	—
Cubic	$\begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{pmatrix}$	$\begin{pmatrix} 3a & -a & -a \\ -a & 3a & -a \\ -a & -a & 3a \end{pmatrix}$	—	$\begin{pmatrix} 2a & a & a \\ a & 2a & a \\ a & a & 2a \end{pmatrix}$

The a-holohedries of centered lattices can be obtained with the aid of the centering matrices as follows:

$$\begin{aligned}
 C\mathbf{M}_s &= \frac{1}{2} \begin{pmatrix} -1 & 1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \mathbf{M}_s \begin{pmatrix} -1 & 1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \\
 F\mathbf{M}_s &= \frac{1}{2} \begin{pmatrix} 1 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 1 \end{pmatrix} \mathbf{M}_s \begin{pmatrix} 1 & 1 & -1 \\ 1 & -1 & 1 \\ -1 & 1 & 1 \end{pmatrix} \\
 I\mathbf{M}_s &= \frac{1}{2} \begin{pmatrix} -1 & 1 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{pmatrix} \mathbf{M}_s \begin{pmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix} \\
 R\mathbf{M}_s &= \frac{1}{3} \begin{pmatrix} 1 & 1 & -2 \\ 1 & -2 & 1 \\ 1 & 1 & 1 \end{pmatrix} \mathbf{M}_s \begin{pmatrix} 1 & 1 & 1 \\ 0 & -1 & 1 \\ -1 & 0 & 1 \end{pmatrix}
 \end{aligned} \tag{10.71}$$

Table 10.4 gives the metric tensors of the 14 Bravais lattices.

10.3.5 Unit, primitive, and Wigner–Seitz cells

The primitive basis vectors of a Bravais lattice, $\mathbf{a}_1, \mathbf{a}_2, \dots, \mathbf{a}_n$, define a six-face structure called a *primitive cell*, with primitive volume

$$\mathbb{V} = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3), \quad (3\text{D})$$

$$\mathbb{A} = \frac{(\mathbf{a}_1 \times \mathbf{a}_2) \cdot (\mathbf{a}_1 \times \mathbf{a}_2)}{|\mathbf{a}_1 \times \mathbf{a}_2|} \quad (2\text{D}). \tag{10.72}$$

Each primitive cell contains, or is associated with, a single point of a Bravais lattice. An infinite repetition of this volume fills the lattice space. However, this primitive cell is not invariant under the operations of the holohedry.

A primitive cell invariant under the operations of the holohedry is a closed polyhedron (polygon) obtained by constructing planes (or lines in 2D) perpendicular to and bisecting the shortest primitive vectors. This polyhedron (polygon) is called a *Wigner–Seitz cell*; it contains one Bravais lattice point and has the same volume as the primitive cell. In addition, it preserves the holohedry of the Bravais lattice: it is left invariant by all the point-group operators of the g-holohedry. The usage of one of these primitive cells depends on the application. Figure 10.10 shows the primitive and Wigner–Seitz cells for the case of a body-centered cubic, while Figure 10.11 displays the corresponding cells for the case of a centered-rectangular mesh.

By contrast, a repetitive cell may be chosen that reflects the holohedry of the lattice, but contains more than one Bravais lattice point. For example, in the case of the

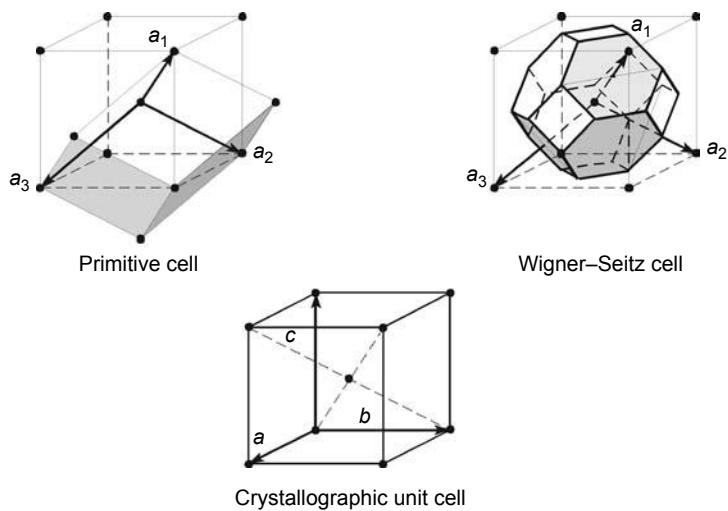


Fig. 10.10. Primitive and unit cells for the body-centered cubic structure.

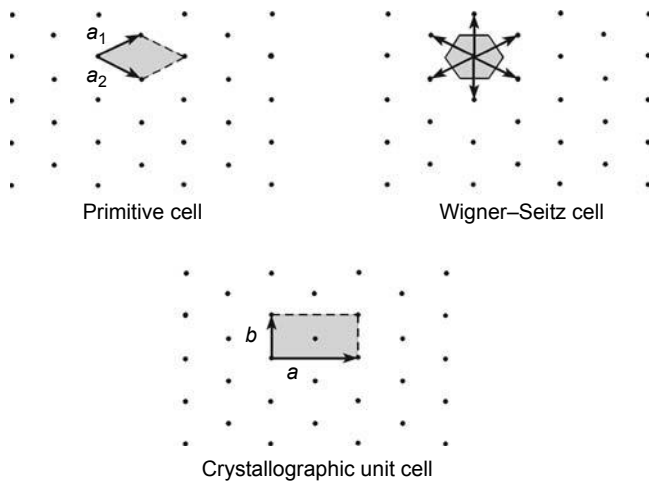


Fig. 10.11. Primitive and unit cells for the two-dimensional centered-rectangular mesh.

body- and face-centered cubic lattices, we find that a cubic unit cell preserves the corresponding holohedry. Such cells are designated *crystallographic unit cells*. They are defined by three vectors **a**, **b**, and **c**, shown in Figure 10.10 (Figure 10.11 for the 2D case). We should note that in many cases unit cells and a standard lattice primitive cell coincide.

10.3.6 The crystal

The construction of a perfect crystal is achieved by superimposing a well-defined pattern or aggregate of atoms, called the *basis*, onto every site of a Bravais lattice. Obviously, this might lower the symmetry of the composite system from the lattice holohedry. Consequently, we expect that the point-group $\mathbb{P}$ of the emergent *crystal* is either a subgroup of the holohedry or, at best, isomorphic to it: $\mathbb{P} \subseteq \mathbb{P}_B$.

Geometric and arithmetic crystal classes

Exhaustively, we identify 32 point-groups in 3D and 10 in 2D, which are subgroups of the seven 3D and four 2D holohedries, respectively. These point-groups are actually conjugacy-classes in $O(2)$ and $O(3)$, and we refer to them as *geometric (g-) classes*, $\mathbb{P}$.

The group-subgroup relations between holohedries and g-classes are listed in Tables 10.5 and 10.6 for 2D and 3D crystallographic systems, respectively.

Table 10.5. *Two-dimensional holohedries and their crystallographic g-classes.*

Crystal system	Holohedries International (Schoenflies)		Point-groups International (Schoenflies)
Oblique	2	($\mathbb{C}_2$)	1 ($\mathbb{E}$), 2 ($\mathbb{C}_2$)
Rectangular	2mm	($\mathbb{C}_{2v}$)	1 ($\mathbb{E}$), 2 ($\mathbb{C}_2$), m ($\mathbb{C}_s$), 2mm($\mathbb{C}_{2v}$),
	222	($\mathbb{D}_2$)	121 ($\mathbb{D}_1$), 222 ($\mathbb{D}_2$)
Square	4mm	($\mathbb{C}_{4v}$)	1 ($\mathbb{E}$), 2 ($\mathbb{C}_2$), 4 ($\mathbb{C}_4$), m ($\mathbb{C}_s$),
			2mm ($\mathbb{C}_{2v}$), 4mm ($\mathbb{C}_{4v}$),
	422	($\mathbb{D}_4$)	222($\mathbb{D}_2$), 422($\mathbb{D}_4$)
Hexagonal	6mm	($\mathbb{C}_{6v}$)	1 ($\mathbb{E}$), 2 ($\mathbb{C}_2$), 3 ($\mathbb{C}_3$), 6 ($\mathbb{C}_6$),
			2mm ($\mathbb{C}_{2v}$), 3m ($\mathbb{C}_{3v}$), 6mm ($\mathbb{C}_{6v}$),
	622	($\mathbb{D}_6$)	222 ($\mathbb{D}_2$), 32 ($\mathbb{D}_3$), 622 ($\mathbb{D}_6$)

The $\mathbb{D}_i$ groups replace the $\mathbb{C}_i$ s for dihedral systems.

Table 10.6. *Classification of the 32 3D crystallographic point-groups according to their holohedries.*

Crystal system	Holohedries International (Schoenflies)	Point-groups International (Schoenflies)
Triclinic	$\bar{1}$ (C_i)	$1 (\mathbb{E}), \bar{1} (C_i)$
Monoclinic	$\frac{2}{m}$ (C_{2h})	$2 (C_2), m (C_{1h}), \frac{2}{m} (C_{2h})$
Orthorhombic	mmm (D_{2h})	$222 (D_2), mm2 (C_{2v}), mmm (D_{2h})$
Tetragonal	$\frac{4}{mmm}$ (D_{4h})	$4 (C_4), 422 (D_4), \frac{4}{m} (C_{4h}), 4mm (C_{4v}), \frac{4}{mmm} (D_{4h}), \bar{4} (S_4), \bar{4}2m (D_{2d})$
Trigonal	$\bar{3}m$ (D_{3d})	$3 (C_3), 32 (D_3), 3m (C_{3v}), \bar{3} (S_6), \bar{3}m (D_{3d})$
Hexagonal	$\frac{6}{mmm}$ (D_{6h})	$6 (C_6), 622 (D_6), \frac{6}{m} (C_{6h}), 6mm (C_{6v}), \frac{6}{mmm} (D_{6h}), \bar{6} (C_{3h}), \bar{6}m2 (D_{3h})$
Cubic	$m\bar{3}m$ (O_h)	$23 (T), m\bar{3} (T_h), 432 (O), \bar{4}3m (T_d), m\bar{3}m (O_h)$

As in the case of geometric and arithmetic representations of holohedries, namely, lattice systems and Bravais classes, a geometric crystal class may contain several arithmetic crystal classes, each arithmetic crystal class $\mathbb{A}$ is a subgroup of an a-holohedry. It is related to its corresponding g-class representation by

$$\mathbb{A} = \mathbf{C}(\mathcal{L}) \mathbb{P} \mathbf{C}^{-1}(\mathcal{L}). \quad (10.73)$$

Such a finite group of integer matrices is also referred to as an *arithmetic point-group*. For each arithmetic point-group there is a unique a-holohedry as a supergroup, it is called the *Bravais group* of the arithmetic point-group. Finally, we define a family of point-groups

Table 10.7. *Standard symbols for crystal families.*

Symbol	Two-dimensional crystal family	Three-dimensional crystal family
a	—	Triclinic (anorthic)
m	Oblique	Monoclinic
o	Rectangular	Orthorhombic
t	Square	Tetragonal
h	Hexagonal	Hexagonal
c	—	Cubic

as the smallest union of point-group systems and Bravais classes of point-groups such that with each crystallographic point-group both its point-group system and its Bravais class belong to the union.

The notions of system and family can be illustrated by the case of the hexagonal family in three dimensions. The metric tensors of all the lattices of this family have two independent parameters. However, they include two systems, those with the rhombohedral lattice holohedry $\bar{3}m$, and those with a hexagonal lattice holohedry $6/mmm$. Symbols for crystal families in two and three dimensions are given in Table 10.7.

The two-dimensional case In contrast to the case of Bravais lattice symmetries, we find that the inversion operation is not mandatory in crystal symmetry. As a consequence, three-fold rotational symmetry is allowed in 2D, and we have g-classes generated from the five rotations 1, 2, 3, 4, and 6 in $\mathcal{O}(2)$. In addition, we have the g-class of reflections through an axis, $m \in \mathcal{O}(2)$, which contains two a-classes for m .

A complete list of arithmetic and geometric classes in 2D is given in Figure 10.12. The horizontal dashed lines establish the correspondence between the 10 geometric classes and their 13 constituent arithmetic classes.

The maximal g-classes are $4mm = \mathcal{C}_{4v}$ and $6mm = \mathcal{C}_{6v}$, which also have unique arithmetic classes $p4mm$ and $p6mm$, respectively. We should caution here that in establishing the distinct a-classes, we must ensure that subgroups appearing in several holohedries are in fact inequivalent arithmetic classes. For example, we find that $\mathcal{C}_s$ and $\mathcal{C}_{2v}$ each give two inequivalent arithmetic classes pm , cm and $p2mm$, $c2mm$, respectively, while the triple occurrence of $\mathcal{C}_2$ corresponds to an equivalence among the ensuing arithmetic classes.

The three-dimensional case In 3D the 32 g-classes, or crystallographic point-groups, together with the 14 Bravais lattices generate 73 a-classes, listed in Table 10.8 according to their holohedry. Table 10.8 also gives the corresponding arithmetic generators, defined in Section 10.5.

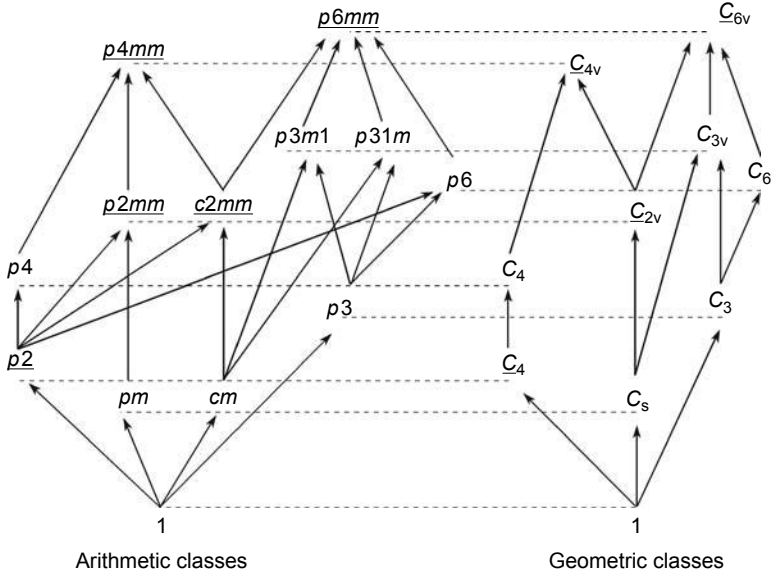


Fig. 10.12. The 13 arithmetic and 10 geometric classes in 2D. Underlined are Bravais classes and crystallographic systems.

10.4 Space-group operations: the Seitz operators

Space-group operations are formed by augmenting translation operations with point-group operations. The space-group associated with a crystallographic system consists of all such combinations of point and translation group operations that leave the system invariant. We use the Seitz operator $(R|\mathbf{w})$ to denote a combined point-group operation R and translation $\mathbf{w}$; it is defined by

$$\mathbf{r}' = (R|\mathbf{w}) \mathbf{r} = R\mathbf{r} + \mathbf{w}, \quad (10.74)$$

where R is a real orthogonal matrix representing the operation R , with determinant $+1$ or -1 for proper or improper rotations, respectively. The translation vector $\mathbf{w}$ can be either a primitive lattice vector $\mathbf{t}$ or a *nonprimitive* vector $\boldsymbol{\tau}$, which is a rational fraction of a primitive vector.

The space-group operation is performed by first operating with the point-group operator followed by the translation-group operator. Thus

$$(R|\mathbf{w}) \mathbf{r} = \mathbf{w} (R\mathbf{r}) = R\mathbf{r} + \mathbf{w}. \quad (10.75)$$

The action of a Seitz operator is pictured in Figure 10.13, along with its inverse, which is defined below. In Figure 10.13(a), the operator C_4^- , acting first, carries the point 1 into point 2. This is followed by the translation operator, $\mathbf{t}$, which carries 2 into 3.

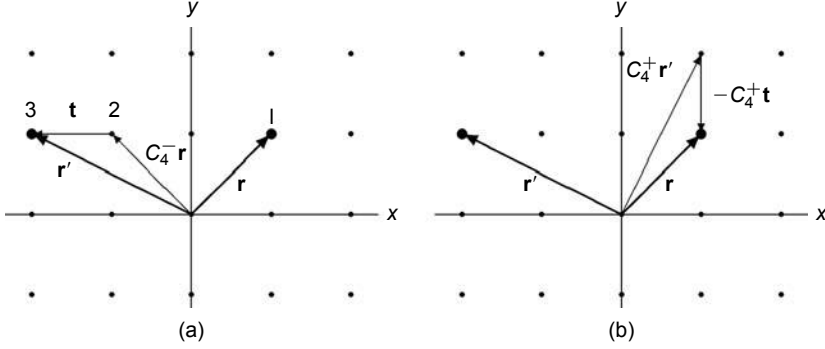


Fig. 10.13. (a) The Seitz operator $(C_4^- | \mathbf{t})$ acting on $\mathbf{r}$, where $\mathbf{t}$ is taken to be the primitive lattice vector in the negative x direction. (b) The inverse operator $(C_4^+ | -C_4^+ \mathbf{t})$ acting on $\mathbf{r}'$.

We reserve the notations E and $\mathbf{0}$ for the identity of the point and translation operations, respectively. The identity operation of the space-group is then $(E | \mathbf{0})$. Pure translations are denoted by $(E | \mathbf{w})$.

Matrix form of the Seitz operators

It is a common practice to combine the linear and translation parts of the Seitz operator into a single matrix form, as

$$(R | \mathbf{w}) = \begin{bmatrix} R & \mathbf{w} \\ \mathbf{0} & 1 \end{bmatrix},$$

where R is a 3×3 matrix, $\mathbf{w}$ a 3×1 vector and $\mathbf{0}$ a 1×3 row-matrix of zeroes. The associated transformation is given by

$$\begin{bmatrix} \mathbf{r}' \\ 1 \end{bmatrix} = \begin{bmatrix} R & \mathbf{w} \\ 0 & 1 \end{bmatrix} \begin{bmatrix} \mathbf{r} \\ 1 \end{bmatrix}. \quad (10.76)$$

10.4.1 Important properties of the Seitz operator

- (i) **The product** The product of two Seitz operators must be defined by

$$(R | \mathbf{a}) (S | \mathbf{b}) = (RS | \mathbf{a} + R\mathbf{b}), \quad (10.77)$$

to conform with the definition of the Seitz operator, since

$$\begin{aligned} (R | \mathbf{a}) (S | \mathbf{b}) \mathbf{r} &= (R | \mathbf{a}) (\mathbf{b} + S\mathbf{r}) \\ &= \mathbf{a} [R(\mathbf{b} + S\mathbf{r})] = \mathbf{a} (R\mathbf{b} + RS\mathbf{r}) \\ &= \mathbf{a} + R\mathbf{b} + RS\mathbf{r} \\ &= (RS | \mathbf{a} + R\mathbf{b}) \mathbf{r}. \end{aligned}$$

- (ii) **The inverse** If we take $(R^{-1}|\mathbf{w}')$ to be the inverse of $(R|\mathbf{w})$ we find that

$$(R|\mathbf{w})(R^{-1}|\mathbf{w}') = (E|\mathbf{w} + R\mathbf{w}') = (E|\mathbf{0}), \quad (10.78)$$

so that we must have $\mathbf{w} + R\mathbf{w}' = \mathbf{0}$, or

$$\mathbf{w}' = -R^{-1}\mathbf{w}, \quad (10.79)$$

and the inverse of the Seitz operator must be

$$(R|\mathbf{w})^{-1} = (R^{-1}|-R^{-1}\mathbf{w}). \quad (10.80)$$

The inverse operation is illustrated in Figure 10.13(b). Note that the inverse operation returns the system to its original configuration, but the *path* traversed is *not* the inverse path. The difference between the path and its inverse is of no fundamental importance. One can always find an origin such that the operations are pure rotations.

- (iii) **Restrictions** In addition to the requirement that the inverse of $(R|\mathbf{w})$ satisfies the relation

$$(R|\mathbf{w})^{-1}(R|\mathbf{w}) = (E|\mathbf{0}),$$

we must also impose the restriction that it must be an element of the space-group. That is, for some operator other than $(R|\mathbf{w})$, say $(R|\mathbf{w}')$, where $(R|\mathbf{w}')$ is an element of the space-group $\mathbb{S}$, it must satisfy

$$(R|\mathbf{w})^{-1}(R|\mathbf{w}') = (R^{-1}|-R^{-1}\mathbf{w})(R|\mathbf{w}') = (E|R^{-1}(\mathbf{w}' - \mathbf{w})), \quad (10.81)$$

where $(E|R^{-1}(\mathbf{w}' - \mathbf{w}))$ must also be an element of $\mathbb{S}$. Since the rotational part of this element is the identity, we must have that $R^{-1}(\mathbf{w}' - \mathbf{w})$ is a lattice vector. Further, since R^{-1} is a point-group operation of the lattice, $\mathbf{w}' - \mathbf{w}$ must itself be a vector that belongs to the translation group $\mathbb{T}(3)$.

- (iv) **Conjugacy operations** The usual conjugacy relation $R^{-1}SR$ becomes, for space-group operations,

$$(R|\mathbf{w})^{-1}(S|\mathbf{u})(R|\mathbf{w}) = (R^{-1}SR|R^{-1}(\mathbf{u} + S\mathbf{w} - \mathbf{w})). \quad (10.82)$$

The restriction that the translational part of the product of two Seitz operators must be a lattice vector is an important one. It is what allows us to express the space-group $\mathbb{S}$ in terms of left cosets of $\mathbb{T}(3)$. It also implies that $\mathbb{T}$ must be an invariant subgroup of $\mathbb{S}$, which we shall prove to be the case when we discuss conjugacy relations for space-groups.

Expressing a group in terms of left cosets of an invariant subgroup was the basis on which we developed the method of inducing Irreps in Chapter 9. We are now assured that we can carry over all the machinery we have previously developed to our present goal of inducing Irreps of space-groups.

We are concerned with two kinds of space-groups, symmorphic and nonsymmorphic.

10.5 Symmorphic and nonsymmorphic space-groups

10.5.1 Symmorphic space-groups

Parts of the material discussed in this section can be found in references [13, 14, 17, 22, 27, 29, 30]. A Bravais lattice space-group combines the point-group operations of its holohedry and its primitive lattice translation operations. Its Seitz operator has the form

$$(R|{}^n\mathbf{t}),$$

so that $(R|\mathbf{0})$ are pure point-group elements. We note that because each a-class is just a point-group representation engendered by primitive lattice vectors, it should be anticipated that it corresponds to a space-group without any nonprimitive lattice translations, and, therefore, there should be exactly 13 2D and 73 3D space-groups that have pure point-group operations. Such space-groups are called *symmorphic space-groups*. It is clear that both the point-group $\mathbb{P}$ and the translation group $\mathbb{T}$ are subgroups of their cov-

Table 10.8. *Arithmetic classes in three-dimensions.*

System	Bravais class	Holohedry	Arithmetic crystal class	Isomorphism class	Generators	Space group number	
Triclinic	P	$P\bar{1}$	$1P$	C_1	1	1	
			$\bar{1}P$	C_2	2	1	
Monoclinic	P	$P\frac{2}{m}$	mP	C_2	3	2	
			$2P$	C_2	4	2	
			$2/mP$	D_2	3, 4	4	
	I	$\frac{2}{I2}m$	mI	C_2	$I3$	2	
			$2I$	C_2	$I4$	1	
			$2/mI$	D_2	$I3, I4$	2	
	Orthorhombic	P	$Pmmm$	$222P$	D_2	4, 5	4
				$2mmP$	D_2	6, 7	10
$mmmP$				$D_2 \times C_2$	3, 6, 7	16	
I		$Immm$	$222I$	D_2	$I4, I5$	2	
			$2mmI$	D_2	$I6, I7$	3	
			$mmmI$	$D_2 \times C_2$	$I3, I6, I7$	4	
C		$Ammm$	$222A$	D_2	$A4, A5$	2	
			$2mm1A$	D_2	$A6, A7$	3	
			$2mm2A$	D_2	$A3, A6$	4	
			$mmmA$	$D_2 \times C_2$	$A3, A6, A7$	6	
	F		$Fmmm$	$222F$	D_2	$F4, F5$	1
				$2mmF$	D_2	$F6, F7$	2

Table 10.8. (*cont.*)

System	Bravais class	Holohedry	Arithmetic crystal class	Isomorphism class	Generators	Space group number
Tetragonal	<i>P</i>	$P\frac{4}{mmm}$	$mmmF$	$D_2 \times C_2$	$F3, F6, F7$	2
			$4P$	C_4	8	3(4)
			$4/mP$	$C_4 \times C_2$	3, 8	4
			$422P$	D_4	8, 9	6(8)
			$4mmP$	D_4	6, 8	8
			$\bar{4}P$	C_4	10	1
			$\bar{4}2m1P$	D_4	9, 10	4
			$\bar{4}2m2P$	D_4	5, 10	4
			$4/mmmP$	$D_4 \times C_2$	3, 6, 8	16
	<i>I</i>	$I\frac{4}{mmm}$	$4I$	C_4	$I8$	2
			$4/mI$	$C_4 \times C_2$	$I3, I8$	2
			$422I$	D_4	$I8, I9$	2
			$4mmI$	D_4	$I6, I8$	4
	<i>I</i>	$I\frac{4}{mmm}$	$\bar{4}I$	C_4	$I10$	1
			$\bar{4}2m1I$	D_4	$I9, I10$	2
			$\bar{4}2m2I$	D_4	$I5, I10$	2
			$4/mmmI$	$D_4 \times C_2$	$I3, I6, I8$	4
Trigonal	<i>P</i>	$R\bar{3}m$	$3R$	C_3	$R11$	1
			$32R$	D_3	$R11, R12$	1
			$\bar{3}R$	C_6	$R13$	1
			$3mR$	D_3	$R11, R14$	2
			$\bar{3}mR$	D_6	$R13, R14$	2
Hexagonal	<i>P</i>	$P\frac{6}{mmm}$	$3P$	C_3	11	2(3)
			$321P$	D_3	14, 5	2(3)
			$322P$	D_3	11, 12	2(3)
			$\bar{3}P$	C_6	13	1
			$3m1P$	D_3	11, 15	2
			$3m2P$	D_3	11, 14	2
			$\bar{3}m1P$	D_6	13, 15	2
			$\bar{3}m2P$	D_6	13, 14	2
			$6P$	C_6	16	4(6)
			$6mmP$	D_6	14, 16	4
			$622P$	D_6	9, 16	4(6)
			$6/mP$	$C_6 \times C_2$	3, 16	2
			$\bar{6}P$	C_6	17	1
			$\bar{6}m21P$	D_6	9, 17	2

Table 10.8. (*cont.*)

System	Bravais class	Holohedry	Arithmetic crystal class	Isomorphism class	Generators	Space group number
Cubic	<i>P</i>	<i>Pm3m</i>	$\bar{6}m22P$	D_6	12, 17	2
			$6/mmmP$	$D_6 \times C_2$	3, 14, 16	4
			$23P$	T	4, 18	2
			$m3P$	$T \times C_2$	2, 4, 18	3
			$432P$	O	8, 19	3(4)
			$\bar{4}3mP$	O	10, 19	2
			$m3mP$	$O \times C_2$	2, 8, 19	4
			$23I$	T	14, 118,	2
			$m3I$	$T \times C_2$	2, 110, 118	2
			$432I$	O	18, 119	2
	<i>I</i>	<i>Im3m</i>	$\bar{4}3mI$	O	110, 119	2
			$m3mI$	$O \times C_2$	2, 18, 119	2
			$23F$	T	$F4, F18$	1
			$m3F$	$T \times C_2$	2, $F4, F18$	2
			$432F$	O	$F8, F19$	2
			$\bar{4}3mF$	O	$F10, F19$	2
	<i>F</i>	<i>Fm3m</i>	$m3mF$	$O \times C_2$	2, $F8, F19$	4

ering space-group $\mathbb{S}$. Table 10.8 gives the number of symmorphic 3D space-groups in each a-class.

As it turns out, only $\mathbb{T}$ is an invariant subgroup of $\mathbb{S}$, since conjugation with any $(R'|\mathbf{t}')$ gives

$$\begin{aligned}(R'|\mathbf{t}')^{-1} (E|\mathbf{t}) (R'|\mathbf{t}') &= (E|R'^{-1}\mathbf{t}) \in \mathbb{T}, \\ (R'|\mathbf{t}')^{-1} (R|\mathbf{0}) (R'|\mathbf{t}') &= (R'^{-1}RR'|R'^{-1}(\mathbf{R}\mathbf{t}' - \mathbf{t}')) \notin \mathbb{P},\end{aligned}$$

since the Bravais lattice has the symmetry of both the translation group $\mathbb{T}$ and the point-group $\mathbb{P}$. Thus $R^{-1}\mathbf{t}$ is a lattice vector and $(E|R^{-1}\mathbf{t})$ is a pure translation of the lattice. This shows that $\mathbb{S}$ is a semidirect product of $\mathbb{T}$ and $\mathbb{P}$,

$$\mathbb{S} = \mathbb{T} \odot \mathbb{P}, \quad (10.83)$$

which is sometimes referred to as an extension of $\mathbb{T}$ by $\mathbb{P}$. Here, we have followed the convention of putting the invariant subgroup as the first member of the semidirect product.

If we were to express a symmorphic space-group in terms of left cosets of $\mathbb{T}(3)$, we would find it most convenient to use as coset representatives the simplest set of Seitz operators, namely, the pure point-group elements $(R_i|\mathbf{0})$ of $\mathbb{P}$ of order p . Setting $R_1 \equiv E$, we would

write

$$\mathbb{S} = \mathbb{T}(E|\mathbf{0}) + \mathbb{T}(R_2|\mathbf{0}) + \mathbb{T}(R_3|\mathbf{0}) + \cdots + \mathbb{T}(R_p|\mathbf{0}). \quad (10.84)$$

Construction of symmorphic space-groups and their notations

With the recipe defined by (10.15) we begin to match the crystallographic group symmetries with the appropriate Bravais lattices. For example, starting with the triclinic we notice that there is only a P-lattice, for which, when matched with the two compatible point-groups $1(\mathbb{E})$ and $\bar{1}(\mathbb{C}_i)$, we obtain the space-groups $P1(\mathbb{E}^1)$ and $P\bar{1}(\mathbb{C}_i^1)$, respectively. The Schoenflies notation is shown in parentheses.

In a similar way, we have two monoclinic lattice structures, P and C , which give rise to the space-groups:

$$P2(\mathbb{C}_2^1), Pm(\mathbb{C}_{1h}^1), P\frac{2}{m}(\mathbb{C}_{2h}^1), \quad \text{and} \quad C2(\mathbb{C}_2^2), Cm(\mathbb{C}_{1h}^2), C\frac{2}{m}(\mathbb{C}_{2h}^2).$$

We notice that in labeling space-groups in the International system we started with the type of Bravais lattice P , I , F , etc., followed by the appropriate point-group. In the Schoenflies notation, the space-group labeling is simply accomplished by augmenting the corresponding point-group notation with a superscript number, indicating its order in the list sharing the same point-group.

Following this procedure we generate the 73 three-dimensional and 13 two-dimensional symmorphic space-groups.

10.5.2 Nonsymmorphic space-groups

Nonsymmorphic space-groups have some elements with nonprimitive lattice translations. Thus, it is important to point out what was implicit in our discussion of the restrictions imposed on the product of Seitz operators; namely, there can be, at most, only one unique nonprimitive lattice vector $\boldsymbol{\tau}_i$ associated with each point-group operator R_i , otherwise the vector $\boldsymbol{\tau}' - \boldsymbol{\tau}_i$ that would appear in the last term of (10.80) might not be a lattice vector.

The need for a nonprimitive translation may ensue for some crystal structures when the superposition of an atomic basis on a Bravais lattice implies that the application of a certain pure point-group operation does not bring the crystal to its original configuration, yet the introduction of an accompanying nonprimitive translation, satisfying the restrictions discussed below, will leave the crystal invariant. In such cases, a general space-group operation assumes the form

$(R|{}^n\boldsymbol{\tau} + {}^n\mathbf{t}).$

(10.85)

A space-group with at least one nonzero $\boldsymbol{\tau}$ is called *nonsymmorphic*.

Clearly, if we were to express a nonsymmorphic space-group in terms of left cosets, we could choose all the ${}^n\mathbf{t}$ to be zero, but one or more of the vectors $\boldsymbol{\tau}_i$ must be nonzero.

The translation group $\mathbb{T}$ remains an *invariant subgroup* of its nonsymmorphic space-group $\mathbb{S}$. For when we perform the conjugacy operation using a general element $(R|\mathbf{a})$, where $\mathbf{a} = \mathbf{v} + \mathbf{t}$, we obtain

$$\begin{aligned} (R|\mathbf{a})^{-1} (E|\mathbf{t}) (R|\mathbf{a}) &= (R^{-1}|-R^{-1}\mathbf{a}) (E|\mathbf{t}) (R|\mathbf{a}) \\ &= (R^{-1}|-R^{-1}\mathbf{a}) (ER|\mathbf{t}) + (E|\mathbf{a}) \\ &= (R^{-1}ER|R^{-1}\mathbf{t} + R^{-1}E\mathbf{a} - R^{-1}\mathbf{a}) \\ &= (E|R^{-1}\mathbf{t}). \end{aligned} \quad (10.86)$$

Nonsymmorphic space-groups have some elements with nonprimitive translations. This implies that none of the pure point-groups are subgroups of nonsymmorphic space-groups; yet it is still possible to identify a quotient or factor group $\mathbb{F}$, which is isomorphic to a point-group, namely

$$\mathbb{F} = \frac{\mathbb{S}}{\mathbb{T}}. \quad (10.87)$$

We may then define right cosets such that

$$\mathbb{S} = \sum_{i=1}^f \mathbb{T} (R_i|\boldsymbol{\tau}_i). \quad (10.88)$$

Screw axes and glide planes

In order to understand the nature of the nonprimitive translations $\boldsymbol{\tau}$ associated with some elements of a point-group, let us consider an operation $(R|\mathbf{u})$, defined about an arbitrary origin, such that

$$\mathbf{r}' = (R|\mathbf{u}) \mathbf{r} = R\mathbf{r} + \mathbf{u},$$

and study the possibility of eliminating the inhomogeneity in this transformation by simply displacing the origin. To this end, we displace the origin by $\mathbf{w}$, and we get

$$\mathbf{s} = \mathbf{r} + \mathbf{w}, \quad (10.89)$$

$$\mathbf{s}' = \mathbf{r}' + \mathbf{w} \quad (10.90)$$

$$\begin{aligned} &= R(\mathbf{s} - \mathbf{w}) + \mathbf{u} + \mathbf{w} \\ &= (R|\mathbf{0}) \mathbf{s} ? \end{aligned} \quad (10.91)$$

This is just the conjugation

$$(E|\mathbf{w}) (R|\mathbf{u}) (E|\mathbf{w})^{-1} = (R|\mathbf{w} + \mathbf{u} - R\mathbf{w}) = (R|\mathbf{0}) ?$$

Satisfying this condition would require that

$$(R - \mathbf{I}) \mathbf{w} = \mathbf{u}. \quad (10.92)$$

It is convenient to solve this equation in the coordinate system where R is diagonal, with eigenvalues $\lambda_1, \lambda_2, \lambda_3$, for example,

$$R = \begin{cases} \begin{pmatrix} e^{i\theta} & 0 & 0 \\ 0 & e^{-i\theta} & 0 \\ 0 & 0 & 1 \end{pmatrix} & \text{proper rotations about } \hat{\mathbf{e}}_3 \text{ axis,} \\ \\ \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} & \text{reflection plane normal to } \hat{\mathbf{e}}_3 \text{ axis.} \end{cases} \quad (10.93)$$

Expressing $\mathbf{u}$ in these coordinates as

$$\mathbf{u} = u_1 \hat{\mathbf{e}}_1 + u_2 \hat{\mathbf{e}}_2 + u_3 \hat{\mathbf{e}}_3 \quad (10.94)$$

we obtain

$$\mathbf{w} = \frac{u_1}{\lambda_1 - 1} \hat{\mathbf{e}}_1 + \frac{u_2}{\lambda_2 - 1} \hat{\mathbf{e}}_2 + \frac{u_3}{\lambda_3 - 1} \hat{\mathbf{e}}_3. \quad (10.95)$$

From (10.93) and (10.95), we arrive at the following:

- (i) For proper rotations only displacements normal to the rotation axis can be eliminated since (10.95) requires $u_3 = 0$, which is the component along the rotation axis as identified by (10.94). Proper rotation operations with nonzero intrinsic translations are referred to as *screw axes*.
- (ii) For reflections only the displacement normal to the reflection plane can be eliminated. Reflection operations with nonzero intrinsic translations are referred to as *glide planes*.

In the case of an n -fold rotation, we have $R^n = E$; while for an arbitrary reflection σ , we have $\sigma^2 = E$. Thus, if we consider a space-group operation $(R|\boldsymbol{\tau}_{\parallel})$ involving a nonprimitive translation vector $\boldsymbol{\tau}_{\parallel}$ along the axis of the proper rotation R , we find that

$$(R|\boldsymbol{\tau}_{\parallel})^n = (R^n|\boldsymbol{\tau}_{\parallel} + R\boldsymbol{\tau}_{\parallel} + R^2\boldsymbol{\tau}_{\parallel} + \cdots + R^{n-1}\boldsymbol{\tau}_{\parallel}), \quad (10.96)$$

where we have made repeated use of the rule for the product of Seitz operators. Now, since $\boldsymbol{\tau}_{\parallel}$ is along the rotation axis of the proper rotation R , we have $R\boldsymbol{\tau}_{\parallel} = \boldsymbol{\tau}_{\parallel}$ and thus the sum of the n translation terms on the right side of (10.96) is just $n\boldsymbol{\tau}_{\parallel}$, so that

$$(R|\boldsymbol{\tau}_{\parallel})^n = (R^n|n\boldsymbol{\tau}_{\parallel}) = (E|\mathbf{t}), \quad (10.97)$$

where $\mathbf{t} \in \mathbb{T}$.

We thus conclude that *the nonprimitive translation associated with an n -fold point-group operation* has to have the form

$$\boldsymbol{\tau}_{\parallel} = \mathbf{t}/n,$$

which restricts $\boldsymbol{\tau}_{\parallel}$ to a submultiple of a primitive lattice translation. Point-group compatibility further restricts the nonprimitive translation to $n = 1, 2, 3, 4$, or 6 . An example with $n = 2$ is shown in Figure 10.14.

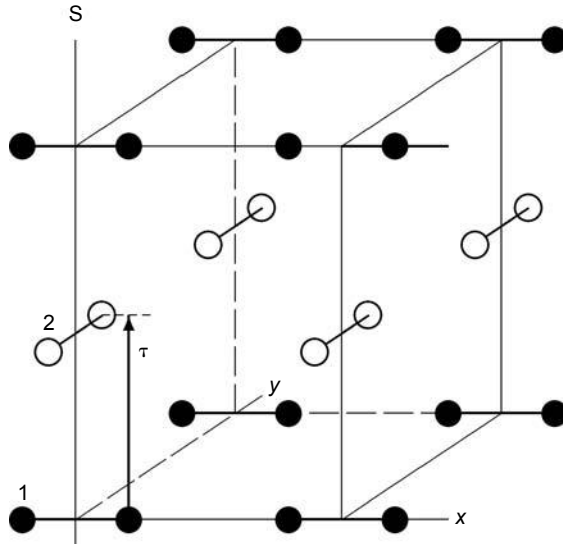


Fig. 10.14. A unit cell belonging to a nonsymmorphic space-group. All atoms are identical. The solid circles denote atoms aligned along the X -axis in the basal plane of the cell. Open circles denote identical atoms in the mid-plane, which are aligned parallel to the Y -axis. The Z -axis is the screw axis. The fractional translation vector τ , which is associated with the screw axis and a glide plane, is given by $\tau = c/2$, where c is the primitive lattice translation perpendicular to the basal plane.

A translation $\tau_{\parallel}$ that is parallel to a glide plane or parallel to a screw axis, combined with a point-group operation, are the fundamental operations admitted in crystallography. As we demonstrated above, this is achieved by selecting appropriate origins whereby this restriction on the nonprimitive vectors can be realized. Nonetheless, in many situations it is more convenient to select a common origin for all the point-group operations, and, hence, we admit some nonstandard compound operations for nonsymmorphic space-groups, a point that we will clarify when we deal with specific problems.

Summing up, we find that two kinds of rotation axes and mirror planes can be specified:

- (i) Axes or planes for which the rotation or reflection is a symmetry of the crystal without an accompanying translation. We denote such operations as *simple*.
- (ii) Axes or planes for which the rotation or reflection is a symmetry of the crystal only when accompanied by a translation parallel to the axis or plane. We denote such operations as *screw axes* or *glide planes*, respectively. In such cases, we can distinguish between two possibilities:
 - (a) A given rotation (reflection) has both simple and screw axes (glide planes); the latter can be eliminated by origin transformation. We call such screw axes (glide planes) *removable*.
 - (b) Screw axes (glide planes) are said to be *essential* when no simple operations can be found.

Thus, the space-group of a crystal is symmorphic if there is a single origin through which the axis of every rotation and the plane of every reflection is simple. A space-group is nonsymmorphic if

- (i) There is at least one essential screw axis or mirror plane.
- (ii) All screw axes and mirror planes are removable, but there is no single origin about which all operations are simple. Surprisingly, only two of the 157 nonsymmorphic Fedorov groups belong to this category: $I2_12_12_1$ (#24) and $I2_13$ (#199).

Nonsymmorphic space-group labeling

As we have seen above, a screw-axis operation involves a rotation about the n -fold axis of symmetry, $n(C_n)$ in the international (Schoenflies) notation, followed by a nonprimitive translation of $\frac{m}{n}$ of the shortest lattice translation vector parallel to the axis. Such an operation is represented by the symbol n_m . Thus, in principle, we may have: $2_1, 3_1, 3_2, 4_1, 4_2, 4_3, 6_1, 6_2, 6_3, 6_4, 6_5$.

The classification of glide planes is given in terms of *axial*, *diagonal (or n -glide)*, or *diamond*. The international notation for these classes of glide planes and its interpretation in terms of the crystallographic a , b , and c is given in Table 10.9.

10.5.3 Point-group of the crystal revisited

We have previously defined the point-group operators of the holohedry by setting to zero all the lattice translations in the space-group operators. We now define the point-group $\mathbb{P}$ of a crystal by setting to zero *all* translations that appear in the space-group operators, including both primitive and nonprimitive lattice translations. We now need to clarify this definition and its implications.

Table 10.9. Classification of glide planes.

Type	Axial			Diagonal			Diamond		
Symbol	a	b	c	n			d		
Glide vector	$\frac{\mathbf{a}}{2}$	$\frac{\mathbf{b}}{2}$	$\frac{\mathbf{c}}{2}$	$\frac{\mathbf{a} + \mathbf{b}}{2},$	$\frac{\mathbf{b} + \mathbf{c}}{2},$	$\frac{\mathbf{c} + \mathbf{a}}{2}$	$\frac{\mathbf{a} \pm \mathbf{b}}{4},$	$\frac{\mathbf{b} \pm \mathbf{c}}{4},$	$\frac{\mathbf{c} \pm \mathbf{a}}{4}$
In addition for				$\frac{\mathbf{a} + \mathbf{b} + \mathbf{c}}{2}$			$\frac{\mathbf{a} \pm \mathbf{b} \pm \mathbf{c}}{4}$		
				Tetragonal and cubic			Tetragonal and cubic		

We have illustrated in Section 10.3 how the point-group symmetry of a crystal may be reduced to a subgroup of the holohedry group $\mathbb{P}_B$ of the Bravais lattice when the lattice is decorated with a basis. Things become a bit more complicated if the atoms that constitute the basis are separated so as to form a glide plane as depicted in Figure 10.15. This creates a nonsymmorphic crystal.

The choice of origin in Figure 10.15 is, in principle, arbitrary, in that a crystal can be constructed starting from any origin. However, in solid state physics applications using group theory, it is important to choose the origin such that all the nontranslational operations form a point-group $\mathbb{P}$, even though this may require that we allow nonstandard compound operations for nonsymmorphic space-groups. If there is a glide translation τ that must be combined with a point-group operation in order to form an allowed space-group operation, some care is required. Thus, in Figure 10.15, we must not choose σ as one of the symmetry operations, even though it is a true plane of reflection symmetry. We must choose σ_v^1 and σ_v^2 , which *must* be associated with τ , to form the space-group operators $(\sigma_v^1|\tau)$ and $(\sigma_v^2|\tau)$. Neither σ_v^1 nor τ alone belongs to the space-group; only the combination $(\sigma_v^1|\tau)$ is a space-group operator. Nonetheless, we define a point-group $\mathbb{P}$ by setting to zero *all* translations in the space-group operators. Defined in this way, σ_v^1 is an element of the point-group $\mathbb{P}$. It is clear that $\mathbb{P}$ is not necessarily a subgroup of $\mathbb{S}$, for in this case σ_v^1 is clearly not an element of $\mathbb{S}$.

We will find that our choice of origin has the compelling advantage that any space-group operation can be represented as a product of operations within the primitive unit cell and a translation operation.

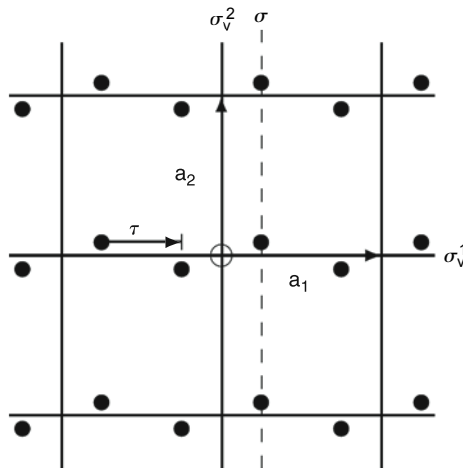


Fig. 10.15. A section of a square net with a basis that introduces a fractional glide translation of $\tau = \mathbf{a}_1/2$. The lines σ_v^1 and σ_v^2 denote reflection operations that are defined only in combination with the glide translation τ . The circle at the intersection of these two lines is taken to be the origin, about which the crystal has a symmetry operation C_2 . The reflection symmetry through the dashed line σ does not pass through the origin and thus does not belong to the point-group operations that keep the origin invariant.

Table 10.10. *Corresponding terms in mathematical and crystallographic terminology.*

Mathematical terminology	Crystallographic terminology
$\mathbb{Z}$ -class	Arithmetic crystal class
$\mathbb{Q}$ -class	Geometric crystal class
Bravais flock	Bravais type
Affine class of space-groups	Space-group type
Lattice basis	Primitive basis
Finite unimodular groups	Crystallographic point-groups
Degree (e.g. space-groups of degree n)	Dimension (e.g. n -dimensional space-groups)
Stabilizers in space-groups of points	Site-symmetry groups

For the crystal lattice of Figure 10.15, the space-group elements belonging to the unit cell are $(E|\mathbf{0})$, $(C_2|\mathbf{0})$, $(\sigma_v^1|\boldsymbol{\tau})$, $(\sigma_v^2|\boldsymbol{\tau})$. Setting all translations to zero gives the set of point-group elements

$$\mathbb{P} = \{(E|\mathbf{0}), (C_2|\mathbf{0}), (\sigma_v^1|\mathbf{0}), (\sigma_v^2|\mathbf{0})\}$$

or, more simply, $\mathbb{P} = \{E, C_2, \sigma_v^1, \sigma_v^2\}$.

10.5.4 Classification of space-groups

We notice that by virtue of the presence of space translations, space-groups do not have fixed-point orbits. However, we usually describe a space-group with respect to a fixed origin. Displacing the origin of a space-group produces another space-group that is physically identical. However, a uniform scaling of the lattice basis vectors results in a space-group; though not identical, it differs only in the scaling of its primitive lattice vectors. By the same token, changing the ratio of the primitive basis $\mathbf{a}$, $\mathbf{b}$ of a rectangular net, or lattice, for example, produces a physically equivalent lattice.

In order to distinguish between these cases, it is appropriate at this point to introduce the terms *space-group* and *space-group type*: The former designates a particular space-group, namely, one that is defined not only by the translational and point symmetry, but also by the corresponding cell parameters, which can be defined through the metric of the lattice. By this token, the space-groups associated with carbon and silicon in the diamond structure are different. *The number of space-groups is thus infinite.*

By contrast, a space-group type is defined only by translational and point symmetry. Thus, in order to determine the type of a particular space-group, we have to transform it into one of the standard representatives of space-group types. The totality of such transformations, or operations: geometric contraction or expansion, dilation, reflection, rotation, shear, and translation, is contained in the affine group $\mathcal{A}$.

Classification of space-group types: affine transformations

The application of affine transformations to determine space-group types is also found in references [26, 34, 35, 36, 37]. An affine group transformation preserves collinearity so that points that initially lie on a straight line still lie on a straight line after transformation. It also preserves the ratios of distances, yet it does not preserve angles or lengths. For example, a transformation of the form

$$\begin{bmatrix} x' \\ y' \end{bmatrix} = \begin{bmatrix} a & -b \\ b & a \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix}$$

results in a rotation by

$$\alpha = \tan^{-1} \left(\frac{-b}{a} \right),$$

and an expansion by $\sqrt{a^2 + b^2}$. In general, an affine transformation can be expressed as

$$\mathbf{r}' = A\mathbf{r} + \mathbf{w},$$

where A is a linear transformation, and $\mathbf{w}$ is a translation. The transformation is *orientation-preserving* if $\det[A] > 0$, and *orientation-reversing* if $\det[A] < 0$.

Thus, in crystallography, the classification of space-group types in n dimensions is defined by their conjugacy with respect to $\mathcal{A}(n)$. This was proposed by Bieberbach in 1910 [33], who demonstrated that:

- (i) for two space-groups, $\mathbb{S}$ and $\mathbb{S}'$, to be isomorphic, there must exist an element $(A|\mathbf{w}) \in \mathcal{A}$, $A \in GL(n, \mathbb{R})$, such that

$$\mathbb{S}' = (A|\mathbf{w}) \mathbb{S} (A|\mathbf{w})^{-1}; \quad (10.98)$$

and that

- (ii) the number of isomorphism classes of space-groups is finite.

Notice that (10.98) implies that, after a rotation, stretching, and shift of origin, one space-group representation becomes identical to the other.

In essence, Bieberbach states that, abstract isomorphism of space-groups is the same as equivalence under affine transformations; it is natural to regard objects as equivalent if they can be transformed into each other by an affine transformation.

Affine group conjugacies allow us to identify 17 isomorphism classes of space-groups (space-group types) in 2D, 13 of them are symmorphic. In 3D there are 219 nonsymmorphic space-group types, 73 of them are symmorphic. However, when conjugation is limited to the orientation-preserving elements of $\mathcal{A}$ with $\det(A) = +1$, we identify 230 nonsymmorphic classes.

In 3D, there are, in all, 230 crystallographic space-groups, 73 of which are symmorphic and the remaining 157 are nonsymmorphic.

In 2D, there are in all 17 space-groups, 13 of which are symmorphic.

The 11 additional classes are nonsymmorphic space-group types that contain only proper rotations, but have screw axes. Since a screw axis can be characterized as right- or left-handed, we find that each of these space-groups has a unique partner with a screw axis of the opposite handedness. Each such pair is referred to as an *enantiomorphic* pair.

Enantiomorphism

The notion of enantiomorphism reveals a subtle difference in how crystallographic objects may be classified. Crystallography deals with objects in physical space, and in some experimental situations the handedness of an object plays a role. In other words, the orientation has to be preserved by a symmetry operation. We are thus obliged to refine our classification scheme to allow only orientation-preserving affine transformations:

Two objects that are equivalent by an affine transformation but not by an orientation-preserving transformation are called an enantiomorphic pair, each member of an enantiomorphic pair is said to be enantiomorphic.

Table 10.11 lists all enantiomorphic pairs of 3D space-group types.

Table 10.11. *Enantiomorphic pairs.*

First member		Second member	
$P4_1$	(C_4^2)	$P4_3$	(C_4^4)
$P4_122$	(D_4^3)	$P4_322$	(D_4^7)
$P4_12_12$	(D_4^4)	$P4_32_12$	(D_4^8)
$P3_1$	(C_3^2)	$P3_2$	(C_3^3)
$P3_112$	(D_3^3)	$P3_212$	(D_3^5)
$P3_121$	(D_3^4)	$P3_221$	(D_3^6)
$P6_1$	(C_6^2)	$P6_5$	(C_6^3)
$P6_2$	(C_6^4)	$P6_4$	(C_6^5)
$P6_122$	(D_6^2)	$P6_522$	(D_6^3)
$P6_422$	(D_6^5)	$P6_222$	(D_6^4)
$P4_332$	(O^6)	$P4_132$	(O^7)

Arithmetic, Bravais, and geometric classes

Space-group types can be sorted into the following, now familiar, classifications:

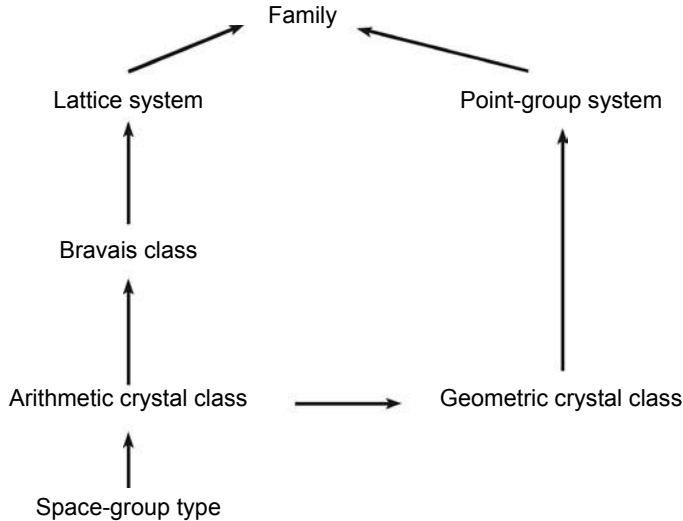


Fig. 10.16. Relation between various crystallographic equivalence concepts.

- (i) **Arithmetic crystal classes** The 230 (17) 3D (2D) space-group types are classified into 73 (13) arithmetic crystal classes: each arithmetic crystal class contains space-group types with the same point-group symmetry and the same type of centering, i.e. based on the conjugacy properties of the representations of their symmetry groups as subgroups of the arithmetic group $GL(3; \mathbb{Z})$ ($GL(2; \mathbb{Z})$). This classification can be established for any space dimensions; see for instance [31, 43, 168].

The main reason for formulating the arithmetic simple-lattice for criterion symmetry is that it describes these structures in a more precise way than the orthogonal framework.

An arithmetic crystal class is designated by a crystallographic point-group symbol, followed by the Bravais lattice symbol. For example, space-group types Pm , Pc and Pn all correspond to the same arithmetic crystal class mP .

- (ii) **Geometric crystal classes** Arithmetic crystal classes are classified, according to their point-group symmetry, into 32 geometric crystal classes. In other words, the arithmetic crystal classes in a given geometric crystal class have the same point symmetry, irrespective of the type of centering.

A geometric crystal class is indicated by the symbol of the corresponding crystallographic point-group; however, it is composed of a set of space-groups.

Examples

Table 10.12. *Space-group types corresponding to the same Bravais class.*

Space-group	Arithmetic crystal class	Bravais class
$P2_1$	$2P$	$\frac{2}{m}P$
Pc	mP	$\frac{2}{m}P$
$P\frac{2_1}{c}$	$\frac{2}{m}P$	$\frac{2}{m}P$

Table 10.13. *Space-group types corresponding to the same geometric crystal class.*

Space-group type	Arithmetic crystal class	Bravais class	Geometric crystal class
Pm	mP	$\frac{2}{m}P$	m
Pc	mP	$\frac{2}{m}P$	m
Cc	mC	$\frac{2}{m}C$	m

Table 10.14. *Space-group types corresponding to the same holohedry*

Space-group type	Arithmetic crystal class	Geometric crystal class	Bravais class	Holohedry	Crystal system
$P2_1$	$2P$	2	$\frac{2}{m}P$	$\frac{2}{m}$	monoclinic
Pm	mP	m	$\frac{2}{m}P$	$\frac{2}{m}$	monoclinic
Pc	mP	m	$\frac{2}{m}P$	$\frac{2}{m}$	monoclinic
$C2_1$	$2C$	2	$\frac{2}{m}C$	$\frac{2}{m}$	monoclinic
Cc	mC	m	$\frac{2}{m}C$	$\frac{2}{m}$	monoclinic

- (iii) **Bravais arithmetic crystal classes** Arithmetic crystal classes corresponding to the arithmetic holohedries of lattices, as, for example

$$1P, \frac{2}{m}P, \frac{2}{m}C, mmmP, mmmC, mmmI, mmmF, 4mmmP, \\ \frac{4}{mmm}I, 3mR, \frac{6}{mmm}P, m3mP, m3mI, m3mF,$$

form the 14 Bravais arithmetic crystal classes or simply Bravais classes in 3D.

A *lattice type* is defined as the class of all simple lattices whose lattice groups, or arithmetic holohedries, belong to the same conjugacy class in $GL(3, \mathbb{Z})$; i.e. share the same point-group and the same type of centering.

- (iv) **Geometric holohedry and crystal systems** The geometric crystal classes corresponding to the lattice holohedries are simply termed holohedries or *geometric-class systems*. In 3D, there are seven holohedries:

$$1, 2/m, mmm, 4/mmm, -3m, 6/mmm, m - 3m;$$

out of the 32 geometric crystal classes, the remaining geometric crystal classes are termed the 25 merohedries.

Commonly, a space-group is associated with the Bravais class of its lattice. In some cases, however, the lattice may accidentally correspond to a higher Bravais class (e.g. the case of a monoclinic crystal whose lattice has $\beta = 90^\circ$). This prevents a reticular classification of space-groups directly in terms of Bravais types of lattices. Space-groups are thus assigned to the Bravais class which corresponds to their point-group: all the space-groups assigned to the same Bravais class belong to the same Bravais flock of space-groups, which are indicated by the symbol of the corresponding Bravais class 2.

10.5.5 Computer generation of space-group matrices

With the classifications given above, we can set up a library of data files that catalogs the generating elements of the 32 point-groups, both in rotational-matrix and permutation representations, and lists the nonprimitive translations of the space-groups associated with each point-group crystal class.

We continue to use the example of the diamond structure as an illustration of the computational methodology for generating the elements of the space-group representatives. To this end we construct a data file that specifies all required information regarding this system, namely,

- (i) Space dimension, ND.
- (ii) Primitive lattice vectors, RL.
- (iii) Atomic positions in primitive cell, RR.
- (iv) Number of chemical elements, NCEL.
- (v) Number of sublattices, NSL.
- (vi) Number of atoms/sublattice, NAT.

File: DIAMOND

```
Print["DIAMOND STRUCTURE"];
a0=4.2 Å
ND=3
RL={{1/2,1/2,0},{0,1/2,1/2},{1/2,0,1/2}}
VV=SG227
NSL=2
NCEL=1
NAT=1
RR={{0,0,0},{1/4,1/4,1/4}}
```

Since the diamond structure belongs to the crystal class O_h , we list below the data file for the O_h crystal class. This file is stored in the library under “Oh”.

It specifies:

- (i) The number of generators of the cubic point-group, NG.
- (ii) The point-group order, g.
- (iii) The permutation Rep of rotation group generators, P. The number of permuted objects is NP.
- (iv) The matrix Rep of rotation group generators, R.

Space-Groups of Crystal-class Oh

```
NG=5
g=48
NP=8
(* C2, Ux, Uxy, C3, I *)
R={{{-1,0,0},{0,-1,0},{0,0,1}},{1,0,0},{0,-1,0},{0,0,-1}},
   {{0,1,0},{1,0,0},{0,0,-1}},{0,0,1},{1,0,0},{0,1,0}},
   {{-1,0,0},{0,-1,0},{0,0,-1}}}
P={{3,4,1,2,7,8,5,6},{6,5,8,7,2,1,4,3},{7,6,5,8,3,2,1,4},
   {6,2,1,5,7,3,4,8},{7,8,5,6,3,4,1,2}}}
```

It lists:

- (v) The nonprimitive translations of all the space-groups of the O_h crystal class. For example, the nonprimitive translations of the space-group $Fd3m$ (diamond structure), which is space-group # 227, are defined by the Array SG227.

```

SG221={{0,0,0},{0,0,0},{0,0,0},{0,0,0},{0,0,0}}
SG222={{0,0,0},{0,0,0},{0,0,0},{0,0,0},{1/2,1/2,1/2}}
SG223={{0,0,0},{0,0,0},{1/2,1/2,1/2},{0,0,0},{0,0,0}}
SG224={{0,0,0},{0,0,0},{1/2,1/2,1/2},{0,0,0},{1/2,1/2,1/2}}
SG225={{0,0,0},{0,0,0},{0,0,0},{0,0,0},{0,0,0}}
SG226={{0,0,0},{0,0,0},{1/2,1/2,1/2},{0,0,0},{0,0,0}}
SG227={{0,0,0},{0,0,0},{1/4,1/4,1/4},{0,0,0},{1/4,1/4,1/4}}
SG228={{0,0,0},{0,0,0},{1/4,1/4,1/4},{0,0,0},{3/4,3/4,3/4}}
SG229={{0,0,0},{0,0,0},{0,0,0},{0,0,0},{0,0,0}}
SG230={{1/2,0,1/2},{1/2,1/2,0},{1/2,0,0},{0,0,0},{0,0,0}};

```

(vi) It also converts the list R of the rotation matrices into matrix form list Rot[i].

```

Array[Rot,{3,3}];
Do[
  B=R[[i]];Rot[i+1]=B(*;
  Print["Rot[" ,i+1,"] = ",MatrixForm[Rot[i+1]]*),{i,1,NG}
]

```

The data contained in files Oh and Diamond are used as input to the program SPGR, which generates the space-group matrix representatives in both g- and a-class form.

Program SPGR

A. Required input data and *Mathematica* packages

Example: *Diamond structure*

```

<< C:file-path/Oh.txt
<< C:file-path/DIAMOND.txt
<< DiscreteMath`Combinatorica`
<< LinearAlgebra`MatrixManipulation`

DIAMOND STRUCTURE

Print["Space Dimension = ", ND]
Print["Lattice Constant a = ", a0]

```



```
Print["Primitive Lattice Vectors in units of a: ",
      MatrixForm[RL]]
Print["Primitive Cell Volume = ", a03*Det[RL], "(Å3)"]
```

The following subprogram uses the information in file DIAMOND to generate the primitive and reciprocal lattice basis vectors:

B. Generate reciprocal lattice vectors

```
G = Array[H, {ND, ND, ND}];
G = {};
Do[
  Do[
    Switch[Or[i == j, i == k, j == k],
      False, GG = Cross[RL[[j]],
        RL[[k]]]/Det[RL];
      AppendTo[G, GG*Signature[{i, j, k}]]
    ]; GG = 0,
  {j, 1, 3}, {k, 1, 3}
], {i, 1, 3}
]
Print["Reciprocal Lattice Vectors in units of 2π/a: ",
      MatrixForm[G]]
```

Next, we construct the matrices of the Seitz representative operators of the space-group *Fd3m* in both the *g*- and *a*-representations. We also create a list **Inv** which contains the inverse elements of the point-group operators as listed in L; this will be useful in generating function transformations.

C. Symmetry operations

```
Print["Number of Generators = ", NG, ", Group Order = ",
      g, ", Number of Objects = ", NP]
VCAR=SG227;
```

⇒

- Point-group elements are best generated in their permutation representation of Array P;
- VC contains nonprimitive vectors of group generators in Cartesian coordinates,
- SYMPH = 0 symmorphic, SYMPH = 1 non-symmorphic).

⇐

1. Generate the a-class matrix generators

```
Do[
  Rota[i] = Transpose[RL].Rot[i].G, {i, 1, NG}
];
Switch[Apply[Plus, VC] == {0, 0, 0},
  True, SYMPH = 0,
  Do[AppendTo[Tau, 0, 0, 0], i, 1, g];
  False, SYMPH = 1;
  Tau = {{0, 0, 0}};
  Do[AppendTo[Tau, VCAR[[i]]], {i, 1, NG}]
  VL = {{0, 0, 0}};
  Do[AppendTo[VL, G.VC[[i]]], {i, 1, NG}]
]
```

2. Generate the remaining Seitz matrix operators

```
L = {Range[NP]};
Do[AppendTo[L, P[[i]]], {i, 1, NG}]
Array[L, {NG + 1}];
nel = Length[L];
f := Permute[L[[i]], L[[j]]]
While[TrueQ[Length[L] < g],
  For[i = 1, i < g, i++,
    For[j = 1, j < (Length[L] + 1), j++,
      Switch[FreeQ[L, f], True,
        AppendTo[L, f]; nel++;
        Rot[nel] = Rot[i].Rot[j];
```

```

        Rota[nel] = Rota[i].Rota[j];
        Switch[SYMPH == 1,
            True,
            TT = Tau[[i]]+Rot[i].Tau[[j]];
            VL[[nel]] = Mod[G.TT,1];
            TT = RL.TT1;
            AppendTo[Tau, TT]
        ]
    ]
]
];
Inv=Map[InversePermutation,L];
m = TableForm[MultiplicationTable[L, Permute]];
RT = MatrixForm[Transpose[Array[Rot,{g}]]];

```

Sometimes it is convenient to change the primitive cell origin, for example in the case of the diamond structure we may find it convenient to use the point $(1/8, 1/8, 1/8)$ as origin, instead of $(0, 0, 0)$. We use the following program to obtain the modified nonprimitive translations, Tau1.

D. Origin displacement and modified nonprimitive translations

```

aa = {1/8,1/8,1/8}; Tau1 = {{0, 0, 0}};
Do[origin = Rot[i] - Rot[1];
    TT = (origin . aa) + Tau[[i]];
    AppendTo[Tau1, TT], {i,2,g}
]

```

10.5.6 Subgroups and supergroups of space-groups

As we have described above, crystal structures may be regarded as infinite geometrical objects endowed with special properties. They manifest a translational repetition of a finite volume, namely the primitive cell. Each primitive cell contains a finite number of atoms, the distribution of which, throughout the crystal, is determined by the discrete

but infinite set of symmetry elements, i.e. the symmetry of a space-group. Thus, when we compare two crystal structures we must consider:

- (i) the relationship among the sets of symmetry operators in an algebraic sense;
- (ii) the relationship among the primitive cells;
- (iii) the relationship among the atomic positions.

We will demonstrate below that a general mathematical procedure, suitable for the treatment of relationships among symmetry operators, primitive cells, and atomic coordinates simultaneously, clearly emerges from the concept of affine mappings [36, 37, 42, 43, 44]. We will define these transformations shortly.

First, we survey some of the basic concepts and provide necessary definitions. Relations between crystal structures imply relations between their space-groups. One form of relations can be discerned from group-subgroup relations between the point-groups of the crystal structures.

Example 10.4

The diamond crystal structure (e.g. silicon) and the zinc-blende structure (e.g. sphalerite ZnS) belong to space-group types $Fd\bar{3}m \equiv \mathbb{O}_h^7$ and $F\bar{4}3m \equiv \mathbb{T}_d^2$, with lattice constants $a_{\text{Si}} = 5.43 \text{ \AA}$ and $a_{\text{ZnS}} = 5.41 \text{ \AA}$, respectively. The zinc-blende structure of ZnS is obtained from the diamond structure of silicon by replacing alternately half of the Si atoms by Zn and half by S, and by adjusting the lattice parameters. The symmetry connection between the two structures is manifest in the relation between their space-groups: the space-group of the zinc blende is a subgroup, of index 2, of that of diamond.

However, relations between two crystal structures may also involve a reduction in the translation group elements on going from one to the other, for example, when we consider I and P lattices that share the same point-group symmetry.

We begin our exploration of such relations, which play a prominent role in the theory of structural phase transitions, by introducing the concept of maximal subgroups.

Maximal subgroups

A *maximal subgroup* $\mathbb{M}$ of a space-group $\mathbb{S}$ implies that there is no other subgroup $\mathbb{H}$ of $\mathbb{S}$ that contains $\mathbb{M}$ as a proper subgroup, i.e.

$$\mathbb{M} \subset \mathbb{H} \subset \mathbb{S}$$

is satisfied only if $\mathbb{H} = \mathbb{S}$.

The number of subgroups or even maximal subgroups of a space-group is infinite, in general. However, by defining the different types of possible subgroups of a space-group we may, under particular conditions, reduce the number to a finite and manageable set.

There are two categories of maximal subgroups [45]: subgroups having the same translation lattice (translationengleich) and subgroups belonging to the same crystal class (klassengleich) as the space-group. Nonmaximal subgroups are infinite in number whereas

translationengleich maximal subgroups are finite in number; on the other hand klassengleich maximal subgroups whose standard symbol is distinct from the space-group standard symbol are also finite in number, whereas maximal subgroups whose standard symbol is the same as for the space-group (isosymbolic subgroups) may be infinite in number.

We now elucidate these concepts by expanding a space-group $\mathbb{S}$ as cosets of its space-subgroup $\mathbb{H}$, namely,

$$\mathbb{S} = \sum_{i=1}^{s/h} S_i \mathbb{H}, \quad S_1 = E.$$

We notice that the subgroup index s/h has a geometric significance: It determines the *dilutation* of symmetry operations of $\mathbb{H}$ compared with those of $\mathbb{S}$. This dilutation can occur in essentially three different ways:

- (i) **Lattice-equal** subgroups $\mathbb{H}_t$ are obtained by reducing the order of the point-group,

$$\mathbb{P}(\mathbb{H}_t) \subset \mathbb{P}(\mathbb{S}),$$

i.e. by eliminating all point symmetry operations of some kind. Such subgroups are called t-subgroups, an abbreviation for the German name *translationengleiche*, because the set of all pure translations is retained. The relation is written as

$$\mathbb{H} \overset{t}{\subset} \mathbb{S}$$

The point-group $\mathbb{P}(\mathbb{S})$ of a space-group $\mathbb{S}$ is a finite group. Hence, the number of t-subgroups, and consequently of maximal t-subgroups is finite. Since a t-subgroup $\mathbb{H}_t \subset \mathbb{S}$ shares the same translation subgroup as a normal subgroup, i.e.

$$\mathbb{T}(\mathbb{H}_t) = \mathbb{T}(\mathbb{S}),$$

there are more cosets in $\mathbb{S} : \mathbb{T}$ than in $\mathbb{H}_t : \mathbb{T}$.

- (ii) **Class-equal** subgroups $\mathbb{H}_k$ are obtained through loss of translations, i.e. by *thinning out* the lattice of translations. In this case we have

$$\mathbb{P}(\mathbb{H}_k) = \mathbb{P}(\mathbb{S}),$$

$$\mathbb{T}(\mathbb{H}_k) \subset \mathbb{T}(\mathbb{S}),$$

and thus the crystal class of the space-group is unchanged. These subgroups are referred to as k-subgroups from the German name *klassengleiche*, and their relation is written as

$$\mathbb{H} \overset{k}{\subset} \mathbb{S}$$

Every space-group $\mathbb{S}$ has an infinite number of maximal k-subgroups. For dimensions 1, 2, and 3, however, it can be shown that the number of maximal k-subgroup types is finite, i.e. if subgroups belonging to the same affine space-group type as $\mathbb{S}$ are excluded.

- (iii) **General** or *allgemein* subgroups which are a combination of (i) and (ii). This type of subgroups is more difficult to survey than the preceding two. In that sense, *every subgroup of a space-group may be regarded as a k-equal subgroup of a t-equal subgroup*

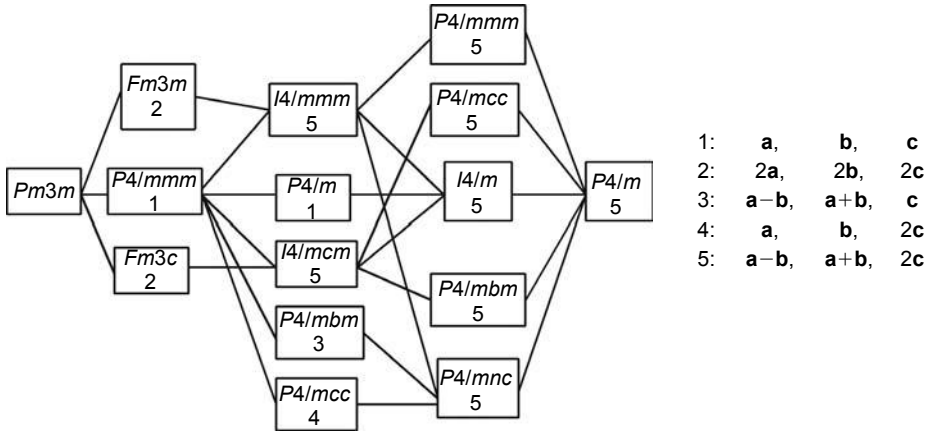


Fig. 10.17. Subgroups of space-group $Pm3m$, ending with $P4/m(\mathbf{a} - \mathbf{b}, \mathbf{a} + \mathbf{b}, 2\mathbf{c})$. From Billiet, *Acta Cryst.* **A37**, 649–652 (1981).

of the space-group. The space-group itself is both a k-equal and a t-equal subgroup. The relation is expressed as

$$\mathbb{H} \overset{t}{\subset} \mathbb{S}$$

Hermann's theorem [46]

- (i) A maximal subgroup $\mathbb{M}$ of a space-group $\mathbb{S}_0$ is either a t-subgroup or a k-subgroup.
- (ii) Any subgroup of a space-group $\mathbb{S}_0$ is a k-equal (Klassengleichen) subgroup of a t-equal (Zellengleichen) subgroup of $\mathbb{S}_0$.

This theorem allows us to identify a subgroup $\mathbb{G} \overset{t}{\subset} \mathbb{S}$, and separate the relation $\mathbb{H} \overset{t}{\subset} \mathbb{S}$ into

$$\mathbb{H} \overset{k}{\subset} \mathbb{G} \overset{t}{\subset} \mathbb{S}.$$

Figure 10.17 depicts the chain of space-subgroups of $Pm3m$ down to $P4/m$. We find that $P4/mmm(\mathbf{a}, \mathbf{b}, \mathbf{c})$ and $P4/m(\mathbf{a}, \mathbf{b}, \mathbf{c})$ are t-equal space-subgroups of $Pm3m(\mathbf{a}, \mathbf{b}, \mathbf{c})$, the former being maximal. While $Fm3m(2\mathbf{a}, 2\mathbf{b}, 2\mathbf{c})$ and $Fm3c(2\mathbf{a}, 2\mathbf{b}, 2\mathbf{c})$ are maximal k-equal.

Generation of k-equal space-subgroups

We discuss here the relations between a k-equal subgroup $\mathbb{H}$, with symmetry operators $(R_H|\mathbf{w}_H)$, and its space-group $\mathbb{S}$, with symmetry operators $(R_S|\mathbf{w}_S)$. Following Bertaut and Billiet [47], this is achieved through the conjugation with respect to a similarity operator $\mathbf{A} = (\mathbf{U}|\boldsymbol{\rho}_0)$, where $\mathbf{U}$ is a 3×3 matrix and $\boldsymbol{\rho}_0$ a column matrix. The matrix $\mathbf{U}$ relates the lattice vectors of $\mathbb{S}$ to those of $\mathbb{H}$, while $\boldsymbol{\rho}_0$ describes the origin of the lattice of $\mathbb{H}$ in the coordinate system of $\mathbb{S}$; the index of $\mathbb{H}$ in $\mathbb{S}$ is equal to $|\det \mathbf{U}|$, and represents the volume ratio of the respective primitive cells. The relation is established in the form of the coefficients of the matrix $\mathbf{U}$ when $\mathbb{S}$ and $\mathbb{H}$ are equivalent. Such subgroups $\mathbb{H}$ with

the same Hermann–Mauguin (HM) space-group symbol as $\mathbb{S}$ are also called *isosymbolic* if they possess the same handedness as $\mathbb{S}$, otherwise they are enantiomorphic.

Each space-group $\mathbb{S}$ associated with a primitive cell $\mathbf{a}_S, \mathbf{b}_S, \mathbf{c}_S$ and an origin O has an infinity of subgroups $\mathbb{H}$ having the same HM space-group symbol, but have an increased primitive cell $\mathbf{a}_H, \mathbf{b}_H, \mathbf{c}_H$ with origin o . $\mathbf{a}_H, \mathbf{b}_H, \mathbf{c}_H$ and $\mathbf{a}_S, \mathbf{b}_S, \mathbf{c}_S$ are related by

$$(\mathbf{a}_H, \mathbf{b}_H, \mathbf{c}_H) = \mathbf{U} (\mathbf{a}_S, \mathbf{b}_S, \mathbf{c}_S), \quad (10.99)$$

where $\mathbf{U}$ has integer coefficients u_{ij} . We follow here an analytical procedure, due to Bertaut and Billiet [47], which relates $\mathbf{U}$ to the generating symmetry operations by an important conjugation relation. When $\det \mathbf{U}$ is restricted to positive values, the handedness of $\mathbb{S}$ is conserved in $\mathbb{H}$.

We consider here the general case where $\det \mathbf{U}$ may be positive as well as negative; the latter allows for a change of handedness; for example, a screw axis 3_1 is changed into a 3_2 axis by an appropriate $\det \mathbf{U} < 0$ transformation.

The conjugation relation

The derivation outlined here is valid for the general form of $\mathbf{U}$, i.e. for integer or noninteger u_{ij} . We use the notation $\mathbf{r}_S(x_S, y_S, z_S)$ and $\mathbf{r}_H(x_H, y_H, z_H)$ as column matrices in $\mathbb{S}$ and $\mathbb{H}$ respectively, describing conventional crystallographic coordinates. We define $\boldsymbol{\rho}_0$ as the column matrix X_0, Y_0, Z_0 which delineates the origin o of the reference system $(o, \mathbf{a}, \mathbf{b}, \mathbf{c})$ of $\mathbb{H}$ in the coordinate system of $\mathbb{S}$, such that

$$\mathbf{r}_S = \boldsymbol{\rho}_0 + \mathbf{U} \mathbf{r}_H. \quad (10.100)$$

The action of a symmetry operator $(R_S | \mathbf{w}_S)$ in $\mathbb{S}$ is defined by

$$\mathbf{r}'_S = (R_S | \mathbf{w}_S) \mathbf{r}_S = R_S \mathbf{r}_S + \mathbf{w}_S, \quad (10.101)$$

and a similar definition for the homologous operator $(R_H | \mathbf{w}_H)$ in $\mathbb{H}$ is given by

$$\mathbf{r}'_H = (R_H | \mathbf{w}_H) \mathbf{r}_H = R_H \mathbf{r}_H + \mathbf{w}_H. \quad (10.102)$$

Using (10.100) we obtain the following relation between $\mathbf{r}'_S$ and $\mathbf{r}'_H$

$$\mathbf{r}'_S = \boldsymbol{\rho}_0 + \mathbf{U} \mathbf{r}'_H. \quad (10.103)$$

Replacing $\mathbf{r}'_S$ and $\mathbf{r}_S$ in (10.101) by their expressions given in (10.103) and (10.100), respectively, we get

$$\mathbf{U} \mathbf{r}'_H = R_S \mathbf{U} \mathbf{r}_H + [R_S - (\mathbb{I})] \boldsymbol{\rho}_0 + \mathbf{w}_S. \quad (10.104)$$

Multiplying (10.102) by $\mathbf{U}$ and substituting for $\mathbf{U} \mathbf{r}'_H$ in (10.104), we obtain the important relation between operators

$$(\mathbf{U} | \boldsymbol{\rho}_0) (R_H | \mathbf{w}_H) = (R_S | \mathbf{w}_S) (\mathbf{U} | \boldsymbol{\rho}_0), \quad (10.105)$$

which can be written as

$$\mathbf{U} R_H = R_S \mathbf{U}, \quad (10.106)$$

$$\mathbf{U} \mathbf{w}_H = \mathbf{w}_S + [R_S - (\mathbb{I})] \boldsymbol{\rho}_0. \quad (10.107)$$

With $\mathbf{w} = \boldsymbol{\tau} + \mathbf{t}$, we rewrite the last equation in the following more convenient form:

$$\mathbf{U} \boldsymbol{\tau}_H - \boldsymbol{\tau}_S - [R_S - (\mathbb{I})] \boldsymbol{\rho}_0 = \mathbf{t}_S, \quad (10.108)$$

since $\mathbf{U} \mathbf{t}_H \in \mathbb{T}_S$. By determining the matrix $\mathbf{U}$ and the vector $\boldsymbol{\rho}_0$ via (10.106) and (10.108), we, in effect, determine the primitive cell in $\mathbb{H}$.

It is instructive at this point to consider three special cases:

- (i) The relation between $\mathbb{T}_S$ and $\mathbb{T}_H$ is obtained by setting $(R_S|\mathbf{w}_S) = (E|\mathbf{t}_S)$ and $(R_H|\mathbf{w}_H) = (E|\mathbf{t}_H)$, so that (10.106) yields

$$\mathbf{U} \mathbf{t}_H = \mathbf{t}_S. \quad (10.109)$$

- (ii) When $\mathbb{S}$ and $\mathbb{H}$ are symmorphic space-groups, we can set $(R_S|\mathbf{w}_S) = (R_S|\mathbf{0})$ and $(R_H|\mathbf{w}_H) = (R_H|\mathbf{0})$, and (10.108) gives

$$[R_S - (\mathbb{I})] \boldsymbol{\rho}_0 = \mathbf{t}_S. \quad (10.110)$$

- (iii) When the origin lies on a screw axis or a glide plane, and the k-equal space-groups share the same origin, i.e. $\boldsymbol{\rho}_0 = \mathbf{0}$, we obtain

$$\mathbf{U} \boldsymbol{\tau}_H - \boldsymbol{\tau}_S = \mathbf{t}_S. \quad (10.111)$$

Example 10.5

Tetragonal systems

The associate holohedral point-group is $4/mmm$. We start with the operation $C_4 =$

$$\begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \text{ and use (10.106) to obtain}$$

$$\mathbf{U} C_4 = C_4 \mathbf{U}$$

$$\begin{bmatrix} u_{12} & -u_{11} & u_{13} \\ u_{22} & -u_{21} & u_{23} \\ u_{32} & -u_{31} & u_{33} \end{bmatrix} = \begin{bmatrix} -u_{21} & -u_{22} & -u_{23} \\ u_{11} & u_{12} & u_{13} \\ u_{31} & u_{32} & u_{33} \end{bmatrix} \Rightarrow \begin{cases} u_{11} = u_{22}, u_{12} = -u_{21}, \\ u_{13} = u_{23} = u_{31} = u_{32} = 0. \end{cases}$$

Thus, for the general tetragonal case we have

$$\mathbf{U} = \begin{bmatrix} u_{11} & u_{12} & 0 \\ -u_{12} & u_{11} & 0 \\ 0 & 0 & u_{33} \end{bmatrix}, \quad \det \mathbf{U} = u_{33} (u_{11}^2 + u_{12}^2).$$

This is strictly true for the isosymbolic groups 4 , $\bar{4}$, and $4/m$.

The remaining subgroups contain mirror planes and/or two-fold axes perpendicular to the four-fold axis. The coincidence of the orientations of such operations in both $\mathbb{S}$ and $\mathbb{H}$ leads to the condition $u_{12} = 0$, and we have

$$\mathbf{U} = \begin{bmatrix} u_{11} & 0 & 0 \\ 0 & u_{11} & 0 \\ 0 & 0 & u_{33} \end{bmatrix}, \quad \det \mathbf{U} = u_{11}^2 u_{33}.$$

An additional possibility arises when the two lower symmetry operations (m or 2) are identical, as for example in 422 or $4mm$, where the orientations of these secondary operations are rotated by $\pi/4$ in $\mathbb{H}$ from those in $\mathbb{S}$. In the case of two-fold rotations we have

$$R_H = C_{2xy} = \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad R_S = C_{2x} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix},$$

and we obtain the extra condition

$$\begin{aligned} \mathbf{U} C_{2xy} = C_{2x} \mathbf{U} &\Rightarrow u_{12} = -u_{11}, \\ \mathbf{U} &= \begin{bmatrix} u_{11} & -u_{11} & 0 \\ u_{11} & u_{11} & 0 \\ 0 & 0 & u_{33} \end{bmatrix}, \quad \det \mathbf{U} = 2u_{33}u_{11}^2. \end{aligned}$$

We find that space-groups

$P22$, $P4mm$, $P4/mmm$, $P4_122$, $P4_222$, $P4_322$, Pcc , $P4/mcc$, $I422$, $I4mm$, $I4/mmm$

allow for these two possibilities.

Parity

- (i) **Screw axes** When the k -equal space-groups share the same origin along a screw axis n_m , we rewrite (10.111) as

$$u_{33} \frac{m}{n} - \frac{m}{n} = \ell,$$

or

$$u_{33} = n \frac{\ell}{m} + 1, \tag{10.112}$$

and since u_{33} is an integer, $n\ell/m$ must also be an integer. As an example, we consider the space-group $P4_1$, for which (10.112) becomes

$$u_{33} = 4\ell + 1,$$

and the index of $\mathbb{H}$ is

$$(4\ell + 1)(u_{11}^2 + u_{12}^2).$$

If we increase the cell dimension along the $\mathbf{c}$ -axis only, thus keeping $u_{11}^2 + u_{12}^2 = 1$; then, for $\ell = 1, 2, 3$, we have isosymbolic subgroups $P4_1$ of index 5, 9, 13, respectively. For the negative values $\ell = -1, -2, -3$, we have $\det \mathbf{U} = -3, -7, -11$, respectively. The negative sign corresponds to a change of handedness, i.e. we obtain enantiomorphic subgroups $P4_3$ of $P4_1$, of index 3, 7, and 11, respectively. At the same time we discern the maximal equivalent subgroups as being the ones with

index 3, 5, 7, 11, and 13, since these are prime numbers. The isosymbolic subgroup P_41 of index 9 is not maximal, since the chain relation

$$P4_1 \rightarrow [3]P4_3 \rightarrow [3]P4_1$$

exists.

(ii) **Glide planes**

- (a) Glide planes perpendicular to a principal axis:

We consider a glide plane operation $n \equiv (\sigma_z|1/2, 1/2, 0)$ in the tetragonal system, for which (10.112) becomes

$$\frac{1}{2}(u_{11} \pm u_{12}) - \frac{1}{2} = \ell \quad \Rightarrow \quad (u_{11} \pm u_{12}) = 2\ell + 1,$$

indicating that u_{11} and u_{12} must have different parities. This is satisfied for $P4/n$ by setting

$$u_{11}^2 + u_{12}^2 = 1, 5, 9, \text{ etc.}$$

By the same token, we have to discard the possibility of $u_{12} = u_{11}$ for $P4/nmm$.

- (b) Glide planes parallel to a principal axis:

We consider the glide plane $b \equiv (\sigma_x|01/20)$ in the tetragonal system, for example $P4bm$, for which (10.112) becomes

$$u_{11} = 2\ell + 1$$

with index $(2\ell + 1)2u_{33}$. Setting $u_{33} = 1$, we find that isosymbolic groups have indices of 1, 3, 5, etc.

10.6 Site-symmetries and the Wyckoff notation

Topics discussed in this section can also be found in [30, 43, 45, 48]. A very efficient and convenient crystallographic classification is to describe a crystal structure by specifying its space-group and identifying occupied orbits, i.e. listing the sets of equivalent sites that are occupied in the crystal. These orbits are called *Wyckoff positions*, and denoted by their Wyckoff (1922) label [185]. Specification of the actual coordinates of the atoms within the unit, or primitive, cell can then be generated by the point-group operations, or may be found, simply, by reference to the *International Tables for Crystallography*. In this section we present the definition and description of the Wyckoff positions, together with their symmetries.

10.6.1 Space-group action and crystallographic orbits

In previous chapters we described the concept of an orbit associated with a point-group $\mathcal{P}$ in n -dimensional Euclidean space, $\mathbb{R}^n$, as the set of points generated by the action of all the elements of $\mathcal{P}$ on a point $\mathbf{r}_0 \in \mathbb{R}^n$, namely,

$$\mathbf{r} = R\mathbf{r}_0, \quad \forall R \in \mathcal{P};$$

this also led to the definition of the stabilizer of $\mathbf{r}_0$ as the subgroup $\mathcal{ST}(\mathbf{r}_0) \subset \mathcal{P}$ that leaves it fixed.

In the realm of crystallography, we first extend this concept of an orbit in nD Euclidean space to the action of its space-group $\mathbb{S}$ on $\mathbf{r}_0$. The action of a symmetry operation $S = (R|\boldsymbol{\tau} + \mathbf{t}) \in \mathbb{S}$ on a point $\mathbf{r}_0 \in \mathbb{R}^n$ generates an equivalent point $\mathbf{r}_S$,

$$\mathbf{r}_S = (R|\boldsymbol{\tau} + \mathbf{t}) \mathbf{r}_0. \quad (10.113)$$

The set of equivalent points generated by all the symmetry operations $S \in \mathbb{S}$ is called a *crystallographic orbit* of $\mathbf{r}_0$ with respect to $\mathbb{S}$, $\mathfrak{O}(\mathbb{S}, \mathbf{r}_0)$, or, a *crystallographic orbit*, for short. The space-group $\mathbb{S}$ is called the *generating space-group of the orbit*, and $\mathbf{r}_0$, its *generator*. Any one of an orbit's points may represent the whole crystallographic orbit; here we chose the point $\mathbf{r}_0$ to be the orbit representative, and used it as its generator.

We can visualize the construction of an nD lattice as the action of its space-group $\mathbb{S}$ on the point $\mathbf{r}_0 = \mathbf{0}$, i.e. the origin, in a continuous nD Euclidean space $\mathbb{R}^n$. Next, we identify a primitive cell Ω , which has the origin as one of its apices, and construct a crystallographic orbit for some point $\mathbf{r}_0 \in \Omega$. We can further elucidate the process of generating such a crystallographic orbit by splitting it into two steps: first, we generate the orbit of the point-group elements of $\mathbb{P}(\mathbb{S})$; second, we generate the full crystallographic orbit with the aid of the action of the elements of $\mathbb{T}^n(\mathbb{S})$, i.e. we generate the translationally equivalent points.

It is then straightforward to realize that the entire nD Euclidean space can be spanned by the infinite set of crystallographic orbits generated by the entire continuous set of points contained in Ω .

Some properties of orbits

We can identify a space-group $\mathbb{E} \supseteq \mathbb{S}$ which leaves an orbit $\mathfrak{O}(\mathbb{S})$, generated by $\mathbb{S}$, fixed. In other words, $\mathbb{E}$ is at least $\mathbb{S}$, or it may be a supergroup of $\mathbb{S}$. It cannot be a continuous

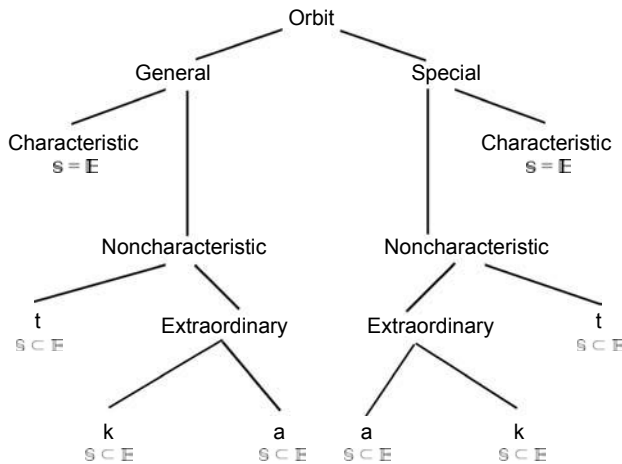


Fig. 10.18. The orbit types [49].

group since there is a minimum length in the translation symmetry. $\mathbb{E}$ is called the *eigen-symmetry (proper or characteristic) space-group* of the orbit $\mathfrak{O}(\mathbb{S})$; it does not depend on $\mathbb{S}$, but is solely a property of the set of points of the orbit.

When $\mathbb{E} \sim \mathbb{S}$ the orbit is called a *characteristic orbit* of $\mathbb{S}$, otherwise it is designated a *noncharacteristic orbit*.

The generating space-group $\mathbb{S}$ of a noncharacteristic orbit has to be a subgroup of the eigensymmetry space-group $\mathbb{E}$ of the orbit. It can then be t-equal, $\mathbb{S} \stackrel{t}{\subset} \mathbb{E}$, k-equal, $\mathbb{S} \stackrel{k}{\subset} \mathbb{E}$, or allgemein, $\mathbb{S} \stackrel{a}{\subset} \mathbb{E}$. In the last two there are lattice translations in $\mathbb{E}$ not contained in $\mathbb{S}$, i.e. $\mathbb{T}_E \supset \mathbb{T}_S$. A noncharacteristic orbit existing under such conditions is termed an *extraordinary orbit* of $\mathbb{S}$.

10.6.2 Site-symmetry subgroups: stabilizers

We find that each point $\mathbf{r}$ of a crystallographic orbit defines its stabilizer, uniquely, as the largest subgroup of $\mathbb{S}$, which maps $\mathbf{r}$ onto itself; such a subgroup is called its **site-symmetry group** [30],

$$\mathcal{G}(\mathbf{r}) = \{S\mathbf{r} = \mathbf{r} \mid S \in \mathbb{S}\}.$$

$\mathcal{G}(\mathbf{r})$ is a finite subgroup of $\mathbb{S}$.

This allows us to classify the points of $\mathbb{R}^n$, with regard to symmetry operations of a space-group $\mathbb{S}$, into two coarse categories:

- (i) A *point of general position*, $\mathbf{r}$, if $\mathcal{G}(\mathbf{r})$ contains the identity element only. Such points generate principal orbits.
- (ii) A *point of special position*, $\mathbf{r}$, if $\mathcal{G}(\mathbf{r})$ contains at least one symmetry operation in addition to E .

As is usually the case with stabilizers, site-symmetry groups belonging to different member points of a crystallographic orbit are conjugate subgroups of $\mathbb{S}$. Hence, a crystallographic orbit consists exclusively either of general points (*general crystallographic orbit*) or of special points (*special crystallographic orbit*). The points of a general orbit bear a one-to-one correspondence with the symmetry operations of $\mathbb{S}$. By contrast, a point of a special orbit corresponds to a complete coset of $\mathbb{S}$ with respect to the stabilizer of that point.

10.6.3 Wyckoff positions and the Wyckoff notation

The subdivision of crystallographic orbit points into two classes, general and special, is too coarse. A finer classification is given in terms of the *Wyckoff positions* with the aid of the relation

$$\mathbf{r}' = \mathbf{r} + \mathbf{t}' = \mathbf{r} \bmod \mathbb{T}, \quad (10.114)$$

where orbit points are related by primitive lattice translations. This allows us to decompose a crystallographic orbit into its translationally equivalent orbits of the point-group $\mathbb{P}(\mathbb{S})$, and to identify one of those point-group orbits as a generator of the crystallographic orbit with respect to $\mathbb{T}(\mathbb{S})$. In other words, we use the set of points comprising the $\mathbb{P}(\mathbb{S})$ -orbit, rather than a single point, as representative of its corresponding crystallographic

orbit. By doing so, we are allowed to limit the relevant group actions to the elements of the crystallographic point-group $\mathbb{P}(\mathbb{S})$ only, and to choose a primitive or a unit cell as the domain of such points for all crystallographic orbits. Each set of equivalent points, belonging to a particular orbit, constitutes a Wyckoff position W_s [45].

In the *International Tables for Crystallography*, Wyckoff positions are classified according to their site-symmetry point-group. The first line gives the general position, while the following lines specify the special positions in order of increasing symmetry. The columns from left to right contain the following:

- (i) The number of equivalent points per unit cell, labeled *multiplicity*:
 $M = \text{index of the site-symmetry group in } \mathbb{P} \times \# \text{ of lattice points per unit cell.}$
- (ii) Site identification by a lower-case Roman letter, *Wyckoff letter*, with a standing for the highest symmetry site.
- (iii) *Oriented site-symmetry*: The site-symmetry symbols display the same sequence as the covering space-group HM symbol, but the site-orientation is depicted by placing a dot wherever the symbols do not contribute to the site-symmetry.
- (iv) *Coordinates*: The coordinates of equivalent points of a Wyckoff position are listed, together with the number of the symmetry-generating element in parentheses (when needed).

Example 10.6

Table 10.15. Wyckoff positions of the planar space-group $c2mm$.

Multiplicity	Wyckoff letter	Site-symmetry	Coordinates	
			$(0, 0)+$	$\left(\frac{1}{2}, \frac{1}{2}\right)+$
8^a	f	1	(1) x, y (3) $\bar{x}, y$	(2) $\bar{x}, \bar{y}$ (4) $x, \bar{y}$
4	e	$.m.^b$	$0, y$	$0, \bar{y}$
4	d	$..m.^b$	$x, 0$	$\bar{x}, 0$
4	c	$2..^b$	$\frac{1}{4}, \frac{1}{4}$	$\frac{3}{4}, \frac{1}{4}$
2	b	$2mm$	$0, \frac{1}{2}$	
2	a	$2mm$	$0, 0$	

^a In the first row we have a multiplicity of eight general points in the unit cell; the first four, corresponding to $(0, 0)+$, are obtained by the symmetry element in parentheses, $(1) \rightarrow E$, $(2) \rightarrow C_2$, $(3) \rightarrow \sigma_y$, $(4) \rightarrow \sigma_x$, the remaining four are obtained from the first four by the primitive translation $(\frac{1}{2}, \frac{1}{2})+$.

^b For Wyckoff positions c, d, e the irrelevant symmetry operations m_y, m_x ; $2, m_x$; $2, m_y$, respectively, are replaced by dots.

The planar space-group $c2mm$ contains two lattice points in the unit cell, $(0,0)$ and $(1/2, 1/2)$. Its point-group $2mm$ comprises E , 2 , m_x , m_y . The corresponding Wyckoff positions are given in Table 10.15.

A closer reflection on the concept of Wyckoff positions reveals that when we prescribe the W_S s of all the atomic species comprising the crystal basis we are actually identifying the corresponding space-group!

We should finally note that the process of applying the translation operations of $T \subset S$ to a given W_S actually produces the corresponding crystallographic orbit, and, consequently, we can speak of *Wyckoff positions of crystallographic orbits* with respect to S .

A program for determining Wyckoff positions of a given crystal

Here, we use program **SPGR** to generate all the symmetry aspects of the crystal. Next, we input information regarding the crystal's atomic basis:

- (i) Number of chemical elements **NCEL**.
- (ii) Number of atoms of chemical element **i**, **NSP[[i]]**.
- (iii) Positions of the **NSP[[i]]** atoms, **RR[[i,j]]**, $j=1 \rightarrow \text{NSP}[[i]]$, in Cartesian coordinates.

Program Wyckoff

Input atomic positions

RATC = **RR**;

1. All vectors **RATC** are expressed in lattice-basis and stored in **RATL**

RATL = {};

```
Do[B = Transpose[RATC[[i, j]]]·RL; AppendTo[RATL, B],
  {i, 1, NCEL}, {j, 1, NSP[[i]]}
]
```

2. Determine the site-stabilizer subgroups

Sitesym = {}; **Wyckoff**={}; **ik** = 0; **iwyk** = 0;

While[**ik**<**NCEL**, **ik**++; **NRM** = **RATL**[[**ik**]];

While[**NRM** ≠ {},

RRK = **NRM**[[1]];

```

While[NRM  $\neq$  {}],
  RRK = NRM[[1]];
  LK = {}; Ltmp = {}; Cosrep = {};
  gr = 0; jk=1;
  Switch[RRK == {0, 0, 0},
    True,
    gr = g;
    AppendTo[Sitesym, Range[g]];
    False,
    Do[
      RK1 = Rota[Inv[[i]]]·(RRK + VL[[i]]);
      RK1 = RK1 - RRK;
      Switch[And[Mod[RK1[[1]],1] == 0,
        Mod[RK1[[2]],1] == 0,
        Mod[RK1[[3]],1] == 0,
        FreeQ[LK, i]],
        True, gr++; AppendTo[LK, i]
      ], {i, 1, g}
    ]; AppendTo[Sitesym, LK];
  ];

indeks = g/gr; Icoset = 1;
Acosrep = {1}; jj = 1; Ltmp = LK;

3. Generate coset Reps of site-symmetry subgroup

While[And[Icoset < indeks, jj < g], jj++;
  Switch[FreeQ[Ltmp, jj], True,
    Icoset++; AppendTo[Acosrep, jj];
    Do[cst = LK[[ij]];
      AppendTo[Ltmp, m[[1, jj, cst]]],
      {ij, 1, Length[LK]}
    ]
  ]
];

```

4. Generate Wyckoff positions

```

RRC= RRK · RL; WK = {RRK};
Do[
  kl = Acosrep[[jj]];
  RK1 = Rota[Inv[[kl]]]·(RRK + VL[[kl]]);
  RK1 = Mod[RK1,1];
  Switch[FreeQ[WK, RK1]],True,
    AppendTo[WK,RK1]
  ],{jj,2,indeks}
];
AppendTo[Wyckoff,WK]; NRM = Complement[NRM,WK];
], {ik, 1, NCEL}
];
Do[
  Print["(", ELMNT[[ik]], ", ", "jk, "] Position at = ",
    RATC[[ik, jk]],", its group of Order ",
      gr, ", is ", LK, ", and its Coset Reps
      are ", Acosrep];
  Print["it has ", indeks, " equivalent
    Wyckoff positions."],
    {ik, 1, NCEL}
];

```

10.6.4 Wyckoff sets: Euclidean and affine normalizers

The classification of the points of the Euclidean space $\mathbb{R}^n$ into Wyckoff positions W_S of a space-group S is unique. However, it is possible to permute equivalent or inequivalent Wyckoff positions through an automorphism, i.e. an isomorphic mapping of S onto itself. These permutations may not preserve the Wyckoff notation label assigned for a given position. It is, therefore, preferable to group together Wyckoff positions that can be permuted by automorphic actions; such groups are designated as *Wyckoff sets* [34, 35, 36, 37, 50, 184].

Automorphic maps may be realized in two ways:

- (i) By an *inner automorphism*, which involves conjugations by elements $S \in S$. Such mappings give rise to conjugate subgroups of S , and do not permute orbits; actually they are the generators of all conjugate site-symmetry groups associated with an orbit.

Thus, two crystallographic orbits of a space-group $\mathbb{S}$ belong to the same Wyckoff position if and only if the site-symmetry groups of any two points, one from the first orbit and one from the second orbit, are conjugate subgroups of $\mathbb{S}$, i.e., if the two site-symmetry groups are mapped onto each other by an inner automorphism of $\mathbb{S}$.

- (ii) By conjugation with elements of a *normalizer* $\mathbb{N}$ of $\mathbb{S}$, in which case the mapping is called an *outer automorphism*. The normalizer, in this case, may be defined with respect to either the covering Euclidean group $\mathcal{E}(n)$, or its covering group $\mathcal{A}(n)$, the *affine group*. $\mathbb{N}$ comprises Euclidean or affine mappings that map $\mathbb{S}$ onto itself.

In order to elucidate the idea of an affine or Euclidean normalizer, we consider the example of the space-group $p2mm(\mathbf{a} = \mathbf{b})$ and its normalizer $p4mm(\mathbf{a})$. The sets of inequivalent special Wyckoff positions for these two plane groups are shown in the following table:

$p2mm$						$p4mm$					
2	h	$\cdot m \cdot$	$\frac{1}{2}, y$	$\frac{1}{2}, \bar{y}$	4	f	$\cdot \cdot m$	x, x	$\bar{x}, \bar{x}$	$\bar{x}, x$	$x, \bar{x}$
2	g	$\cdot m \cdot$	$0, y$	$0, \bar{y}$	4	e	$\cdot m \cdot$	$x, \frac{1}{2}$	$\bar{x}, \frac{1}{2}$	$\frac{1}{2}, x$	$\frac{1}{2}, \bar{x}$
2	f	$\cdot \cdot m$	$x, \frac{1}{2}$	$\bar{x}, \frac{1}{2}$	4	d	$\cdot m \cdot$	$x, 0$	$\bar{x}, 0$	$0, x$	$0, \bar{x}$
2	e	$\cdot \cdot m$	$x, 0$	$\bar{x}, 0$	4	c	$2mm \cdot$	$\frac{1}{2}, 0$	$0, \frac{1}{2}$		
1	d	$2mm$	$\frac{1}{2}, \frac{1}{2}$		1	b	$4mm$	$\frac{1}{2}, \frac{1}{2}$			
1	c	$2mm$	$\frac{1}{2}, 0$								
1	b	$2mm$	$0, \frac{1}{2}$								
1	a	$2mm$	$0, 0$		1	a	$4mm$	$0, 0$			

We then find the following relations

$$\begin{array}{ccc}
 p4mm : & e & d & c \\
 & \downarrow & \downarrow & \downarrow \\
 p2mm : & \underbrace{f \quad h} & \underbrace{e \quad g} & \underbrace{b \quad c}
 \end{array}$$

Thus, the plane group $p4mm$ maps each of the above pairs of Wyckoff positions into each other; it basically interchanges the x - and y -axes. Each pair then forms a Wyckoff set.

We may generalize this idea by stating that the mappings of $\mathbb{N}$, which are not symmetry operations of $\mathbb{S}$, may transfer one Wyckoff position of $\mathbb{S}$ onto an inequivalent Wyckoff position. A collection of all those Wyckoff positions of a space-group $\mathbb{S}$ which may be permuted by such automorphism of $\mathbb{S}$ into a single set is called a Wyckoff set.

In group-theoretical terms, a *Wyckoff set with respect to $\mathbb{S}$* consists of all points $\mathbf{r}$ for which the site-symmetry groups are conjugate subgroups of $\mathbb{N}$.

We may further discern the difference between Wyckoff positions and Wyckoff sets of $\mathbb{S}$ by the following statement:

Any Wyckoff position of $\mathbb{S}$ is mapped onto itself by all elements of $\mathbb{S}$, but not necessarily by all the elements of $\mathbb{N} \supset \mathbb{S}$. By contrast, any Wyckoff set is transformed onto itself by those elements of $\mathbb{N}$ which are not contained in $\mathbb{S}$. Alternatively, we may speak of a *Wyckoff set of crystallographic orbits*.

Wyckoff sets present a coarser classification of crystallographic orbits, since two crystallographic orbits of a space-group $\mathbb{S}$ belong to the same Wyckoff set if and only if the site-symmetry groups of any two points from the first and the second orbit are conjugate subgroups of the Euclidean or affine normalizer of $\mathbb{S}$, i.e. if the two site-symmetry groups are mapped onto each other by an outer automorphism of $\mathbb{S}$.

Accordingly, all orbits of the same Wyckoff position belong to one and the same Wyckoff set. Therefore, the assignment of orbits to Wyckoff sets also defines an equivalence relation on the Wyckoff positions of a space-group. We further stipulate that we can assign Wyckoff sets to space-group types, and hence we can talk about *Wyckoff set types*! In other words:

When two space-groups $\mathbb{S}$ and $\mathbb{S}'$ belong to the same space-group type, i.e. they are equivalent with respect to some affine map, then their corresponding Wyckoff sets, with respect to the same affine map, belong to the same Wyckoff set type.

The affine normalizer $\mathcal{N}_A(\mathbb{S})$

We define the affine normalizer, $\mathcal{N}_A(\mathbb{S})$, of $\mathbb{S}$ as the subgroup of $\mathcal{A}(n)$ whose elements $(\mathbf{A}, \mathbf{a}) \in \mathcal{N}_A(\mathbb{S})$ satisfy the affine conjugation mapping

$$(\mathbf{A}, \mathbf{a}) (R|\mathbf{w}) (\mathbf{A}, \mathbf{a})^{-1} = (R'|\mathbf{w}'), \quad (R|\mathbf{w}), (R'|\mathbf{w}') \in \mathbb{S}, \quad (10.115)$$

where $\mathbf{w} = \mathbf{t} + \boldsymbol{\tau}$. This follows directly from the definition of a normalizer of $\mathbb{S}$, which requires that $\mathbb{S}$ be a normal subgroup of $\mathcal{N}_A(\mathbb{S})$. We note that since $\mathbb{S}$ is a subgroup of $\mathcal{N}_A(\mathbb{S})$, the latter may contain translations, $\mathbf{a} \notin \mathbb{S}$. Moreover, these translations form a normal subgroup of $\mathcal{N}_A(\mathbb{S})$, and since any such a translation must be an isometry, they have to satisfy the relation

$$\mathcal{T}[\mathcal{N}_A(\mathbb{S})] = \mathcal{T}[\mathcal{N}_E(\mathbb{S})],$$

where $\mathcal{T}[\mathcal{N}_E(\mathbb{S})]$ is the translation group of the Euclidean normalizer of $\mathbb{S}$. $\mathcal{T}[\mathcal{N}_A(\mathbb{S})]$ need not be discrete; in fact, it is found to be continuous in some cases.

Following Boisen, Gibbs, and Wondatschek [50], who adopt an approach similar to that of Bertaut and Billiet [47], we explicitly write (10.115) as

$$(\mathbf{A}\mathbf{R}\mathbf{A}^{-1}|\mathbf{a} + \mathbf{A}\mathbf{w} - \mathbf{A}\mathbf{R}\mathbf{A}^{-1}\mathbf{a}) = (R'|\mathbf{w}'),$$

and expand it further as

$$\mathbf{A}\mathbf{R}\mathbf{A}^{-1} = R', \quad (10.116)$$

$$\mathbf{a} + \mathbf{A}\mathbf{w} - R'\mathbf{a} = \mathbf{w}'. \quad (10.117)$$

The translations of $\mathcal{N}_{\mathcal{A}}(\mathbb{S})$ In order to determine $\mathbf{a}$, we focus on pure translations of $\mathcal{N}_{\mathcal{A}}(\mathbb{S})$, by setting $\mathbf{A} = E$. Hence, (10.116) gives $R = R'$, and (10.117) is reduced to

$$\mathbf{a} + \mathbf{w} - R\mathbf{a} = \mathbf{w}'$$

or

$$(\mathbb{I} - R)\mathbf{a} = \mathbf{w}' - \mathbf{w} = \mathbf{t}' - \mathbf{t} \in \mathbb{T}.$$

This simplification does not impose any restrictions on the choice of $\mathbf{a}$.

Next, we use the fact that $(R|\mathbf{w})$ and $(R|\mathbf{w}')$ are elements of $\mathbb{S}$ to obtain the relation that

$$(R|\mathbf{w}') (R|\mathbf{w})^{-1} = (E|\mathbf{t}' - \mathbf{t})$$

is actually a translation in $\mathbb{S}$.

We choose a primitive basis for $\mathbb{S}$, so that $\mathbf{t}' - \mathbf{t}$ consists of integers, and $R \in GL(n, \mathbb{Z})$, $\forall R \in \mathbb{P}(\mathbb{S})$. It then follows that

$$(\mathbb{I} - R)\mathbf{a} \in \mathbb{Z}^n \quad \forall R \in \mathbb{P}(\mathbb{S}). \quad (10.118)$$

As only the matrix parts of $\mathbb{S}$ occur in (10.118), *the result is the same for all space-group types of the same arithmetic crystal class.*

It is sufficient to solve (10.118) for a set of generators of $\mathbb{P}(\mathbb{S})$. This follows from the argument that when R_1 and R_2 satisfy (10.118), then there exist $\mathbf{z}_1$ and $\mathbf{z}_2$ in $\mathbb{Z}^n$ such that

$$R_1\mathbf{a} = \mathbf{a} + \mathbf{z}_1 \quad \text{and} \quad R_2\mathbf{a} = \mathbf{a} + \mathbf{z}_2$$

and hence

$$R_2 R_1 \mathbf{a} = R_2(\mathbf{a} + \mathbf{z}_1) = \mathbf{a} + \mathbf{z}_2 + R_2 \mathbf{z}_1.$$

Since $R_2 \in GL(n, \mathbb{Z})$, we find that $\mathbf{z}_2 + R_2 \mathbf{z}_1 \in \mathbb{Z}^n$. Hence, $R_2 R_1$ satisfies (10.118) whenever R_1 and R_2 satisfy (10.118). Since $\mathbb{P}(\mathbb{S})$ is finite,

$$R^r = E, \quad \text{or} \quad R^{-1} = R^{r-1},$$

so that R^{-1} is a positive power of R . The set of all $(E, \mathbf{a})$ satisfying (10.118) can then be easily found.

Example 10.7

Determine the translations of $\mathcal{N}_{\mathcal{A}}(\mathbb{S})$ for space-groups of the arithmetic crystal class $422P$, which belongs to the tetragonal system

We apply the two generators

$$R_1 = C_{4z} = \begin{pmatrix} 0 & \bar{1} & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \text{and} \quad R_2 = U_y = \begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}.$$

We now need to find those columns $\mathbf{a}$ that satisfy (10.118) for R_1 and R_2 simultaneously. For R_1 , we have

$$\begin{pmatrix} 1 & 1 & 0 \\ \bar{1} & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix} = \begin{pmatrix} a_1 + a_2 \\ -a_1 + a_2 \\ 0 \end{pmatrix} = \begin{pmatrix} z_1 \\ z_2 \\ z_3 \end{pmatrix} \Rightarrow \begin{cases} a_1 = (z_1 - z_2)/2, \\ a_2 = (z_1 + z_2)/2, \\ \text{No condition,} \end{cases}$$

$$\begin{pmatrix} 2 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 2 \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix} = \begin{pmatrix} 2a_1 \\ 0 \\ 2a_3 \end{pmatrix} = \begin{pmatrix} z_1 \\ z_2 \\ z_3 \end{pmatrix} \Rightarrow \begin{cases} a_1 = (z_1 - z_2)/2, \\ \text{No condition,} \\ a_3 = (z_3 + z_3)/2, \end{cases}$$

where z_1 , z_2 , and z_3 are integers. Thus, we obtain $a_1 \equiv a_2 \equiv a_3 = 0, 1/2 \pmod{1}$, which shows that the translations of $\mathcal{N}_{\mathcal{A}}(\mathbb{S})$ for this arithmetic class form a C -centered lattice with $\mathbf{c}' = 1/2 \mathbf{c}$!

The matrix components of the normalizer $\mathcal{N}_{\mathcal{A}}(\mathbb{S})$ Our strategy here is based on using (10.116) to determine the $\mathbf{A}$ s. We first have to establish two points: we note that the set of matrices $\mathbf{A}$ in $\mathcal{N}_{\mathcal{A}}(\mathbb{S})$ forms a point-group $\mathbb{P}[\mathcal{N}_{\mathcal{A}}(\mathbb{S})]$, in the same manner that we define $\mathbb{P}(\mathbb{S})$. We establish the second point by setting $R = E$ in (10.116); we then get $R' = E$, and find that (10.117) reduces to

$$\mathbf{A}\mathbf{t} = \mathbf{t}', \quad \forall \mathbf{A}.$$

Since $\mathbf{t}$ and $\mathbf{t}'$ in (10.117) are columns of integers, we must have $\mathbf{A} \in GL(n, \mathbb{Z})$, and $\mathbb{P}[\mathcal{N}_{\mathcal{A}}(\mathbb{S})] \subset GL(n, \mathbb{Z})$.

We are now ready to solve (10.116) armed with the above two facts, namely

$$\mathbf{A}\mathbf{R}\mathbf{A}^{-1} = \mathbf{R}' \implies \mathbf{A}, \mathbf{R}, \mathbf{R}' \in GL(n, \mathbb{Z}), \quad \mathbf{R}, \mathbf{R}' \in \mathbb{P}(\mathbb{S}). \quad (10.119)$$

The solutions of (10.119) form the normalizer, $\mathcal{N}[\mathbb{P}(\mathbb{S})]$ in $GL(n, \mathbb{Z})$. Again it is sufficient to determine $\mathbf{A}$ for a set of generators of $\mathbb{P}(\mathbb{S})$ only.

Example 10.8

$$\mathcal{N}[\mathbb{P}(mm2C)]$$

The arithmetic holohedry of the base-centered orthorhombic lattice is $mm2c$; its primitive basis, expressed in terms of the standard orthogonal basis $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$, is

$$\mathbf{a}_p = 1/2\mathbf{a} - 1/2\mathbf{b}, \quad \mathbf{b}_p = 1/2\mathbf{a} + 1/2\mathbf{b}, \quad \mathbf{c}_p = \mathbf{c},$$

which corresponds to the centering matrix

$$B = \frac{1}{2} \begin{pmatrix} 1 & -1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix}.$$

The point-group comprises E , 2_z , m_x , m_y , which, when referred to the primitive basis have the following matrix representation:

$$2_z = \begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \sigma_x = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

We write $\mathbf{A}$ in the form

$$\mathbf{A} = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix},$$

(10.119) requires R and R' to be in the same class, which implies that they should have similar realizations, for example that both are n -fold rotations or reflections. In the present case, the normalizer must map $2_z \rightarrow 2_z$, and either $\sigma_x \rightarrow \sigma_y$ or $\sigma_x \rightarrow \sigma_x$. Thus, setting $R = 2_z$ requires that R' must also be 2_z . Equation (10.119) then gives

$$\mathbf{A} = 2_z \mathbf{A} 2_z^{-1} \Rightarrow \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} & -a_{13} \\ a_{21} & a_{22} & -a_{23} \\ -a_{31} & -a_{32} & a_{33} \end{pmatrix},$$

which reduces to

$$\mathbf{A}_{2_z, 2_z}(p) = \begin{pmatrix} a_{11} & a_{12} & 0 \\ a_{21} & a_{22} & 0 \\ 0 & 0 & a_{33} \end{pmatrix},$$

with the proviso that it has integer entries, and that

$$\det(\mathbf{A}_{2_z, 2_z}(p)) = a_{33}(a_{11}a_{22} - a_{12}a_{21}) = \pm 1.$$

In $mm2C$, the two reflections σ_x and σ_y are inequivalent with respect to an inner automorphism, i.e. they belong to different classes, but they can be mapped into each other by the outer automorphism of the normalizer, since they have the same physical trait. We can then map, for example, σ_x either onto itself: $\sigma_x = \mathbf{A}\sigma_x\mathbf{A}^{-1}$, or onto σ_y : $\sigma_y = \mathbf{A}\sigma_x\mathbf{A}^{-1}$. In the first case, the solution is

$$\mathbf{A}_{\sigma_x, \sigma_x}(p) = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{12} & a_{11} & a_{13} \\ a_{31} & a_{31} & a_{33} \end{pmatrix},$$

which is the normalizer of $1m1C$ referred to the primitive basis. In the case $\sigma_y = \mathbf{A}\sigma_x\mathbf{A}^{-1}$ the solution is

$$\mathbf{A}_{\sigma_y, \sigma_x}(p) = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ -a_{12} & -a_{11} & -a_{13} \\ a_{31} & a_{31} & a_{33} \end{pmatrix}.$$

Combining the conditions of $\mathbf{A}_{2_z, 2_z}(p)$ with those of $\mathbf{A}_{\sigma_x, \sigma_x}(p)$ or $\mathbf{A}_{\sigma_y, \sigma_x}(p)$ and taking

into account that $\mathbf{A}$ is unimodular, we get

$$\mathbf{A}_{\sigma_x, \sigma_x, 2_z}(Cp) = \begin{pmatrix} a_{11} & a_{12} & 0 \\ a_{12} & a_{11} & 0 \\ 0 & 0 & \pm 1 \end{pmatrix}$$

or

$$\mathbf{A}_{\sigma_y, \sigma_x, 2_z}(Cp) = \begin{pmatrix} a_{11} & a_{12} & 0 \\ -a_{12} & -a_{11} & 0 \\ 0 & 0 & \pm 1 \end{pmatrix}, \quad (10.120)$$

respectively. There are two possible choices of the matrix entries: (i) $a_{11} = 0$ and $a_{12} = \pm 1$, (ii) $a_{12} = 0$ and $a_{11} = \pm 1$. This gives rise to 16 matrices which, when defined in terms of an appropriate basis, is equivalent to $4/mmmP$, and forms the group $\mathcal{N}[\mathbb{P}(mm2C)]$.

$\mathcal{N}[\mathbb{P}(mm2C)]$ in the standard basis

Since the matrix representation of 2_z is the same in the primitive and in the standard basis, the form of $\mathbf{A}_{2_z, 2_z}(s)$ is the same as that of $\mathbf{A}_{2_z, 2_z}(p)$. Thus the set $\{\mathbf{A}_{2_z, 2_z}(p)\}$ of matrices of the form of $\mathbf{A}_{2_z, 2_z}(p)$ is the normalizer of $112P$, a space subgroup of the standard lattice.

Transforming to the standard basis by $\mathbf{A}_{\sigma_x \sigma_x}(s) = B \mathbf{A}_{\sigma_x \sigma_x}(p) B^{-1}$, we obtain

$$\mathbf{A}_{\sigma_x, \sigma_x}(s) = \begin{pmatrix} a_{11} + a_{12} & 0 & a_{13} \\ 0 & a_{11} - a_{12} & 0 \\ 2a_{31} & 0 & a_{33} \end{pmatrix}.$$

Again, since $\mathbf{A}_{\sigma_x, \sigma_x}(s)$ is unimodular, $a_{11} - a_{12} = \pm 1$, $a_{11} + a_{12}$, a_{33} must be odd, and $2a_{31}$ is even. Similarly, we obtain

$$\mathbf{A}_{\sigma_y, \sigma_x}(s) = \begin{pmatrix} 0 & a_{12} - a_{11} & 0 \\ -a_{11} - a_{12} & 0 & -a_{13} \\ 2a_{31} & 0 & a_{33} \end{pmatrix}.$$

The role of inversion in defining $\mathcal{N}_{\mathcal{A}}(\mathbb{S})$ The operation of inversion commutes with all affine mappings, it therefore has no effect on defining directly the elements of $\mathcal{N}_{\mathcal{A}}(\mathbb{S})$ as a generator. Thus, when the generators of $\mathbb{P}(\mathbb{S})$ comprise only proper rotations and the inversion, the normalizer is defined completely by the proper rotations. However, the introduction of the inversion may change the normalizer in groups that already contain improper rotations. This can be seen in the point-group of Example 10.8, namely $mm2$, where the mapping was restricted to $2_z \rightarrow 2_z$, and either $\sigma_y \rightarrow \sigma_x$ or $\sigma_y \rightarrow \sigma_y$. The point-group mmm , generated as $mm2 \otimes \{E, \sigma_z\}$, contains the inversion, since in this case it has $\frac{2_x}{\sigma_x} \frac{2_y}{\sigma_y} \frac{2_z}{\sigma_z}$. The normalizer may now interchange the two-fold rotations $\{2_x, 2_y, 2_z\}$, and there are more combinations to consider. The actual allowed permutations then depend on the arithmetic crystal class considered, and thus the centering of the lattice. We find,

for example, that

$$\mathcal{N}_{\mathcal{A}}(mmmI) \supset \mathcal{N}_{\mathcal{A}}(mm2I)$$

while

$$\mathcal{N}_{\mathcal{A}}(mmmC) = \mathcal{N}_{\mathcal{A}}(mm2C)$$

because 2_z cannot be mapped onto 2_x or 2_y due to the C centering.

Constructing $(\mathbf{A}, \mathbf{a}) \in \mathcal{N}_{\mathcal{A}}(\mathbb{S})$ We first demonstrate that we have to consider the solutions of (10.116) and (10.117) only for a set of generators $(R|\mathbf{w}) \in \mathbb{S}$. Thus, we consider the product of two elements $(R_1|\mathbf{w}_1)$ and $(R_2|\mathbf{w}_2)$, each satisfying (10.116) and (10.117), namely,

$$(R_2|\mathbf{w}_2)(R_1|\mathbf{w}_1) = (R_2R_1|\mathbf{w}_2 + R_2\mathbf{w}_1).$$

We find that

$$\begin{aligned} \mathbf{A}(R_2R_1)\mathbf{A}^{-1} &= (\mathbf{A}R_2\mathbf{A}^{-1})(\mathbf{A}R_1\mathbf{A}^{-1}) = R'_2R'_1, \quad \Rightarrow (R_2R_1)' = R'_2R'_1, \\ \mathbf{w}'_1 &= \mathbf{a} + \mathbf{A}\mathbf{w}_1 - \mathbf{A}R_1\mathbf{A}^{-1}\mathbf{a}, \\ \mathbf{w}'_2 &= \mathbf{a} + \mathbf{A}\mathbf{w}_2 - \mathbf{A}R_2\mathbf{A}^{-1}\mathbf{a}, \\ \mathbf{w}'_2 + R'_2\mathbf{w}'_1 &= \mathbf{a} + \mathbf{A}(\mathbf{w}_2 + R_2\mathbf{w}_1) - R'_2R'_1\mathbf{a}, \end{aligned}$$

which demonstrates that $(R_2|\mathbf{w}_2)(R_1|\mathbf{w}_1)$ satisfies (10.116) and (10.117). For each space-group, it is then sufficient to apply (10.117) to a set of generating matrices among the solutions of (10.116).

When forming the combination $(\mathbf{A}, \mathbf{a}) \in \mathcal{N}_{\mathcal{A}}(\mathbb{S})$ care must be taken to ensure that it satisfies (10.117), i.e. a given solution $\mathbf{A}$ of (10.116) must also satisfy (10.117) for some $\mathbf{a}$. Again, since $\mathcal{N}_{\mathcal{A}}(\mathbb{S})$ is a group, it suffices to determine its defining set of generators.

For symmorphic space-groups, $\mathbf{w} = \mathbf{t}$, and $\mathbf{A}$ satisfying (10.116) has the solution $(\mathbf{A}, \mathbf{0})$ of (10.117) because $\mathbf{t}$ and $\mathbf{t}'$ can always be taken set to $\mathbf{0}$.

For nonsymmorphic groups, a case sometimes arises where some generators $\mathbf{A}$ of (10.116) may not satisfy (10.117) for any $\mathbf{a}$ and so the group $\mathcal{N}[\mathbb{P}(\mathbb{S})] = \{\mathbf{A}\}$ does not constitute $\mathbb{P}[\mathcal{N}_{\mathcal{A}}(\mathbb{S})]$. In order to ensure that the appropriate $\mathbb{P}[\mathcal{N}_{\mathcal{A}}(\mathbb{S})]$ is found, we adopt the following procedure. Let

$$\mathcal{U} = \{\mathbf{A} | \mathbf{A} \text{ satisfies (10.117)}\},$$

then two scenarios emerge:

- (i) The index of $\mathcal{U}$ in $\mathcal{N}[\mathbb{P}(\mathbb{S})]$ is a prime number, in which case $\mathcal{U}$ must be a maximal subgroup of $\mathcal{N}[\mathbb{P}(\mathbb{S})]$, and we find

$$\mathcal{U} = \mathbb{P}[\mathcal{N}_{\mathcal{A}}(\mathbb{S})].$$

- (ii) When the index of $\mathcal{U}$ in $\mathcal{N}[\mathbb{P}(\mathbb{S})]$ is not a prime number, $\mathcal{U}$ might not be maximal, and we must consider subgroups of $\mathcal{N}[\mathbb{P}(\mathbb{S})]$ which are supergroups of $\mathcal{U}$ and check them to find $\mathbb{P}[\mathcal{N}_{\mathcal{U}}(\mathbb{S})]$. This can be done by considering additional generators to those of $\mathcal{U}$ that produce subgroups of $\mathbb{P}[\mathcal{N}_{\mathcal{U}}(\mathbb{S})]$.

Example 10.9

Determine the normalizers of space-groups $P422$ (89), $P4_122$ (91), $P4_222$ (93) or $P4_322$ (95), where the space-group number is given in parentheses.

We begin with determining the normalizer for the point-group 422. Using the generators given in Example 10.7, and realizing that the $\mathbb{S}$ operation conjugated by $\mathcal{N}_u(\mathbb{S})$ must have the same physical properties, i.e. reflections, n -fold rotations, etc. Accordingly, we obtain the relations

$$\mathbf{A}_{C_4, C_4} = \mathbf{A}_{C_4, C_4^3} = \begin{pmatrix} a & b & 0 \\ -b & a & 0 \\ 0 & 0 & c \end{pmatrix}, \quad c = \pm 1, \quad a^2 + b^2 = 1 \quad \begin{cases} a = \pm 1, b = 0, \\ b = \pm 1, a = 0, \end{cases}$$

$$\mathbf{A}_{U_y, U_y} = \begin{pmatrix} a & 0 & d \\ 0 & b & 0 \\ e & 0 & c \end{pmatrix}, \quad \text{with } b = \pm 1, \quad ac - de = 1,$$

$$\mathbf{A}_{U_y, U_x} = \begin{pmatrix} 0 & b & 0 \\ d & 0 & e \\ f & 0 & c \end{pmatrix}, \quad \text{with } b = \pm 1, \quad ef - cd = 1.$$

Combining these conditions we obtain

$$\mathbf{A} = \begin{pmatrix} a & b & 0 \\ -b & a & 0 \\ 0 & 0 & c \end{pmatrix}, \quad c = \pm 1, \quad a^2 + b^2 = 1 \quad \begin{cases} a = \pm 1, b = 0, \\ b = \pm 1, a = 0, \end{cases}$$

which defines the elements of the point-group $4/mmm = 422 \otimes \bar{1}$ as $\mathcal{N}[422]$.

We now introduce the translations we found in Example 10.7 above, and from the outset we obtain $C4/mmm$, a nonstandard setting having

$$\frac{1}{2}(\mathbf{a} - \mathbf{b}), \quad \frac{1}{2}(\mathbf{a} + \mathbf{b}), \quad \frac{1}{2}\mathbf{c}$$

with respect to the basis of $\mathbb{S}$. Next, we check the compatibility of the point-group $4/mmm$ for each of the four space-groups. We use the conjugation of $(4|\tau_4) \in 4_i22, i = 0, 1, 2, 3$, with respect to the inversion operation in $C4/mmm$, $(\mathcal{I}|\mathbf{t})$, which should leave the operation unchanged. With $\tau = 0, 1/4, 1/2, 3/4$, we obtain

$$\begin{aligned} & (\mathcal{I}|\mathbf{t})(C_{4z}|\tau)(\mathcal{I}|\mathbf{t}) \\ &= \begin{pmatrix} \bar{1} & 0 & 0 & | & l \\ 0 & \bar{1} & 0 & | & m \\ 0 & 0 & \bar{1} & | & n \end{pmatrix} \begin{pmatrix} 0 & \bar{1} & 0 & | & 0 \\ 1 & 0 & 0 & | & 0 \\ 0 & 0 & 1 & | & \tau \end{pmatrix} \begin{pmatrix} \bar{1} & 0 & 0 & | & l \\ 0 & \bar{1} & 0 & | & m \\ 0 & 0 & \bar{1} & | & n \end{pmatrix} \\ &= \begin{pmatrix} 0 & \bar{1} & 0 & | & l+m \\ 1 & 0 & 0 & | & -l+m \\ 0 & 0 & 1 & | & -\tau \end{pmatrix} = (C_{4z}|\tau). \end{aligned}$$

This relation is satisfied only when $\tau = 0$ or $\tau = 1/2$. Hence the normalizers of $P422$ and $P4_222$ contain inversions, and we have

$$\mathcal{N}(P422) = \mathcal{N}(P4_222) = C4/mmm$$

with $\mathbf{c}' = 1/2\mathbf{c}$, which is equivalent to $P4/mmm$.

Now, in order to determine the normalizers of $\mathbb{S} = P4_122$ and $\mathbb{S} = P4_322$, we explore the k-equal supergroup of $\mathbb{S}$ which includes the additional translations as determined above, namely, $C422$. In fact, the normalizer of $P4_122$ and $P4_322$ is $C4_222$, referred to the basis $\mathbf{a}' = \mathbf{a}$, $\mathbf{b}' = \mathbf{b}$, $\mathbf{c}' = 1/2\mathbf{c}$, which is equivalent to $P4_222$.

Example 10.10

Determine the normalizer of space-group No. 59,

$$Pmmn = C_{2v} + \left(\mathfrak{I} \left| \begin{smallmatrix} a & b & c \\ 2 & 2 & 2 \end{smallmatrix} \right. \right) C_{2v},$$

with generators

$$\sigma_x = \left(\begin{array}{ccc|c} \bar{1} & 0 & 0 & 1/2 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{array} \right), \sigma_y = \left(\begin{array}{ccc|c} 1 & 0 & 0 & 0 \\ 0 & \bar{1} & 0 & 1/2 \\ 0 & 0 & 1 & 0 \end{array} \right), \sigma_z = \left(\begin{array}{ccc|c} 1 & 0 & 0 & 1/2 \\ 0 & 1 & 0 & 1/2 \\ 0 & 0 & \bar{1} & 0 \end{array} \right).$$

We first determine the $\mathbf{a}$ s; from (10.118) we have

$$\begin{pmatrix} 2 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix}, \begin{pmatrix} 0 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix}, \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 2 \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix} = \begin{pmatrix} z_1 \\ z_2 \\ z_3 \end{pmatrix} \in \mathbb{Z}^3$$

which gives

$$a_1, a_2, a_3 = 0, 1/2 \pmod{1};$$

hence the generators of $\mathbb{T}[\mathcal{N}_A(Pmmn)]$ are

$$\mathbf{a}' = \frac{1}{2}\mathbf{a}, \quad \mathbf{b}' = \frac{1}{2}\mathbf{b}, \quad \mathbf{c}' = \frac{1}{2}\mathbf{c}.$$

As for the point-group, we find that

$\mathbf{A}\sigma_z = \sigma_z\mathbf{A}$	$\mathbf{A}\sigma_z = \sigma_y\mathbf{A}$	$\mathbf{A}\sigma_z = \sigma_x\mathbf{A}$	$\mathbf{A}\sigma_y = \sigma_y\mathbf{A}$
$\begin{pmatrix} a & d & o \\ f & b & 0 \\ 0 & 0 & c \end{pmatrix}$	$\begin{pmatrix} a & d & 0 \\ 0 & 0 & g \\ h & k & 0 \end{pmatrix}$	$\begin{pmatrix} a & 0 & 0 \\ 0 & b & g \\ 0 & k & c \end{pmatrix}$	$\begin{pmatrix} a & 0 & e \\ 0 & b & 0 \\ h & 0 & c \end{pmatrix}$
$c = \pm 1,$	$g = \pm 1,$	$a = \pm 1,$	$b = \pm 1,$
$ab - fd = \pm 1$	$ak - dh = \pm 1,$	$bc - gk = \pm 1,$	$ac - eh = \pm 1,$

provide sufficient relations to generate the 48 unimodular matrix representatives of the point-group $m3m$, namely,

$$\begin{pmatrix} \pm 1 & 0 & 0 \\ 0 & \pm 1 & 0 \\ 0 & 0 & \pm 1 \end{pmatrix} \quad \begin{pmatrix} \pm 1 & 0 & 0 \\ 0 & 0 & \pm 1 \\ 0 & \pm 1 & 0 \end{pmatrix} \quad \begin{pmatrix} 0 & 0 & \pm 1 \\ 0 & \pm 1 & 0 \\ \pm 1 & 0 & 0 \end{pmatrix}$$

$$\begin{pmatrix} 0 & \pm 1 & 0 \\ 0 & 0 & \pm 1 \\ \pm 1 & 0 & 0 \end{pmatrix} \quad \begin{pmatrix} 0 & 0 & \pm 1 \\ \pm 1 & 0 & 0 \\ 0 & \pm 1 & 0 \end{pmatrix} \quad \begin{pmatrix} 0 & \pm 1 & 0 \\ \pm 1 & 0 & 0 \\ 0 & 0 & \pm 1 \end{pmatrix}$$

We should note that

$$Pmmn(\mathbf{a}, \mathbf{b}, \mathbf{c}) \stackrel{k}{\subset} Pmmm(\mathbf{a}', \mathbf{b}', \mathbf{c}') \stackrel{t}{\subset} Pm3m(\mathbf{a}', \mathbf{b}', \mathbf{c}'),$$

which suggests that the next step is to check the compatibility of $Pm3m(\mathbf{a}', \mathbf{b}', \mathbf{c}')$ as a normalizer; we choose

$$3_d = \begin{pmatrix} 0 & 0 & 1 & | & 0 \\ 1 & 0 & 0 & | & 0 \\ 0 & 1 & 0 & | & 0 \end{pmatrix} \quad \text{and} \quad 2_d = \begin{pmatrix} 0 & 0 & 1 & | & 0 \\ 0 & \bar{1} & 0 & | & 0 \\ 1 & 0 & 0 & | & 0 \end{pmatrix}$$

as additional generators for $Pm3m$. We find that neither 3_d nor 2_d satisfy all of the equations

$$3_d(\sigma_k|\tau_k)3_d^{-1} = (\sigma_l|\tau_l),$$

$$k, l = x, y, z,$$

$$2_d(\sigma_k|\tau_k)2_d^{-1} = (\sigma_l|\tau_l).$$

However, before concluding that $Pmmm(\mathbf{a}', \mathbf{b}', \mathbf{c}')$ is the normalizer, we should check the remaining possibilities: $4_z/mmm$ and $4_x/mmm \equiv 4_y/mmm$ by testing the corresponding generators

$$2_d\left(\frac{4_z}{mmm}\right) = \begin{pmatrix} 0 & 1 & 0 & | & 0 \\ 1 & 0 & 0 & | & 0 \\ 0 & 0 & \bar{1} & | & 0 \end{pmatrix} \quad \text{and} \quad 2_d\left(\frac{4_x}{mmm}\right) = \begin{pmatrix} \bar{1} & 0 & 0 & | & 0 \\ 0 & 0 & 1 & | & 0 \\ 0 & 1 & 0 & | & 0 \end{pmatrix}$$

respectively. We find that $2_d(4_z/mmm)$ gives

$$2_d\left(\frac{4_z}{mmm}\right)(\sigma_x|\tau_x)2_d\left(\frac{4_z}{mmm}\right)^{-1} = (\sigma_y|\tau_y),$$

$$2_d\left(\frac{4_z}{mmm}\right)(\sigma_y|\tau_y)2_d\left(\frac{4_z}{mmm}\right)^{-1} = (\sigma_x|\tau_x),$$

$$2_d\left(\frac{4_z}{mmm}\right)(\sigma_z|\tau_z)2_d\left(\frac{4_z}{mmm}\right)^{-1} = (\sigma_z|\tau_z),$$

hence the normalizer is

$$P \frac{4_z}{mmm} (\mathbf{a}', \mathbf{b}', \mathbf{c}').$$

The affine normalizers of the two-dimensional groups are obtained from the affine normalizers of the space-groups by inspection.

The Euclidean normalizers of the two- and three-dimensional space-groups are obtained by discarding the affine elements which do not leave the quadratic form of the lattice invariant, i.e. $\mathcal{N}_E$ is the intersection of the affine normalizers with the group of all isometries. Note that this concerns the matrix parts of the operations. Moreover, matrix orthogonality does not guarantee the mapping to be an isometry. For example, in the case of a conventional (P) monoclinic lattice, the operation σ_x

$$\sigma_x \mathbf{g} \sigma_x^{-1} = \begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} a & d & 0 \\ d & b & 0 \\ 0 & 0 & c \end{pmatrix} \begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} a & -d & 0 \\ -d & b & 0 \\ 0 & 0 & c \end{pmatrix}$$

is orthogonal but is not an isometry.

Whereas the affine normalizers of all space-groups of the same space-group type belong to the same affine type of groups, the Euclidean normalizers depend on the symmetry of the lattice. The Euclidean normalizers listed in the literature are those of space-groups for which the lattices correspond to the space-group symmetry (characteristic lattices) and are not accidentally ones of higher symmetry.

10.6.5 Examples of two- and three-dimensional crystals

Two-dimensional nonsymmorphic crystals

Primitive rectangular with $p2mg$ space-group symmetry As the label $p2mg$ indicates, the two-dimensional crystal has a two-fold symmetry along the z -axis, a mirror plane, and a glide plane. Figure 10.19 shows a typical two-dimensional nonsymmorphic crystal with space-group $p2mg$. The reflection planes σ_x and σ_y are represented by gray stripes. The σ_y reflection plane is located such that no nonprimitive vector is required; however, if it is shifted to coincide with the x -axis, a nonprimitive translation of $\boldsymbol{\tau} = \frac{b}{2} \hat{\mathbf{y}}$ would be required. A typical reflection through the σ_x plane is represented by $1 \rightarrow 1'$ and $2 \rightarrow 2'$, returning to the original configuration requires a nonprimitive displacement of $\boldsymbol{\tau} = \frac{b}{2} \hat{\mathbf{y}}$. As can be seen from Figure 10.19, a C_2 rotation about the origin O does not require a nonprimitive translation; however, if we move the origin to coincide with the intersection of the σ_x and σ_y planes, C_2 acquires a nonprimitive translation, $\boldsymbol{\tau}$. Thus, the representative coset elements of the group are given by $(E|\mathbf{0}), (C_2|\boldsymbol{\tau}), (\sigma_x|\boldsymbol{\tau}), (\sigma_y|\mathbf{0})$.

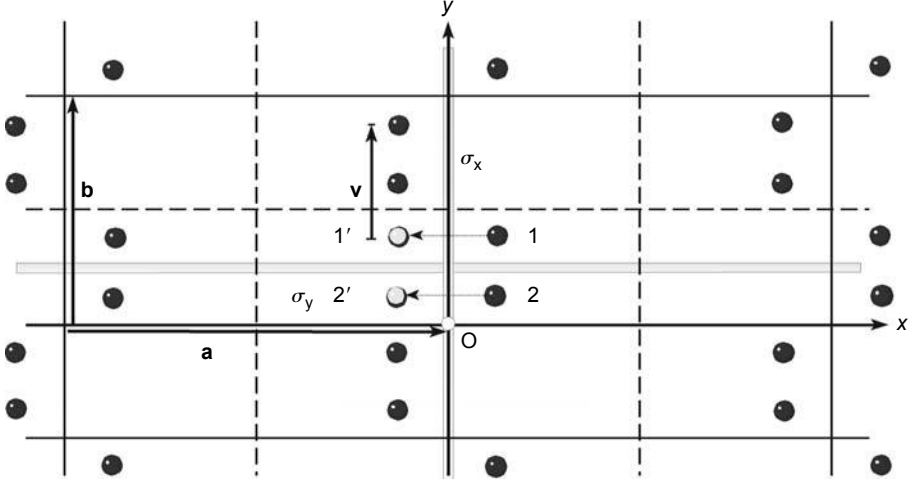


Fig. 10.19. The two-dimensional primitive rectangular mesh with space-group $p2mg$. Only σ_x involves a nonprimitive vector $\tau = \frac{b}{2} \hat{y}$.

The Wyckoff positions are:

$$4 \quad c \quad 1 \quad (x, y), (\bar{x}, \bar{y}), \left(x, \frac{1}{2} - y\right), \left(\bar{x}, \frac{1}{2} + y\right).$$

$$2 \quad a \quad 2 \quad (0, 0), \left(0, \frac{1}{2}\right)$$

There is only one set of special points a .

Affine normalizer $p4mm(\mathbf{a}', \mathbf{b}')$, $\mathbb{T}[\mathcal{N}_{\mathcal{A}}(p2mg)] = \mathbf{a}' = \frac{1}{2} \mathbf{a}$, $\mathbf{b}' = \frac{1}{2} \mathbf{b}$.

Primitive rectangular with $p2gg$ space-group symmetry Figure 10.20 shows the two-dimensional nonsymmorphic crystal with space-group $p2gg$. The space-group label indicates that in addition to a two-fold symmetry along the z -axis, there is a g -plane perpendicular to the x -axis, and a second g -plane normal to the y -axis. The reflection planes σ_x and σ_y are represented by gray stripes. σ_x and σ_y are placed such that the nonprimitive vectors lie in the respective reflection planes, namely, $\tau_x = \frac{b}{2} \hat{y}$ and $\tau_y = \frac{a}{2} \hat{x}$. Typical reflections through these planes are shown, together with the associated nonprimitive displacements. Again, we see from Figure 10.20 that a C_2 rotation about the origin is not associated with a nonprimitive translation. We can thus write the representative elements of $p2mg$ as: $(E|\mathbf{0})$, $(C_2|\mathbf{0})$, $(\sigma_x|\tau_x)$, $(\sigma_y|\tau_y)$.

If the reflection planes are shifted so that they coincide with the x - and y -axes, the representative elements take the form: $(E|\mathbf{0})$, $(C_2|\mathbf{0})$, $(\sigma_x|\tau)$, $(\sigma_y|\tau)$, where now $\tau = \frac{a}{2} \hat{x} + \frac{b}{2} \hat{y}$.

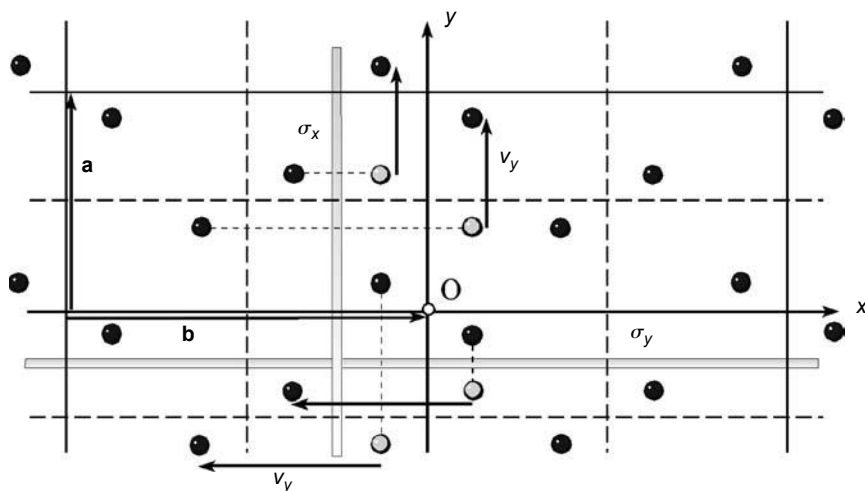


Fig. 10.20. The two-dimensional primitive rectangular mesh with space-group $p2gg$. σ_x and σ_y involve nonprimitive vectors $\tau_x = \frac{b}{2} \hat{y}$ and $\tau_y = \frac{a}{2} \hat{x}$.

The Wyckoff positions are:

$$4 \quad c \quad 1 \quad (x, y), (\bar{x}, \bar{y}), \left(\frac{1}{2} + x, \frac{1}{2} - y\right), \left(\frac{1}{2} - x, \frac{1}{2} + y\right)$$

$$2 \quad b \quad 2 \quad \left(\frac{1}{2}, 0\right), \left(0, \frac{1}{2}\right)$$

$$2 \quad a \quad 2 \quad (0, 0), \left(\frac{1}{2}, \frac{1}{2}\right).$$

As we see, there are two sets of special points a and b.

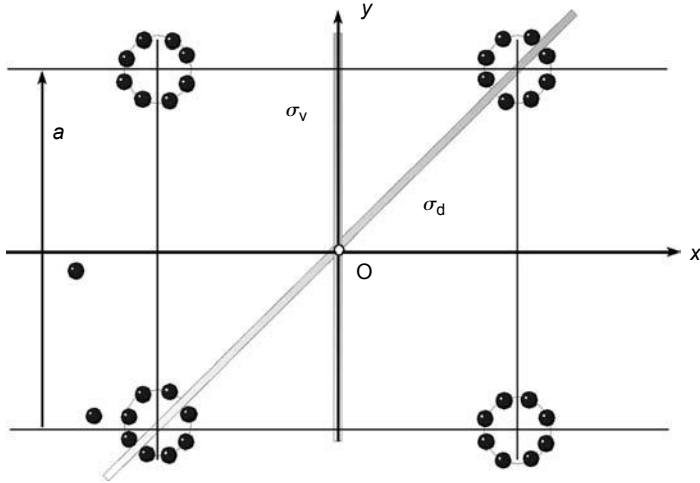
$p2gg$ has the same affine normalizer as $p2mg$.

Primitive square with $p4mm$ space-group symmetry The $p4mm$ space-group is symmorphic, and has a four-fold z -axis and two inequivalent pairs of reflection planes. The point-group operations represent the factor group and are given by $(E|\mathbf{0})$, $(C_2|\mathbf{0})$, $(C_4|\mathbf{0})$, $(C_4^{-1}|\mathbf{0})$, $(\sigma_v^x|\mathbf{0})$, $(\sigma_v^y|\mathbf{0})$, $(\sigma_d^1|\mathbf{0})$, $(\sigma_d^2|\mathbf{0})$.

The Wyckoff positions are:

$$8 \quad g \quad 1 \quad (x, y), (\bar{x}, \bar{y}), (x, \bar{y}), (\bar{x}, y), (y, x), (\bar{y}, \bar{x}), (y, \bar{x}), (\bar{y}, x)$$

$$4 \quad f \quad m \quad (x, x), (\bar{x}, \bar{x}), (x, \bar{x}), (\bar{x}, x).$$

Fig. 10.21. The symmorphic space-group $p4mm$ of the square mesh.

4	e	m	$(0,0), \left(x, \frac{1}{2}\right), \left(\bar{x}, \frac{1}{2}\right), \left(\frac{1}{2}, x\right), \left(\frac{1}{2}, \bar{x}\right)$
4	d	m	$(0,0), (x,0), (\bar{x},0), (0,x), (0,\bar{x})$
2	c	$2mm$	$\left(\frac{1}{2}, 0\right), \left(0, \frac{1}{2}\right)$
1	b	$4mm$	$\left(\frac{1}{2}, \frac{1}{2}\right)$
1	a	$4mm$	$(0,0)$

There are six sets of special points a – f . $p4mm$ has the same affine normalizer as the previous two space-groups.

Three-dimensional nonsymmorphic crystals

The rutile structure $P \frac{4_2}{m} \frac{2_1}{n} \frac{2}{m} \left(P \frac{4_2}{mnm} \right)$ The rutile structure is found in TiO_2 crystals. As shown in Figure 10.22 it has a primitive tetragonal Bravais lattice with primitive vectors

$$\mathbf{a}_1 = a \hat{\mathbf{x}}, \quad \mathbf{a}_2 = a \hat{\mathbf{y}}, \quad \mathbf{a}_3 = c \hat{\mathbf{z}},$$

hence the primitive and crystallographic cells are identical, and contain two Ti and four O atoms. The point-group of the crystal is $\mathbb{D}_{4h}$ with 16 group elements. The locations of

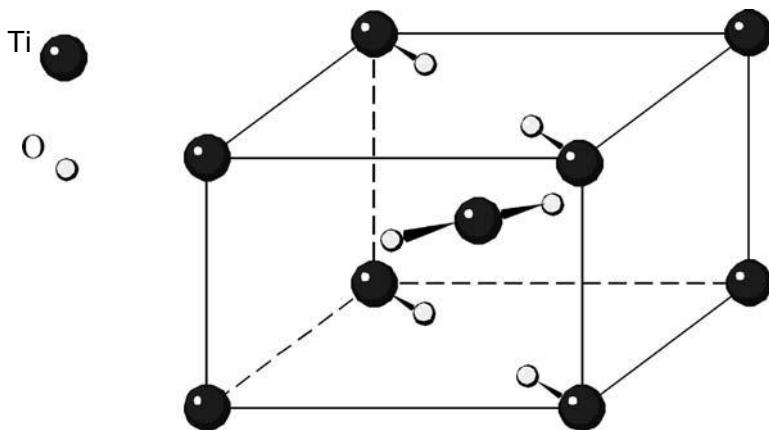


Fig. 10.22. The rutile structure.

the Ti atoms in the unit cell are $(0, 0, 0); (1/2, 1/2, 1/2)$, while the O atoms are located at $\pm(u, u, 0); \pm(1/2 + u, 1/2 - u, 1/2)$, where for TiO_2 $u = 0.31a$. It has the nonsymmorphic space-group $P \frac{4_2}{m} \frac{2_1}{n} \frac{2}{m}$ (abbreviated form $P \frac{4_2}{mnm}$). The International notation indicates that there is:

- a four-fold screw-axis along $\hat{\mathbf{z}}$ with a nonprimitive translation of $2c/4 = c/2$, with a mirror plane normal to it;
- two-fold screw-axes along $\hat{\mathbf{x}}$ and $\hat{\mathbf{y}}$ with normal n-glide planes;
- two-fold axes along the diagonals in the base-plane, with normal mirror planes.

The 16 representative operations isomorphic to the operation of $\mathbb{D}_{4h}$ are

$$(E|\mathbf{0}), (C_2|\mathbf{0}), (C_{2\bar{x}}|\mathbf{0}), (C_{2\bar{y}}|\mathbf{0}), (I|\mathbf{0}), (\sigma_h|\mathbf{0}), (\sigma_d|\mathbf{0}), (\sigma_d|\mathbf{0}), \\ (C_4|\boldsymbol{\tau}), (C_4^{-1}|\boldsymbol{\tau}), (C_{2x}|\boldsymbol{\tau}), (C_{2y}|\boldsymbol{\tau}), (S_4|\boldsymbol{\tau}), (S_4^{-1}|\boldsymbol{\tau}), (\sigma_{vx}|\boldsymbol{\tau}), (\sigma_{vy}|\boldsymbol{\tau}),$$

where $\boldsymbol{\tau} = (\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3)/2$. The nonprimitive vector $\boldsymbol{\tau}$ corresponds to an origin taken at the center of the unit cell, namely, $(1/2, 1/2, 1/2)$. However, with appropriate similarity transformations, it is possible to reduce the nonprimitive translations associated with rotations to lie along the rotation axis, and those for reflections to lie in the reflection planes. For example, the nonprimitive translation associated with C_4 can be reduced to $(c/2)\hat{\mathbf{z}}$ by the similarity transformation

$$\left(E \middle| -\frac{a}{2} \hat{\mathbf{y}}\right) (C_4|\boldsymbol{\tau}) \left(E \middle| \frac{a}{2} \hat{\mathbf{y}}\right) = \left(C_4 \middle| \frac{c}{2} \hat{\mathbf{z}}\right).$$

The Wyckoff positions are:

16	k	1	$(x, y, z), (\bar{x}, \bar{y}, \bar{z}), (\bar{x}, \bar{y}, z), (x, y, \bar{z})$ $(y, x, z), (y, x, \bar{z}), (\bar{y}, \bar{x}, z), (\bar{y}, \bar{x}, \bar{z})$ $\left(\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z\right), \left(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z\right)$ $\left(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z\right), \left(\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z\right)$ $\left(\frac{1}{2} + y, \frac{1}{2} - x, \frac{1}{2} - z\right), \left(\frac{1}{2} + y, \frac{1}{2} - x, \frac{1}{2} + z\right)$ $\left(\frac{1}{2} - y, \frac{1}{2} + x, \frac{1}{2} - z\right), \left(\frac{1}{2} - y, \frac{1}{2} + x, \frac{1}{2} + z\right)$
8	j	..m	(x, x, z)
8	i	m..	$(x, y, 0)$
8	h	2..	$\left(0, \frac{1}{2}, z\right)$
8	g	m.2m	$(x, \bar{x}, 0), (\bar{x}, x, 0), \left(\frac{1}{2} + x, \frac{1}{2} + x, \frac{1}{2}\right), \left(\frac{1}{2} - x, \frac{1}{2} - x, \frac{1}{2}\right)$
4	f	m.2m	$(x, x, 0), (\bar{x}, \bar{x}, 0), \left(\frac{1}{2} + x, \frac{1}{2} - x, \frac{1}{2}\right), \left(\frac{1}{2} - x, \frac{1}{2} + x, \frac{1}{2}\right)$
4	e	2.mm	$(0, 0, z), (0, 0, -z), \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2} + z\right), \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2} - z\right)$
4	d	$\bar{4}$	$\left(0, \frac{1}{2}, \frac{1}{4}\right), \left(0, \frac{1}{2}, \frac{3}{4}\right), \left(\frac{1}{2}, 0, \frac{1}{4}\right), \left(\frac{1}{2}, 0, \frac{3}{4}\right)$
4	c	2/m..	$\left(0, \frac{1}{2}, 0\right), \left(\frac{1}{2}, 0, 0\right), \left(0, \frac{1}{2}, \frac{1}{2}\right), \left(\frac{1}{2}, 0, \frac{1}{2}\right)$
2	b	m.mm	$\left(0, 0, \frac{1}{2}\right), \left(\frac{1}{2}, \frac{1}{2}, 0\right)$
2	a	m.mm	$(0, 0, 0), \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$

There are six sets of special points $a - f$.

The affine normalizer is $I4/mmm$.

The Hexagonal close-packed structure $P \frac{6_3}{m} \frac{2}{m} \frac{2}{c} \left(P \frac{6_3}{mmc} \right), \mathbb{D}_{6h}^4$

As the label indicates, this structure has a primitive hexagonal Bravais lattice with primitive lattice vectors:

$$\mathbf{a}_1 = \frac{a}{2} \left(\sqrt{3} \hat{\mathbf{x}} - \hat{\mathbf{y}} \right), \quad \mathbf{a}_2 = a \hat{\mathbf{y}}, \quad \mathbf{a}_3 = c \hat{\mathbf{z}},$$

and two atoms per unit cell, located at $(0, 0, 0)$ and $(1/3, 2/3, 1/2)$.

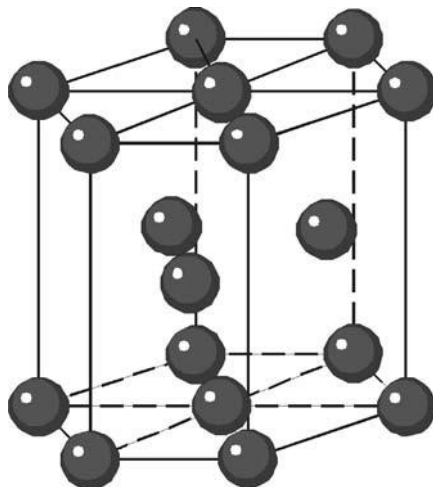
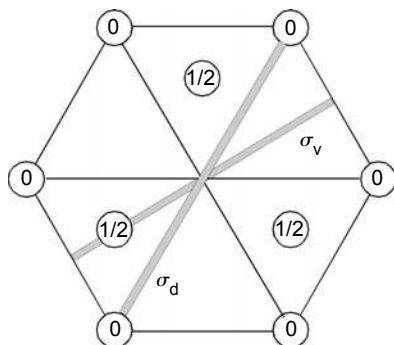


Fig. 10.23. The hexagonal close-packed structure.

Fig. 10.24. Horizontal projection of the rutile structure. The elevation of each atom in the unit cell is indicated. Also shown as gray stripes are the two inequivalent reflection planes σ_v and σ_d .

There are 24 representative elements of this group; below we list 12 typical operators, and it is quite straightforward to discern the remaining 12,

$$(E|\mathbf{0}), (C_3|\mathbf{0}), (C_2''|\mathbf{0}), (S_6|\mathbf{0}), (\sigma_h|\mathbf{0}), (\sigma_v|\mathbf{0}), \\ (I|\boldsymbol{\tau}), (C_6|\boldsymbol{\tau}), (C_2|\boldsymbol{\tau}), (C_2'|\boldsymbol{\tau}), (S_3|\boldsymbol{\tau}), (\sigma_d|\boldsymbol{\tau}),$$

with $\boldsymbol{\tau} = (0, 2a/3, c/2)$.

The affine normalizer is $P6/mmm(\mathbf{a}_1, \mathbf{a}_2, \mathbf{c}/2)$.

10.7 Fourier space crystallography

The recent discovery of incommensurate and quasi-crystalline systems revealed that a unifying description of symmetry operations, inclusive of these systems as well as regular crystals, is to be found in Fourier space rather than real physical space. This revelation evoked Mermin to make the following comment,

... it is a misfortune of intellectual history that the space-group classification of crystallography was developed in real space to categorize periodic structures, rather than in Fourier space to categorize diffraction patterns consisting of sharp Bragg peaks. This was first remarked upon in a little cited paper by Arthur Bienenstock and P. P. Ewald, 1962. That their work has for thirty years had no impact on textbook treatment of space-groups, or on the *International Tables for Crystallography* ..., I attribute in part to the enormous inertia of well established methods.

However, we believe that our preceeding presentation of crystallography in real space is of pedagogical value vis-à-vis developing the underlying basic concepts, including symmorphic and nonsymmorphic space-groups, yet we also realize that such an approach becomes rather cumbersome, when called for to elucidate the ideas behind quasi-periodic systems.

We therefore find it pedagogically rather prudent to present a detailed characterization of Fourier space symmetries [51, 52, 53], and establish methods for describing and classifying crystallographic space-groups in this space in anticipation of the development of the symmetry of quasi-periodic systems in Chapter 18. We warn the reader that at times the presentation may seem redundant and unnecessary at this stage; the real purpose of this presentation, however, is to allow the reader to develop a certain degree of agility in manipulating symmetry operations in Fourier space and learn how to translate these methods to their counterparts in real physical space. Such empowerment will be quite helpful when dealing with quasi-crystalline systems, which, by definition, lack periodicity in their physical space, although they exhibit periodicity in higher dimensional spaces. Here, we capitalize on the dual reciprocity between real and Fourier space in crystalline systems to elucidate the development of some underlying concepts concerning manifest symmetries in Fourier space, and to establish the physical connections between Fourier and real spaces.

10.7.1 Reciprocal space, reciprocal lattice, and diffraction patterns

A crystal can be represented by some density function $\rho(\mathbf{r})$ that remains invariant under the action of the defining space-group. Although $\rho(\mathbf{r})$ can be a continuous function, its Fourier transform $\mathbf{P}(\mathbf{q})$, as manifest in its diffraction pattern, is always a discrete function defined only at the *reciprocal lattice points*. Yet $\mathbf{P}(\mathbf{q})$ is a complete image of ρ in reciprocal space. Thus, any transformation property of ρ in physical space, such as symmetry operations, must have its equivalent in Fourier space.

This can be clearly seen when we consider the crystal as a decoration ρ on a periodic lattice Λ in real dD Euclidean space, with a defined holohedry. We require that ρ be invariant both under some subgroup of the holohedry, and under the infinitely countable

set of translation vectors $\mathbf{t}$ defining Λ , namely

$$\rho(\mathbf{r} + \mathbf{t}) = \rho(\mathbf{r}), \quad \forall \mathbf{t} \in \Lambda. \quad (10.121)$$

Each $\mathbf{t}$ can be defined in terms of d independent primitive basis vectors $\mathbf{a}_i$ as

$$\mathbf{t} = \sum_{i=1}^d m_i \mathbf{a}_i, \quad (10.122)$$

where the m_i s are integer coefficients.

Taking the Fourier transform of (10.121), we write

$$\int \rho(\mathbf{r}) e^{i\mathbf{q} \cdot \mathbf{r}} d\mathbf{r} = P(\mathbf{q}) = \int \rho(\mathbf{r} + \mathbf{t}) e^{i\mathbf{q} \cdot \mathbf{r}} d\mathbf{r} = e^{-i\mathbf{q} \cdot \mathbf{t}} P(\mathbf{q}), \quad (10.123)$$

where $P(\mathbf{q})$ is a complex function with the proviso that $P(-\mathbf{q}) = P^*(\mathbf{q})$, since ρ is a real positive function. Equation (10.123) requires that

$$\mathbf{q} \cdot \mathbf{t} = 2n\pi \Rightarrow \mathbf{q} = \mathbf{G} \in \Lambda^*, \quad (10.124)$$

where the reciprocal lattice vectors $\mathbf{G}$ are defined on the dual lattice Λ^* in a companion *dual* space, identified as reciprocal space. Equation (10.124) together with (10.123) demonstrate that symmetry translations $\mathbf{t}$ in physical space effect phase shifts at the discrete Λ^* points, which are integer multiples of 2π .

Dual lattice Λ^* has the point-group symmetry of the holohedry of Λ . It also displays translation invariance with respect to an infinitely countable set of $\mathbf{G}$ -vectors. A $\mathbf{G}$ -vector can be expressed in terms of a set of d primitive reciprocal basis lattice vectors $\mathbf{b}_i$, as

$$\mathbf{G} = \sum_{i=1}^d h_i \mathbf{b}_i, \quad (10.125)$$

where again h_i are integers. Alternatively, we may represent Λ^* by the set of integers $(h_1, h_2, \dots, h_d)$ and label it *index-space*, a practice adopted in identifying and labeling diffraction patterns.

The set $\mathbf{b}_i$ bears a definite mathematical relation to the $\mathbf{a}_i$ s, namely,

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi \delta_{ij}. \quad (10.126)$$

The discrete configuration delineated by amplitudes $P(\mathbf{G})$ on the discrete reciprocal lattice, namely,

$$\rho(\mathbf{r}) = \sum_{\mathbf{G}} P(\mathbf{G}) e^{i\mathbf{G} \cdot \mathbf{r}} = \sum_{\mathbf{G}} |P(\mathbf{G})| e^{i(\mathbf{G} \cdot \mathbf{r} + 2\pi\varphi_{\mathbf{G}})}, \quad (10.127)$$

defines the corresponding diffraction pattern, where the Fourier components $|P(\mathbf{G})|$ reflect the Bragg peak intensities in scattering experiments. The intensities of these Bragg peaks tend to get weaker with increase in magnitude of the $\mathbf{G}$ vectors; reflecting the smooth distribution of the density function in the unit cell.

The phase $\varphi_{\mathbf{G}}$ cannot be extracted from scattering experiments, but is indispensable in the construction of space-group representations in Fourier space. Since ρ is a positive function, we require that

$$\varphi_0 = 0,$$

as a necessary, but by no means sufficient, condition for making the weights the Fourier transform of a positive function.

10.7.2 Action of space-group operators in Λ^*

Since, by definition, a space-group operation, generally of the form $(R|\boldsymbol{\tau})$, should leave $\rho(\mathbf{r})$ invariant, we require

$$\rho'(\mathbf{r}) = (R|\boldsymbol{\tau})\rho(\mathbf{r}) = \rho(R^{-1}(\mathbf{r} - \boldsymbol{\tau})) = \rho(\mathbf{r}),$$

or

$$\begin{aligned} \sum_{\mathbf{G} \in \Lambda^*} \mathbf{P}(\mathbf{G}) e^{i\mathbf{G} \cdot \mathbf{r}} &= \sum_{\mathbf{G} \in \Lambda^*} e^{iR\mathbf{G} \cdot \boldsymbol{\tau}} \mathbf{P}(\mathbf{G}) e^{iR\mathbf{G} \cdot \mathbf{r}} \\ &= \sum_{\mathbf{G} \in \Lambda^*} e^{i\mathbf{G} \cdot \boldsymbol{\tau}} \mathbf{P}(R^{-1}\mathbf{G}) e^{i\mathbf{G} \cdot \mathbf{r}}, \end{aligned} \quad (10.128)$$

and we obtain the relation

$$\mathbf{P}(R\mathbf{G}) = e^{iR\mathbf{G} \cdot \boldsymbol{\tau}} \mathbf{P}(\mathbf{G}) = e^{2\pi i \phi_R(\mathbf{G})} \mathbf{P}(\mathbf{G}), \quad (10.129)$$

where

$$2\pi \phi_R(\mathbf{G}) = R\mathbf{G} \cdot \boldsymbol{\tau} = \mathbf{G} \cdot R^{-1}\boldsymbol{\tau}. \quad (10.130)$$

Equation (10.129) defines the relations

$$|\mathbf{P}(R\mathbf{G})| = |\mathbf{P}(\mathbf{G})|, \quad (10.131)$$

$$\varphi_{R\mathbf{G}} = \phi_R(\mathbf{G}) + \varphi_{\mathbf{G}}. \quad (10.132)$$

Two comments are in order at this point:

- Since the reality of ρ requires $|\mathbf{P}(-\mathbf{G})| = |\mathbf{P}(\mathbf{G})|$, the intensities observed in scattering experiments must be invariant under inversion $\mathcal{I}$. Thus, if the point-group of ρ , $\mathcal{P}$, does not contain $\mathcal{I}$, the point-group of $|\mathbf{P}(\mathbf{G})|$ is

$$\mathcal{P}_{\text{Laue}} = \mathcal{P} \otimes \bar{1}.$$

$\mathcal{P}_{\text{Laue}}$ is called the *Laue group*, and $\mathcal{P}_{\text{Laue}} \supset \mathcal{P}$.

- The phase change $\phi_R(\mathbf{G})$ due to space-group action depends specifically on both $(R|\boldsymbol{\tau})$ and $\mathbf{G}$. Hence, the set of $\phi_R(\mathbf{G})$ associated with $(R|\boldsymbol{\tau}) \in \mathbb{S}$ can be used to classify the action of different space-groups $\mathbb{S}$, in Fourier space.

Writing

$$\boldsymbol{\alpha} = R^{-1}\boldsymbol{\tau} = \sum_i \alpha_i \mathbf{a}_i$$

and substituting it together with (10.125) in (10.130), we get

$$\phi_R(\mathbf{G}) = \sum_i h_i \alpha_i \pmod{1}. \quad (10.133)$$

Equation (10.133) has two consequences:

- (i) Its linear composition form allows us to limit the $\phi_R(\mathbf{G})$ computations to the set $\phi_R(\mathbf{b}_i) = \alpha_i$, and we write

$$\phi_R(\mathbf{G}) = \sum_i h_i \phi_R(\mathbf{b}_i).$$

- (ii) It also allows us to represent the action of the operator $(R|\boldsymbol{\tau})$ on the 3D Λ^* by the matrix

$$(R|\boldsymbol{\tau}) \Rightarrow \begin{pmatrix} R & | & \mathbf{0} \\ \boldsymbol{\alpha} & | & 1 \end{pmatrix} \begin{pmatrix} h_1 \\ h_2 \\ h_3 \\ \varphi_{\mathbf{G}} \end{pmatrix} \quad (10.134)$$

where $\mathbf{0}$ is a 3×1 null vector, and $0 < \alpha_i < 1$. Moreover, the R matrices are engendered on the primitive basis $\mathbf{b}_i$; alternatively, they may be obtained from those of the standard primitive lattice with the aid of centering matrices.

Next, we use the space-group composition law,

$$\begin{aligned} [(R_1|\boldsymbol{\tau}_1)(R_2|\boldsymbol{\tau}_2)] \rho(\mathbf{r}) &= \rho([(R_1 R_2)^{-1} | -R_2^{-1} \boldsymbol{\tau}_2 - (R_1 R_2)^{-1} \boldsymbol{\tau}_1] \mathbf{r}), \\ \rho(R_1 R_2 \mathbf{G}) &= \exp [-i(R_1 [R_2 \mathbf{G}] \cdot \boldsymbol{\tau}_1) + R_2 \mathbf{G} \cdot \boldsymbol{\tau}_2] \rho(\mathbf{G}), \end{aligned} \quad (10.135)$$

to obtain the *linear group compatibility condition*

$$\phi_{R_1 R_2}(\mathbf{G}) = \phi_{R_1}(R_2 \mathbf{G}) + \phi_{R_2}(\mathbf{G}).$$

(10.136)

This composition law allows further reduction in the number of computed phases. Since all point-groups can be constructed, with the aid of *generating relations*, from a small set of generating elements $\mathbf{R}_i$ – with the exception of mmm , which has three generators, all other 3D point-groups have two generators – the computation of $\phi_R(\mathbf{b}_i)$ is limited to these generators.

The generating relations assume two forms: $\mathbf{R}_i^n = E$, and $\mathbf{R}_i \mathbf{R}_j \mathbf{R}_i = \mathbf{R}_i$. Noting that

$$\phi_E(\mathbf{G}) = 0 \rightarrow \begin{pmatrix} \mathbb{I} & \mathbf{0} \\ 0 & 0 & 1 \end{pmatrix},$$

we find that the corresponding group compatibility relations are

$$\phi_{\mathbf{R}_i}((1 + \mathbf{R}_i + \mathbf{R}_i^2 - I + \cdots + \mathbf{R}_i^{n-1}) \mathbf{G}) = 0, \quad (10.137)$$

$$\phi_{\mathbf{R}_i}(\mathbf{R}_j \mathbf{R}_i \mathbf{G}) + \phi_{\mathbf{R}_j}(\mathbf{R}_i \mathbf{G}) + \phi_{\mathbf{R}_i}(\mathbf{G}) - \phi_{\mathbf{R}_j}(\mathbf{G}) = 0. \quad (10.138)$$

We find that the action of space-groups on lattices in Fourier space involves the assignment of phases to the Fourier coefficients. We can then classify space-groups in Fourier space according to the corresponding set of phases that is consistent with the action of its symmetry operations on the lattice.

Symmorphic space-groups redefined

We may define a space-group as symmorphic when there is a single origin about which every point-group operation is a symmetry of the crystal with $\tau = \mathbf{0}$. Which in Fourier space translates to

$$\phi_R(\mathbf{G}) = 0 \pmod{1}, \quad \forall R \in \mathbb{P}, \text{ and } \mathbf{G} \in \mathbb{T},$$

with respect to that origin.

10.7.3 Equivalent space-groups, gauge transformations

In order to define the different symmetry classes of space-groups we have to define the equivalence relation among seemingly different space-groups.

Gauge transformations and equivalent space-groups

Two density functions $\rho(\mathbf{r})$ and $\rho'(\mathbf{r})$, defined on a real-space lattice Λ , such that

$$\rho'(\mathbf{r}) = \rho(\mathbf{r} - \mathbf{d}), \quad \mathbf{d} \notin \Lambda \quad (10.139)$$

must have equivalent space-group symmetry. Their Fourier components, defined on the dual lattice Λ^* , are related by

$$\mathbf{P}'(\mathbf{G}) = e^{i\mathbf{G} \cdot \mathbf{d}} \mathbf{P}(\mathbf{G}) = e^{i2\pi\chi(\mathbf{G})} \mathbf{P}(\mathbf{G}), \quad 0 < \chi(\mathbf{G}) < 1, \quad (10.140)$$

where $\chi(\mathbf{G}) = \mathbf{G} \cdot \mathbf{d}/2\pi$ is called a *gauge function*, in analogy with the gauge functions of electrodynamics, since it has no effect on macroscopic properties of the crystal. Conversely, we say that two densities, defined on a lattice, are equivalent if there exists a gauge function relating their Fourier components.

We establish a linear composition law of χ in two steps, with the aid of (10.140): First, we get $\chi(\mathbf{0}) = 0$, second, substituting $\sum_i \mathbf{G}_i = \mathbf{0}$ we find that

$$\sum_i \chi(\mathbf{G}_i) = 0, \quad \text{when } \sum_i \mathbf{G}_i = \mathbf{0}. \quad (10.141)$$

Equation (10.141) can be used to generate the gauge function on the lattice as follows: Starting with $\mathbf{b}_i - \mathbf{b}_i = \mathbf{0}$ we obtain

$$\chi(-\mathbf{b}_i) = -\chi(\mathbf{b}_i),$$

then, with the aid of $\mathbf{G} - \sum_i h_i \mathbf{b}_i = \mathbf{0}$, we obtain

$$\chi(\mathbf{G}) = \sum_i h_i \chi(\mathbf{b}_i).$$

Equation (10.129) gives

$$\begin{aligned} \mathbf{P}(R\mathbf{G}) &= e^{2\pi i \phi_R(\mathbf{G})} \mathbf{P}(\mathbf{G}), \\ \mathbf{P}'(R\mathbf{G}) &= e^{2\pi i \phi'_R(\mathbf{G})} \mathbf{P}'(\mathbf{G}), \end{aligned}$$

which together with (10.140) provide the *gauge transformation relation*

$$\phi'_R(\mathbf{G}) - \phi_R(\mathbf{G}) = \chi(R\mathbf{G}) - \chi(\mathbf{G}) = \chi([R - \mathbb{I}]\mathbf{G}) \quad (10.142)$$

that establishes the equivalence between two space-groups.

The concept of gauge function and gauge transformation have trivial interpretation in the case of crystallographic space-groups, as we shall show below. However, they assume a more general form and provide a unique means of classifying space-groups of quasi-crystallographic systems in Fourier space, as we will demonstrate in Chapter 18.

If we designate as $\mathbb{S}$ and $\mathbb{S}'$ the space-groups of ρ and ρ' , respectively, then a close examination of (10.142) shows that in the case of crystallographic systems it reduces to

$$R\mathbf{G} \cdot (\boldsymbol{\tau}' - \boldsymbol{\tau}) = (R - \mathbb{I})\mathbf{G} \cdot \mathbf{d} \Rightarrow \boldsymbol{\tau}' - \boldsymbol{\tau} = (R - \mathbb{I})\mathbf{d},$$

which conforms with the discussion of Section 10.5.2, especially (10.92).

Symmetry types of densities are classified as having gauge-equivalent classes of phase functions.

Gauge transformations and symmorphic space-groups

In the light of the idea of gauge transformations, we may identify a class of space-groups as symmorphic if there exists a gauge in which every phase function vanishes (modulo unity).

Example 10.11

The 3D tetragonal system

With the aid of the method outlined above we will establish a classification scheme for the space-groups corresponding to index-space having tetragonal symmetry.

There are two different space lattices in this system: the first is P and the second may be either I or F , depending on the choice of axes (the equivalence of these two is left as an exercise). In order to obtain the usual body-centered setting in physical space, we choose a face-centered setting for the index-space, with primitive basis:

$$\mathbf{b}_1 = (1/a, 1/a, 0), \quad \mathbf{b}_2 = (1/a, 0, 1/c), \quad \mathbf{b}_3 = (0, 1/a, 1/c).$$

The Bravais lattice has $4/mmm$ holohedral symmetry, but the crystal $P(\mathbf{G})$ -function may reduce the symmetry in index-space to that of any of the complex point subgroups of $4/mmm$ formed by (10.134) type operators, namely those based on 4 , $\bar{4}$, $4/m$, $\bar{4}2m$ and $4mm$. We write the point operation matrices in terms of the standard P and the F lattices,

the latter is obtained with the aid of the centering matrix $1/2 \begin{pmatrix} 1 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 1 \end{pmatrix}$ and its inverse

$$\begin{pmatrix} 1 & 1 & -1 \\ 1 & -1 & 1 \\ -1 & 1 & 1 \end{pmatrix}.$$

- (i) **Space-group class 4** The generator is a four-fold rotation about the c -axis which we denote by the matrix operator $\mathfrak{C}_4$; its standard and F Reps are

$$\mathfrak{C}_4^s = \begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ \alpha_1 & \alpha_2 & \alpha_3 & 1 \end{pmatrix} \Rightarrow \mathfrak{C} = \begin{pmatrix} 0 & 0 & -1 & 0 \\ -1 & 0 & 0 & 0 \\ 1 & 1 & 1 & 0 \\ \alpha_1 & \alpha_2 & \alpha_3 & 1 \end{pmatrix}$$

satisfying the generating relation $\mathfrak{C}_4^4 = \mathbb{I}$, which on the index-space becomes

$$\begin{pmatrix} h_1 \\ h_2 \\ h_3 \\ \varphi_{\mathbf{G}} \end{pmatrix} = \mathfrak{C}_4^4 \begin{pmatrix} h_1 \\ h_2 \\ h_3 \\ \varphi_{\mathbf{G}} \end{pmatrix} = \begin{pmatrix} \mathbb{I} & & & \\ -2\alpha_2 - 2\alpha_3 & 2\alpha_2 + 2\alpha_3 & 2\alpha_2 + 2\alpha_3 & 1 \end{pmatrix} \begin{pmatrix} h_1 \\ h_2 \\ h_3 \\ \varphi_{\mathbf{G}} \end{pmatrix},$$

implying that

$$\begin{aligned} \alpha_2 + \alpha_3 &= 0 \pmod{1}, \\ \alpha_2 + \alpha_3 &= \frac{1}{2} \pmod{1}, \end{aligned}$$

which gives rise to the two inequivalent space-groups

$$I(F)4 \rightarrow \alpha_1 = \alpha_2 = \alpha_3 = 0,$$

$$I(F)4_1 \rightarrow \alpha_1 = \mathbf{b}_1 \cdot \mathbf{R}^{-1} \boldsymbol{\tau} = 1/2, \alpha_2 = \mathbf{b}_2 \cdot \mathbf{R}^{-1} \boldsymbol{\tau} = 3/4, \alpha_3 = \mathbf{b}_2 \cdot \mathbf{R}^{-1} \boldsymbol{\tau} = 3/4.$$

- (ii) **Space-group class $\bar{4}$** This group has a four-fold rotary-inversion axis parallel to l , denoted $\mathfrak{S}_4$.

$$\mathfrak{S}_4^s = \begin{pmatrix} 0 & 1 & 0 & 0 \\ \bar{1} & 0 & 0 & 0 \\ 0 & 0 & \bar{1} & 0 \\ \beta_1 & \beta_2 & \beta_3 & 1 \end{pmatrix} \Rightarrow \mathfrak{S}_4 = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \\ -1 & -1 & -1 & 0 \\ \beta_1 & \beta_2 & \beta_3 & 1 \end{pmatrix}.$$

Table 10.16. *Nonprimitive vectors for class 4 space-groups.*

$\mathbb{S}$	E	C_4	C_2	C_4^3
$I(F)4$	$(0, 0, 0)$	$(0, 0, 0)$	$(0, 0, 0)$	$(0, 0, 0)$
$I(F)4_1$	$(0, 0, 0)$	$(0, a/2, c/4)$	$(0, 0, 0)$	$(0, a/2, c/4)$
$\mathbf{R}^{-1}\boldsymbol{\tau}$		$(a/2, 0, c/4)$		$(a/2, 0, c/4)$

We require that $\mathfrak{S}_4^4 = \mathbb{I}$ on the index-space. We find, however, by matrix multiplication, that

$$\mathfrak{S}_4^4 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$

Thus, β_1 , β_2 , and β_3 are arbitrary parameters and there is a single space-group in the class.

- (iii) **Space-group class $4/m$** The generators are C_4 and a normal mirror plane which we denote $\mathfrak{H}$, such that

$$\mathfrak{H}^s = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \bar{1} & 0 \\ \gamma_1 & \gamma_2 & \gamma_3 & 1 \end{pmatrix} \Rightarrow \mathfrak{H} = \begin{pmatrix} 1 & 1 & 1 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & \bar{1} & 0 & 0 \\ \gamma_1 & \gamma_2 & \gamma_3 & 1 \end{pmatrix}.$$

The group has the three generating relations,

$$\mathfrak{H}^2 = \mathfrak{C}_4^4 = \mathbb{I}, \quad \mathfrak{H} \mathfrak{C}_4 = \mathfrak{C}_4 \mathfrak{H}.$$

$\mathfrak{C}_4^4 = \mathbb{I}$	$\mathfrak{H}^2 = \mathbb{I}$	$\mathfrak{H} \mathfrak{C}_4 = \mathfrak{C}_4 \mathfrak{H}$
$2\alpha_2 + 2\alpha_3 = 0$	$2\gamma_1 + \gamma_2 + \gamma_3 = 0$	$\alpha_2 + \alpha_3 + \gamma_1 + \gamma_2 = 0$
	$\gamma_2 - \gamma_3 = 0$	$\alpha_2 - \alpha_3 + \gamma_1 + \gamma_3 = 0$
		$\alpha_2 - \alpha_3 + \gamma_1 - \gamma_3 = 0.$
$\alpha_2 + \alpha_3 = 0, 1/2$	$\gamma_1 + \gamma_2 = 0, 1/2$	$\alpha_2 + \alpha_3 + \gamma_1 + \gamma_2 = 0$
	$\gamma_2 = \gamma_3$	$\gamma_3 = 0, 1/2$
		$\alpha_2 - \alpha_3 + \gamma_1 = 0, 1/2$

Table 10.17. *Nonprimitive vectors for class 4 space-groups.*

$\mathbb{S}$	E S_4^3	C_4 σ_h	C_2 S_4	C_4^3 $\mathcal{I}$
$I(F)4/m$	(0, 0, 0)	(0, 0, 0)	(0, 0, 0)	(0, 0, 0)
$I(F)4_1/a$	(0, 0, 0)	(0, $a/2$, $c/4$)	(0, 0, 0)	(0, $a/2$, $c/4$)
$\mathbf{R}^{-1}\boldsymbol{\tau}$		($a/2$, 0, $c/4$)		

and we obtain the two allowed space-group classes for point-group class $4/m$ in the face-centered index-space:

$$\begin{aligned}
 I(F)4/m &\rightarrow \alpha_1 = \alpha_2 = \alpha_3 = \gamma_1 = \gamma_2 = \gamma_3 = 0 \\
 I(F)4_1/a &\rightarrow \alpha_1 = 1/2, \quad \alpha_2 = \alpha_3 = \frac{1}{4}, \quad \gamma_1 = \frac{1}{2}, \quad \gamma_2 = \gamma_3 = 0.
 \end{aligned}$$

(iv) **Space-group class $4mm$ (C_{4v})** The generators are $\mathfrak{C}_4$ and the mirror plane

$$\mathfrak{M}^s = \begin{pmatrix} \bar{1} & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ \gamma_1 & \gamma_2 & \gamma_3 & 1 \end{pmatrix} \Rightarrow \mathfrak{M} = \begin{pmatrix} 0 & -1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 1 & 1 & 1 & 0 \\ \gamma_1 & \gamma_2 & \gamma_3 & 1 \end{pmatrix},$$

with the generating relations

$$\begin{aligned}
 \mathfrak{C}_4^4 &= \mathbb{I} & \mathfrak{M}^2 &= \mathbb{I} & (\mathfrak{C}_4 \mathfrak{M})^2 &= \mathbb{I} \\
 2\alpha_2 + 2\alpha_3 &= 0 & \gamma_1 + \gamma_2 + 2\gamma_3 &= 0 & \alpha_2 + \alpha_3 + \gamma_2 + \gamma_3 &= 0 \\
 & & \gamma_1 - \gamma_2 &= 0 & 2\alpha_1 - 2\gamma_2 &= 0 \\
 & & & & 2\alpha_1 + 2\alpha_2 + 2\alpha_3 + 2\gamma_3 &= 0 \\
 \alpha_2 + \alpha_3 &= 0, 1/2 & \gamma_2 + \gamma_3 &= 0, 1/2 & \alpha_2 + \alpha_3 + \gamma_2 + \gamma_3 &= 0 \\
 & & \gamma_1 &= \gamma_2 & \alpha_1 - \gamma_2 &= 0, 1/2 \\
 & & & & \alpha_1 + \alpha_2 + \alpha_3 + \gamma_3 &= 0, 1/2
 \end{aligned}$$

(a) $\alpha_2 + \alpha_3 = 0$

1. All phase angles vanish, symmorphic space-group $I(F)4mm$.
2. The α s vanish, $\gamma_3 = \gamma_2 = \gamma_1 = \frac{1}{2}$, nonsymmorphic space-group $I(F)4cm$.

(b) $\alpha_2 + \alpha_3 = 1/2$

1. $I(F)4_1md \Rightarrow \alpha_1 = 1/2, \alpha_2 = \alpha_3 = 1/4, \gamma_1 = \gamma_2 = 0, \gamma_3 = 1/2$.
2. $I(F)4_1cd \Rightarrow \alpha_1 = 1/2, \alpha_2 = \alpha_3 = 1/4, \gamma_1 = \gamma_2 = 0, \gamma_3 = 1/2$.

Table 10.18. *Nonprimitive vectors for class 4mm space-groups.*

$\mathbb{S}$	E	C_4	C_2	C_4^3	σ_x	σ_y	σ_{xy}	$\sigma_{\bar{x}y}$
$I(F)4mm$	(0, 0, 0)	(0, 0, 0)	(0, 0, 0)	(0, 0, 0)	(0, 0, 0)	(0, 0, 0)	(0, 0, 0)	(0, 0, 0)
$I(F)4cm$	(0, 0, 0)	(0, 0, 0)	(0, 0, 0)	(0, 0, 0)	$(0, 0, \frac{c}{2})$	$(0, 0, \frac{c}{2})$	$(0, 0, \frac{c}{2})$	$(0, 0, \frac{c}{2})$
$\mathbf{R}^{-1}\boldsymbol{\tau}$					$(0, 0, \frac{c}{2})$			
$I(F)4_1md$	(0, 0, 0)	$(0, \frac{a}{2}, \frac{c}{4})$	(0, 0, 0)	$(0, \frac{a}{2}, \frac{c}{4})$	(0, 0, 0)	(0, 0, 0)	$(0, \frac{a}{2}, \frac{c}{4})$	$(0, \frac{a}{2}, \frac{c}{4})$
$\mathbf{R}^{-1}\boldsymbol{\tau}$		$(\frac{a}{2}, 0, \frac{c}{4})$						
$I(F)4_1cd$	(0, 0, 0)	$(0, \frac{a}{2}, \frac{c}{4})$	(0, 0, 0)	$(0, \frac{a}{2}, \frac{c}{4})$	$(0, 0, \frac{c}{2})$	$(0, 0, \frac{c}{2})$	$(\frac{a}{2}, 0, \frac{c}{4})$	$(\frac{a}{2}, 0, \frac{c}{4})$
$\mathbf{R}^{-1}\boldsymbol{\tau}$		$(\frac{a}{2}, 0, \frac{c}{4})$			$(0, 0, \frac{c}{2})$			

10.7.4 Extinctions in Fourier space

An interesting manifestation arises in Fourier space when the space-group contains stabilizers of some $\mathbf{G}$ vectors, i.e. $R\mathbf{G} = \mathbf{G}$, with some of the stabilizer elements having nonzero nonprimitive vectors attached to them. As we will show, this has a direct impact on the corresponding diffraction pattern, it gives rise to the phenomenon of *missing Bragg peaks*.

First, we note that when $R\mathbf{G} = \mathbf{G}$, (10.142) yields

$$\phi'_R(\mathbf{G}) - \phi_R(\mathbf{G}) = \chi([R - \mathbb{I}]\mathbf{G}) = 0 \pmod{1},$$

i.e. $\phi_R(\mathbf{G})$ is gauge invariant.

Second, we find that in such cases we encounter contradicting results from (10.129), namely, we find that for $(R|\boldsymbol{\tau})$ in the stabilizer of $\mathbf{G}$,

$$\begin{aligned} \mathbf{P}(R\mathbf{G}) &= \mathbf{P}(\mathbf{G}), & \text{since } R\mathbf{G} &= \mathbf{G}, \\ \mathbf{P}(R\mathbf{G}) &= e^{iR\mathbf{G} \cdot \boldsymbol{\tau}} \mathbf{P}(\mathbf{G}), & \text{since } \boldsymbol{\tau} &\neq \mathbf{0}, \end{aligned}$$

thus, if $R\mathbf{G} \cdot \boldsymbol{\tau}/2\pi$ is not an integer, the only way to satisfy both conditions is that $\mathbf{P}(\mathbf{G}) = 0$. Thus, $\mathbf{P}$ must vanish at such $\mathbf{G}$ s, and we say that *the Bragg peak at $\mathbf{G}$ is extinguished*. We should, therefore, recognize that extinctions are solely associated with screw axes and glide planes. If we know the phase functions $\phi_R(\mathbf{G})$, we can predict the ensuing extinctions.

However, when a centered lattice is expressed in terms of the basis vectors of its standard lattice, we may expect extinctions to emerge for some $\mathbf{G}$ vectors, which, as we will show in part (2) of the following example, can be easily determined in index-space.

Example 10.12

(1) **Monoclinic space-group** $P\frac{2_1}{b}$

This space-group comprises the coset Reps

$$(E|000), (I|000), \left(C_2^z \left| \frac{a}{2} \frac{b}{2} \frac{c}{2} \right.\right), \left(\sigma_z \left| \frac{a}{2} \frac{b}{2} \frac{c}{2} \right.\right).$$

- (i) Extinctions associated with the screw z -axis 2_1 arise from the condition $\mathbf{G} \cdot \left(00\frac{c}{2}\right) \neq 0 \pmod{1}$. Writing $\mathbf{G} = \sum_i h_i \mathbf{b}_i$, we obtain extinctions at

$$(h_1 h_2 h_3) \Rightarrow h_3 = 2n + 1.$$

- (ii) Extinctions associated with the glide plane σ_z arise from the condition $\mathbf{G} \cdot \left(0\frac{b}{2}0\right) \neq 0 \pmod{1}$, and give rise to extinctions at

$$(h_1 h_2 h_3) \Rightarrow h_2 = 2n + 1.$$

(2) **Centering** The body-centered (I) lattice

When an I lattice is delineated in terms of the basis vectors of its standard (P) lattice, namely $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$, then the intensity of a diffraction peak $I(\mathbf{G})$, $G = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$, is given by

$$\begin{aligned} I(hkl) &\propto \sum_{\mathbf{t}} e^{i\mathbf{G} \cdot \mathbf{t}} \left[1 + \exp \left(i\mathbf{G} \cdot \left(\frac{a}{2} \frac{b}{2} \frac{c}{2} \right) \right) \right] \\ &= 1 + \exp [i(h+k+l)\pi], \end{aligned}$$

and we find that intensities at $h+k+l = 2n+1$ are extinguished.

Similarly, we obtain the following extinctions for other centered lattices:

$$\begin{aligned} \mathbf{A} &\Rightarrow k+l = 2n+1 \\ \mathbf{B} &\Rightarrow h+l = 2n+1 \\ \mathbf{C} &\Rightarrow h+k = 2n+1 \\ &\quad h+k \\ \mathbf{F} &\Rightarrow h+l = 2n+1 \\ &\quad k+l \end{aligned}$$

Exercises

- 10.1 Use the integers 1, 2, 3, etc. to label each of the lattice points in Figure 10.13a whose x -coordinates are such that $x \geq 0$. Perform the space-group operation $(C_4^-|\mathbf{t})$ on each of these numbered lattice points and label the resulting lattice points by $1', 2'$, etc. Find

the new origin such that the space-group operations $(C_4^-|\mathbf{t})$ just carried out can be described as pure rotations about the new origin.

- 10.2 Show that body-centered and face-centered tetragonal lattices are equivalent.
- 10.3 Derive the a-holohedry matrices of the generators C_{4z} , C_{3xyz} , $\mathcal{I}$ of the face-centered cubic structure.
- 10.4 Sketch the unit cell of Figure 10.14 as viewed along the screw axis. With the use of the solid and open circles to distinguish atoms in the basal plane from those in the mid-plane, identify the glide plane. What is the Seitz operator that takes atom 1 to the position of atom 2?
- 10.5 Show that for the two-dimensional space-group $p2mg$

$$(\sigma_x|\boldsymbol{\tau})(\sigma_y|\boldsymbol{\tau})\mathbf{r} = (\sigma_x\sigma_y|\boldsymbol{\tau} + \sigma_x\boldsymbol{\tau})\mathbf{r} = -\mathbf{r}.$$

Show explicitly that $(\sigma_x|\boldsymbol{\tau})(\sigma_y|\boldsymbol{\tau})$ is its own inverse.

- 10.6 Explain the difference between the crystallographic point-groups $3m$ and $m\bar{3}$. Explain why $m\bar{3}(\mathcal{T}_h)$ is not holohedral despite the fact that it contains a center of inversion.
- 10.7 Explain why no face-centered lattices appear in the tetragonal system.
- 10.8 Show that monoclinic I (body-centered) lattices are possible, but not new; that is, show that $2C$ is not a distinct lattice but that $2A$ and $2B$ are.
- 10.9 Use the reasoning presented in Section 10.5.2 to demonstrate that symmetry operations involving improper rotations cannot be accompanied by a nonprimitive translation $\boldsymbol{\tau}$, except $\bar{2}(S_2)$.
- 10.10 Discuss the reasons for the classification of the point-groups $\mathcal{C}_{3h}$ and $\mathcal{S}_6$ among the hexagonal and trigonal systems.
- 10.11 Write down an explicit form of the following Seitz operators:

- (i) a c -glide plane at $x, 1/4, z$,
- (ii) a 2_1 axis along $[0, y, 1/4]$,
- (iii) an n -glide plane at $x, 0, z$,
- (iv) a 4_2 axis along $[1/4, 0, z]$.

Discuss the action of the following sequence of symmetry operations:

- (i) (a) followed by (b),
 - (ii) (c) followed by (d) on the point (x, y, z) . Repeat the argument when the sequence of operations is reversed.
- 10.12 Enumerate all n -glide plane operators that appear in the space-group $P4nc(\mathcal{C}_{4v}^6)$, #104. Show that there are two types of nonprimitive translations, namely, $(\mathbf{b} + \mathbf{c})/2$ and $(\mathbf{a} + \mathbf{b} + \mathbf{c})/2$. Discuss the action of these glide planes on a point x, y, z .

- 10.13 Write down the Seitz operator form for the symmetry operations effecting the following mappings:

$$\begin{aligned}(x, y, z) &\rightarrow (1/2 - x, 1/2 - x, 1/2 + z) \\(x, y, z) &\rightarrow (1/2 + z, 1/2 - y, +z) \\(1/4 + x, 1/4 + y, 1/4 + z) &\rightarrow (1/2 + x, y, 1/2 + z) \\(y - x, y, 2/3 - z) &\rightarrow (y - x, -x, 1/3 + z)\end{aligned}$$

- 10.14 Discuss the action of the operations of the nonsymmorphic space-group $P\frac{4_2}{m}\frac{2_1}{n}\frac{2}{m}$ of the rutile structure, presented in Section 10.6.5, on a wavefunction $\psi(x, y, z)$.
- 10.15 What are the crystallographic point-groups and the site-symmetry of the (a) Wyckoff position for the following space-groups: $P\bar{4}m2$, $P\bar{4}c2$, $P3m1$, $R\bar{3}c$, and 123 ?
- 10.16 Consider the space-group $Pban$. Write out all the essential symmetry operations with respect to a *fixed* origin taken at
- (i) the intersection of the two-fold axes,
 - (ii) a center of inversion.
- 10.17 The matrices representing an n -glide plane operation normal to a , and an a -glide plane operation normal to b are

$$\begin{pmatrix} \bar{1} & 0 & 0 & 0 \\ 0 & 1 & 0 & 1/2 \\ 0 & 0 & 1 & 1/2 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \quad \begin{pmatrix} 1 & 0 & 0 & 1/2 \\ 0 & \bar{1} & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$

Determine the nature and orientation of the symmetry operator arising from the combination of the two operators given.

- 10.18 Consider a crystallographic point-group rotation operation $R \in \mathbb{P} \subset \mathcal{SO}(3)$. Next, consider a unit sphere centered about the origin; the axis of rotation of R intersects the sphere at two points, its *poles of rotation*. Each element of $\mathcal{SO}(3)$ has two such poles.

We consider two poles p_1 and p_2 as *equivalent* if they are related through some $R \in \mathbb{P}$ by

$$p_2 = R p_1.$$

This definition allows us, through the action of $\mathbb{P}$, to define a stabilizer $\mathcal{G}_p \subset \mathbb{P}$ of a pole p as

$$p = \mathcal{G}_p p.$$

- (i) Expand $\mathbb{P}$ in terms of cosets of $\mathcal{G}_p$.
- (ii) How many poles are equivalent to p , in other words, what is the size of the equivalence class of p ?
- (iii) Enumerate the subgroups of $\mathbb{P}$ conjugate to $\mathcal{G}_p$.
- (iv) How many elements of $\mathbb{P}$ are there in the union of all conjugate subgroups of $\mathcal{G}_p$ other than the identity?

- (v) Excluding the identity, show that equating the number of nonidentity elements $\mathbb{P}$ to the total number of nonidentity elements in all the equivalence classes of poles leads to the relation

$$2 \left(1 - \frac{1}{p} \right) = \sum_{i=1}^m \left(1 - \frac{1}{g_p^m} \right),$$

where p is the order of $\mathbb{P}$, m is the total number of distinct equivalent pole classes, and g_p the order of $\mathcal{G}_p$.

- (vi) The above relation can be used to determine all possible finite subgroups of $\mathcal{SO}(3)$:

- (a) Show that the limits of ∞ and 2 that can be imposed on p lead to the inequalities

$$2 > 2(1 - (1/p)) > 1, \quad 1 > (1 - (1/g_p^m)) \geq 1/2.$$

- (b) Show, by considering the inequality

$$p \geq g_p \geq 2,$$

that the only possible values m can assume are 2 and 3.

- (c) Show that the case of $m = 2$ leads to cyclic point-groups.
 (d) Show that for the case of $m = 3$, the relation

$$\frac{1}{n_1} + \frac{1}{n_2} + \frac{1}{n_3} = 1 + \frac{2}{N} > 1,$$

with $n_1 \geq n_2 \geq n_3$, requires that $n_3 = 2$.

- (e) Show that the inequality $n_1 \geq n_2 \geq n_3$ then requires that n_2 takes on the values 2 and 3 only.
 (f) What values can n_1 assume for $n_2 = n_3 = 2$? Show that the corresponding groups are $\mathcal{D}_n$.
 (g) Repeat part (iv) for $n_2 = 3$. What are the corresponding point-groups?

10.19 The perovskite structure, with the formula ABX_3 (A and B are cations and X anions) belongs to the space-group $Pm\bar{3}m$ ($\mathcal{O}_h^1$). The unit cell coordinates of orbit representative atoms are:

$$\begin{array}{ll} A & \text{at } (1/2, 1/2, 1/2) \\ B & \text{at } (0, 0, 0) \\ X & \text{at } (1/2, 0, 0) \end{array}$$

- (i) Identify the corresponding Wyckoff positions, and determine the new coordinates if the origin is moved to the A cation site.
 (ii) Determine the appropriate space-subgroup and its type that emerge when:
 (a) The A and B cations are displaced, by differing amounts, along the $[001]$ direction.
 (b) The A and B cations are displaced, by differing amounts, along the $[110]$ direction.

- (c) The A and B cations are displaced, by differing amounts, along the $[111]$ direction.
- (d) Neighboring coplanar anion octahedra are rotated in opposite directions about their z -axes.

10.20 Determine the Wyckoff positions for the space-group $P23(T^1)$.

10.21 Both the graphite and wurtzite (AB) structures belong to the space-group $P6_3mc(C_{6v}^4)$. Their unit cell coordinates are given in the table below.

Graphite			Wurtzite		
$(0, 0, 0)$	$(0, 0, 1/2)$	A	$(1/3, 2/3, 0)$	$(2/3, 1/3, 1/2)$	
$(1/3, 2/3, 0)$	$(2/3, 1/3, 1/2)$	B	$(1/3, 2/3, u)$	$(2/3, 1/3, u + 1/2)$	

Determine their respective Wyckoff positions.

11

Space-groups: Irreps

We have shown in the previous chapter that the periodicities of perfect crystals, as well as their rotational symmetries are completely described by their space-groups. Since these groups are infinitely countable, it is not possible to apply methods like Burnside's to determine their Irreps. Moreover, we alluded, in the introduction of Chapter 9, to the fact that the method of induction of Irreps is perfectly suited for such cases; as a matter of fact, it was one of the primary motives for developing the induction technique in this book. We have also shown in the previous chapter that the subgroup of translations $\mathbb{T}$ of a space-group $\mathbb{S}$ is always an invariant subgroup of $\mathbb{S}$, as such it plays a central role in the application of the induction process to space-groups. It is, therefore, appropriate to start this chapter with the development of Irreps of the translation group.

11.1 Irreps of the translation group

Although translation groups are of infinite order, it is possible to determine their Irreps without the aid of induction. Generally, the most convenient way to provide a mathematical description of an infinite lattice is by means of periodic boundary conditions. By imposing periodic boundary conditions, we make all the translations finite, limited by the length of the period chosen. We can then use the methods of finite group theory. For a one-dimensional lattice, with a translation group $\mathbb{T}_1$, we can do this by considering a lattice segment of length $L = Na$, where N is the number of lattice points and a is the primitive lattice constant, the magnitude of the primitive lattice vector $\mathbf{a}$. We then impose the condition that a function defined on the lattice must have the periodicity of the lattice segment Na . If N is sufficiently large we find all that is physically significant.

To generate the Irreps of $\mathbb{T}_1$, we first choose a generating function ϕ and use the mathematical artifact that this function is periodic over a translation Na ,

$$\phi(x \pm Na) = \phi(x), \quad (11.1)$$

where a is the generating translation, and then allow $N \rightarrow \infty$. Operating on the basis function $\phi(x)$ with the translation function operator a generates a representation of $\mathbb{T}_1$. Now we know from Section 10.1.1 that elements of the translation group are Abelian, thus its Irreps are one-dimensional. This means that if $\phi(x)$ is a basis function for an Irrep of

$\mathbb{T}_1$, we must have

$$a \phi(x) = \phi(x - a) = \chi(a) \phi(x), \quad (11.2)$$

where the first step in the equation has been illustrated in Chapter 1 and where the character, $\chi(a)$, is the one-dimensional matrix Irrep that is generated. Then, using the assumed periodicity of $\phi(x)$, we find

$$a^N \phi(x) = \chi^N(a) \phi(x) = \phi(x - Na) = \phi(x), \quad (11.3)$$

which leads to N solutions, the N primitive roots of unity:

$$\begin{aligned} \chi(a) &= [1]^{1/N} = \exp \left[-i \frac{2m\pi}{N} \right] \\ &= \exp \left[-i \left(\frac{2m\pi}{Na} \right) a \right] \\ &= \exp(-ik_m a); \\ m &= -(N-1)/2, \dots, -1, 0, 1, \dots, N/2. \end{aligned} \quad (11.4)$$

The choice of a minus sign in the exponent of the roots of unity is for convenience, as will be explained shortly. The restriction on m is chosen to serve two purposes:

- (i) it restricts the number of Irreps to N , the number of classes, and
- (ii) as discussed below, it defines $k_m = 2\pi m/Na = 2\pi m/L$, which is familiar in solid state physics as the wavevector $\mathbf{k}$, such that it is restricted to the first Brillouin zone.

Now consider the F-operator a acting on the function $\exp(ik_m x)$. We get

$$a \exp(ik_m x) = \exp(ik_m (x - a)) = \exp(-ik_m a) \exp(ik_m x),$$

which is just the product of the Irrep $\exp(-ik_m a)$ and the original function $\exp(ik_m x)$. We have generated an Irrep in agreement with (11.4). It is the reason for our choice of a minus sign in the exponent of (11.4).

We can now take the limit $N \rightarrow \infty$ and identify the Irreps of $\mathbb{T}_1$ as

$$^{(k)}\Delta(a^s) = [\exp(-ik a)]^s = \exp(-ik sa), \quad (11.5)$$

with $-\pi/a < k \leq \pi/a$. Any Irrep $^{(k')}\Delta(a^s)$ with k' lying outside this domain is *equivalent* to an Irrep $^{(k)}\Delta(a^s)$, with k lying inside it, such that

$$k' = k \pm (2n\pi/L). \quad (11.6)$$

The interval of k -space defined by

$$-\frac{\pi}{a} < k \leq \frac{\pi}{a} \quad (11.7)$$

is known as the first Brillouin zone, or simply the Brillouin zone. All information concerning a periodic function with period a is contained within this zone. The Irreps of $\mathbb{T}_1$ are thus labeled by the points k belonging to the first Brillouin zone. The concept of Brillouin zones plays a key role in the development of space-groups.

It is now straightforward to define the Irreps of $\mathbb{T}_n$ as those of direct product groups:

$$\begin{aligned} {}^{(n)\mathbf{k}}\Delta({}^n\mathbf{t}) &= \exp(-i {}^n\mathbf{k} \cdot {}^n\mathbf{t}) \\ &= \prod_{j=1}^n \exp(-ik_j t_j), \end{aligned} \quad (11.8)$$

where

$${}^n\mathbf{t} = \sum_{j=1}^n m_j \mathbf{a}_j,$$

and $\mathbf{a}_j$ is the lattice generator for the j th dimension. To simplify the notation, we drop the superscript $\mathbf{n}$. This is also motivated by the fact that most of the applications of space-groups and their Irreps will involve one, two, and three dimensions. In application, the dimension of the Euclidean space involved will be clear. Thus, we simply write the Irreps of $\mathbb{T}$ as

$${}^{(\mathbf{k})}\Delta(\mathbf{t}) = \exp(-i \mathbf{k} \cdot \mathbf{t}). \quad (11.9)$$

11.1.1 Brillouin zones and the reciprocal lattice

Historically, Brillouin zones have been introduced in solid state physics in the context of reciprocal space, the staple of the theory of crystal diffraction. They serve to identify and delineate the states of crystalline quasi-particles, such as electrons, phonons, magnons, etc. Each Bravais lattice has a corresponding *reciprocal-space lattice* with primitive reciprocal-space base vectors $\mathbf{b}_i$ defined as contravariant vectors with respect to the Bravais lattice primitive vectors, according to the condition

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi \delta_{ij}. \quad (11.10)$$

This leads to the relations

$$\mathbf{b}_i = \frac{2\pi}{\Omega} (\mathbf{a}_j \times \mathbf{a}_k), \quad i, j, k = 1, 2, 3 \text{ cyclic}, \quad (11.11)$$

where Ω is the volume of the primitive cell. A general reciprocal lattice vector $\mathbf{G}$ is given, in terms of the primitive reciprocal lattice vectors, by

$$\mathbf{G} = \sum_{i=1}^3 m_i \mathbf{b}_i, \quad (11.12)$$

where m_i is a positive or negative integer.

The Brillouin zone in reciprocal space is analogous to the Wigner–Seitz unit cell of real space. It is a cell centered about the origin in reciprocal space, which we often refer to as $\mathbf{k}$ -space, and defined such that all values of $\mathbf{k}$ that correspond to a point on the surface of the first Brillouin zone satisfy

$$2\mathbf{k} \cdot \mathbf{G} + G^2 = 0, \quad (11.13)$$

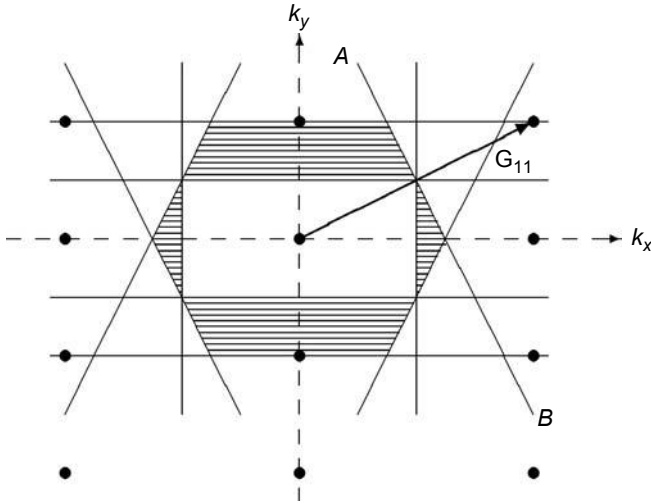


Fig. 11.1. Brillouin zones for a 1×2 rectangular net. The first Brillouin zone is the open rectangle centered at the origin. The second Brillouin zone consists of two shaded triangles and the two shaded quadrilaterals that surround the first Brillouin zone.

where the reciprocal lattice vectors $\mathbf{G}$ are selected to be the shortest vectors that lead to an enclosed zone. Equation (11.13) is the Bragg equation written in terms of the wavevector $\mathbf{k}$ and reciprocal lattice vector $\mathbf{G}$.

In group theory, the concept of the Brillouin zone arises quite naturally from the translational symmetry of the lattice, in much the same way that Newton's law of conservation of momentum arises from the translational invariance of space. In that spirit, we can think of Bragg's equation as the equation that defines the unit cell in $\mathbf{k}$ -space, centered on $\mathbf{k} = 0$, which we call the Brillouin zone.

A two-dimensional example of Brillouin zones is shown in Figure 11.1. Three-dimensional examples appear in the context of applications in Chapter 14.

Brillouin zones are constructed as follows: $\mathbf{G}$ -vectors are drawn from the origin to neighboring reciprocal lattice points. Planes are constructed to be perpendicular to and bisect these $\mathbf{G}$ -vectors. Such planes satisfy Bragg's equation, $2\mathbf{k} \cdot \mathbf{G} = G^2$. For example, in Figure 11.1, the plane denoted by the line AB is the perpendicular bisector of the reciprocal lattice vector $\mathbf{G}_{11}$. All $\mathbf{k}$ -vectors that originate at the origin and terminate somewhere on the line AB satisfy Bragg's equation, thus the line AB is a Brillouin zone boundary. Apart from the k_x - and k_y -axes, which are shown as dashed lines, and the shaded regions, all the remaining lines correspond to those planes that satisfy Bragg's equation for *some* $\mathbf{G}$ -vector. The central cell (here a rectangle) defines the first Brillouin zone. The polygons that surround and border the first Brillouin zone (here, two triangles and two quadrilaterals) make up the second Brillouin zone. The pieces of the second Brillouin zone can be translated to fit exactly into the first Brillouin zone if they are translated by appropriate reciprocal lattice vectors. One does not *fold* them into the first zone; they are translated.

The Brillouin zone is constructed from the bisection of reciprocal lattice vectors, which are derived from the primitive translation vectors of the Bravais lattice. Thus, the Brillouin zone has no geometric symmetry other than that which it derives from the Bravais lattice to which it is attached. It is defined only in terms of the translational symmetry of the Bravais lattice and is independent of the contents of the unit cell or the symmetry of the basis.

Test for wavevectors in the first Brillouin zone

We present here a simple program that tests whether a given wavevector lies inside, outside, or on the boundary of the first Brillouin zone (BZ).

Brillouin zone test

Example: face-centered cubic lattice

Input data

$$A = \begin{bmatrix} 1/2 & 1/2 & 0 \\ 0 & 1/2 & 1/2 \\ 1/2 & 0 & 1/2 \end{bmatrix}; \quad \Leftrightarrow \quad \text{primitive lattice basis}$$

```
Print["Primitive Lattice Vectors : ",MatrixForm[A]]
```

1. Generate reciprocal lattice vectors

```
B = {};
```

```
Do[
```

```
Do[
```

```
Switch[Or[i == j, i == k, j == k],  
      False, GG = Cross[A[[j]], A[[k]]]/Det[A];
```

```
AppendTo[B,GG*Signature[{i, j, k}]]
```

```
];
```

```
GG = 0,{j, 1, 3},{k, 1, 3}
```

```
],{i, 1, 3}
```

```
]
```

$$B = \begin{bmatrix} 1 & 1 & -1 \\ -1 & 1 & 1 \\ 1 & -1 & 1 \end{bmatrix}; \quad \Leftrightarrow \quad \text{reciprocal lattice basis}$$

```

Print["Reciprocal Lattice basis : ",MatrixForm[B]]
Print["B = ",MatrixForm[B]];

2. Test whether wavevector  $[1/2, 1/2, 1/2]$  lies inside, outside, or
on boundary of BZ.

Y = Transpose[A] · B;
Print["Y = ", MatrixForm[Y]];
Q = {1/2, 1/2, 1/2}; ⇔ wavevector in Cartesian coordinates
Print["Q =",MatrixForm[Q]];
QG = Transpose[A] · Q; ⇔ wavevector in reciprocal lattice coordinates
Print["QG = ",MatrixForm[QG]];
SQG = {}; ⇔ contains the signs of individual QG components
Do[
  Switch[QG[[i]] == 0, True,
    AppendTo[SQG, 1],
    False, AppendTo[SQG, Sign[QG[[i]]]]
  ], {i, 1, 3}
]
Print["SQG = ", SQG]
GX = {}; ⇔ contains the G vectors that define the BZ boundaries

(a) Generate B(i), B(i) + B(j), B(1) + B(2) + B(3)

Do[
  AppendTo[GX, SQG[[i]] B[[i]]], {i, 1, 3}
];
Do[
  Switch[i < j,True, GF = SQG[[i]] B[[i]] + SQG[[j]] B[[j]];
    AppendTo[GX, GF] ], {i, 1, 3}, {j, 1, 3}
];
AppendTo[GX,SQG[[1]] G[[1]]+SQG[[2]] G[[2]]+SQG[[3]] G[[3]]];
Print["GX = ", MatrixForm[GX]];

⇒ WV=-1,0,1 for Q inside, on boundary, or outside BZ, respectively.

```

```

WV = 0;
P = {};
(b) Test if  $\mathbf{Q} \cdot \mathbf{G} >, =, < (1/2)\mathbf{G} \cdot \mathbf{G}$ , P contains  $\mathbf{Q} \cdot \mathbf{G} - (1/2)\mathbf{G} \cdot \mathbf{G}$ 

Do[
AppendTo[P,  $\mathbf{Q} \cdot \mathbf{GX}[[i]] - (\mathbf{GX}[[i]] \cdot \mathbf{GX}[[i]]/2)$ ],
{i, 1, Length[GX]}
]
Print["P = ", P]
Q lies outside BZ
Do[
Switch[P[[i]] > 0, True, WV = 1],
{i, 1, Length[GX]}
Q lies inside BZ
PP = 0;
Do[
Switch[P[[i]] < 0, True, PP += -1],
{i, 1, Length[GX]}
]
PP = Length[GX] + PP;
Switch[PP == 0, True, WV = -1];
Print["WV = ", WV]

```

11.1.2 Symmetry projection operators of $\mathbb{T}$ and Bloch functions

Since the Irreps of $\mathbb{T}$ are one dimensional, we only have symmetry projection operators of the Wigner type. According to (6.17) they are written as

$${}^{(\mathbf{k})}\mathcal{P} = \frac{1}{N} \sum_{\mathbf{t}} {}^{(\mathbf{k})}\Delta^*(\mathbf{t}) (E|\mathbf{t}), \quad (11.14)$$

where, for convenience, it is conventional to include a finite number, N , of translation vectors, and implicitly assume that $N \rightarrow \infty$. When we apply the Wigner operator ${}^{(\mathbf{k})}\mathcal{P}$ to

a function $\phi(\mathbf{r})$ we obtain an unnormalized basis function of the Irrep $(\mathbf{k})$ of the form

$$\begin{aligned} {}^{(\mathbf{k})}\Psi(\mathbf{r}) &= {}^{(\mathbf{k})}\mathcal{P}\phi(\mathbf{r}) \\ &= \frac{1}{N} \sum_{\mathbf{t}} e^{i\mathbf{k}\cdot\mathbf{t}} (E|\mathbf{t})\phi(\mathbf{r}) \\ &= \frac{1}{N} \sum_{\mathbf{t}} e^{i\mathbf{k}\cdot\mathbf{t}} \phi(\mathbf{r}-\mathbf{t}). \end{aligned} \quad (11.15)$$

This form of ${}^{(\mathbf{k})}\Psi(\mathbf{r})$ is known as a Bloch function. It is easy to see that ${}^{(\mathbf{k})}\Psi(\mathbf{r})$ is a basis function for the Irrep $(\mathbf{k})$, since, for any $\mathbf{t}' \in \mathbb{T}$ we have

$$\begin{aligned} (E|\mathbf{t}') {}^{(\mathbf{k})}\Psi(\mathbf{r}) &= \frac{1}{N} \sum_{\mathbf{t}} e^{i\mathbf{k}\cdot\mathbf{t}} (E|\mathbf{t}')\phi(\mathbf{r}-\mathbf{t}) \\ &= \frac{1}{N} \sum_{\mathbf{t}} e^{i\mathbf{k}\cdot\mathbf{t}} \phi(\mathbf{r}-\mathbf{t}-\mathbf{t}') \\ &= \frac{1}{N} \sum_{\mathbf{t}} e^{i\mathbf{k}\cdot(\mathbf{t}+\mathbf{t}')} \phi(\mathbf{r}-\mathbf{t}) \\ &= e^{-i\mathbf{k}\cdot\mathbf{t}'} {}^{(\mathbf{k})}\Psi(\mathbf{r}). \end{aligned}$$

As we will demonstrate below, basis functions for space-groups are restricted to a particular form known as Bloch functions.

A slightly modified form of a Bloch function may be obtained from the solution of the Schrödinger equation for a particle in a periodic potential $V(\mathbf{r})$, and can be written as

$$\Psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}), \quad (11.16)$$

where $u_{\mathbf{k}}(\mathbf{r})$ also has the periodicity of the potential and $\mathbf{k}$ is a vector in the reciprocal lattice, usually restricted to the first Brillouin zone. Thus, a Bloch function may be described as a plane wave $e^{i\mathbf{k}\cdot\mathbf{r}}$ modulated by a function $u_{\mathbf{k}}(\mathbf{r})$ having the periodicity of the lattice. The periodicity of $V(\mathbf{r})$ is the periodicity of the lattice, and the $\mathbf{k}$ -vector is defined only to within a reciprocal lattice vector $\mathbf{G}$, and is generally restricted to the first Brillouin zone. We will show all this explicitly when we deal with the electronic band structure of solids. Again, we can easily demonstrate that this form of Bloch functions serve as basis functions for Irreps of the translation group. Applying a translation space-group F-operator to $\Psi_{\mathbf{k}}(\mathbf{r})$ generates an Irrep of the translation group:

$$\begin{aligned} (E|\mathbf{t})\Psi_{\mathbf{k}}(\mathbf{r}) &= (E|\mathbf{t})e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) \\ &= e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{t})} u_{\mathbf{k}}(\mathbf{r}-\mathbf{t}) \\ &= e^{-i\mathbf{k}\cdot\mathbf{t}} e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) \\ &= e^{-i\mathbf{k}\cdot\mathbf{t}} \Psi_{\mathbf{k}}(\mathbf{r}) \\ &= \Psi_{\mathbf{k}}(\mathbf{r}) {}^{(\mathbf{k})}\Delta(E|\mathbf{t}), \end{aligned}$$

where the third line follows from the periodicity $u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r}-\mathbf{t})$, and the last line follows from (11.9) for the Irreps of the translation group.

11.1.3 Point-groups and conjugate Irreps of the translation group

When we apply a general space-group operator $(R|\mathbf{w})$ to the Wigner operator $^{(\mathbf{k})}\mathcal{P}$ where $\mathbf{w} = \mathbf{v} + \mathbf{t}'$, we find that

$$\begin{aligned}
 (R|\mathbf{w})^{(\mathbf{k})}\mathcal{P} &= \frac{1}{N} \sum_{\mathbf{t}} {}^{(\mathbf{k})}\Delta^*(\mathbf{t}) (R|\mathbf{w}) (E|\mathbf{t}) \\
 &= \frac{1}{N} \sum_{\mathbf{t}} {}^{(\mathbf{k})}\Delta^*(\mathbf{t}) (R|R\mathbf{t} + \mathbf{w}) \\
 &= \frac{1}{N} \sum_{\mathbf{t}} {}^{(\mathbf{k})}\Delta^*(\mathbf{t}) (E|R\mathbf{t}) (R|\mathbf{w}) \\
 &= \frac{1}{N} \sum_{\mathbf{t}} {}^{(\mathbf{k})}\Delta^*(R^{-1}\mathbf{t}) (E|\mathbf{t}) (R|\mathbf{w}). \tag{11.17}
 \end{aligned}$$

Since $e^{i\mathbf{k}\cdot R^{-1}\mathbf{t}} = e^{iR\mathbf{k}\cdot\mathbf{t}}$, we infer that $^{(\mathbf{k})}\Delta^*(R^{-1}\mathbf{t}) = {}^{(R\mathbf{k})}\Delta^*(\mathbf{t})$, and obtain

$$\begin{aligned}
 (R|\mathbf{w})^{(\mathbf{k})}\mathcal{P} &= \frac{1}{N} \sum_{\mathbf{t}} {}^{(R\mathbf{k})}\Delta(\mathbf{t}) (E|\mathbf{t}) (R|\mathbf{w}) \\
 &= {}^{(R\mathbf{k})}\mathcal{P} (R|\mathbf{w}), \tag{11.18}
 \end{aligned}$$

or

$$(R|\mathbf{w})^{(\mathbf{k})}\mathcal{P} (R|\mathbf{w})^{-1} = {}^{(R\mathbf{k})}\mathcal{P}.$$

(11.19)

Thus, we conclude that ${}^{(R\mathbf{k})}\Delta$ is an Irrep conjugate to $^{(\mathbf{k})}\Delta$. We should note that we define $R\mathbf{k}$ modulo a reciprocal lattice vector, namely,

$$R\mathbf{k} = \mathbf{k}' + \mathbf{G} \sim \mathbf{k}', \tag{11.20}$$

where $\mathbf{k}'$ lies in the first Brillouin zone. We should also stress the fact that ${}^{(R\mathbf{k})}\Delta$ is *identical* to $^{(\mathbf{k}')}\Delta$, i.e. ${}^{(R\mathbf{k})}\Delta = {}^{(\mathbf{k}')}\Delta$, since

$$e^{iR\mathbf{k}\cdot\mathbf{t}} = e^{i(\mathbf{k}'+\mathbf{G})\cdot\mathbf{t}} = e^{i\mathbf{k}'\cdot\mathbf{t}}.$$

We recall that the matrix representative of a group operator in a conjugate Irrep is just the matrix representative of the conjugate operator in the original Irrep. Here, we are concerned with the translation group operator $(E|\mathbf{t})$ and its conjugate translation group operator $(E|R^{-1}\mathbf{t})$, which we have just found. We find that the conjugate Irreps are

$$\begin{aligned}
 {}^{(R\mathbf{k})}\Delta (E|\mathbf{t}_i) &= {}^{(\mathbf{k})}\Delta (E|R^{-1}\mathbf{t}_i) \\
 &= \exp(-i\mathbf{k}\cdot R^{-1}\mathbf{t}_i) = \exp(-iR\mathbf{k}\cdot\mathbf{t}_i) \\
 &= {}^{(R\mathbf{k})}\Delta (E|\mathbf{t}_i) = {}^{(\mathbf{k}')}\Delta (E|\mathbf{t}_i), \tag{11.21}
 \end{aligned}$$

where

$$\mathbf{k}' = R\mathbf{k} + \mathbf{G}.$$

11.1.4 Orbits and little-groups

We now need to adapt some of the definitions and concepts introduced in Chapter 9 to accommodate the new terminology of space-groups. We will then be prepared to move on to the induction of space-group Irreps following the same general procedure we previously used for point-groups.

The introduction of conjugate Irreps of the translation group above reveals the presence of orbits, superorbits, and little-groups [12, 13, 30, 31]. The set of all conjugate Irreps qualifies as a superorbit. We, then, may differentiate conjugate Irreps into sets, each comprising mutually equivalent conjugate Irreps. The maximal set of mutually inequivalent representative conjugate Irreps constitutes an orbit. Since Irreps of $\mathbb{T}$ are labeled in terms of the wavevector $\mathbf{k}$, we may attribute orbits and little-groups to $\mathbf{k}$. Thus:

The orbit of $\mathbf{k}$ is the set of all inequivalent mutually conjugate Irreps, $^{(\mathbf{k}')} \Delta$, i.e. the *orbit* of the Irrep $^{(\mathbf{k})} \Delta$.

Moreover, since the set of representative wavevectors of the orbit are amenable to a graphic display in the Brillouin zone, as shown in Figure 11.2, it has been coined a *star of $\mathbf{k}$* . Thus:

The star of $\mathbf{k}$, denoted by $^* \mathbf{k}$, is the set of all mutually *inequivalent* $\mathbf{k}$ -vectors that are related by $R\mathbf{k}$, where R ranges over all operations of the point-group.

The order of the star can be at most equal to the order of the point-group $\mathcal{P}$ associated with the space-group $\mathbb{S}$.

Figure 11.2 shows eight $\mathbf{k}$ -vectors in the two-dimensional Brillouin zone of a square net that are generated by the set of point-group operations $R\mathbf{k}$, $R \in \mathcal{C}_{4v}$. This set of symmetry-related $\mathbf{k}$ -vectors forms the star of $\mathbf{k}$. We will find that the star of $\mathbf{k}$ provides an irreducible basis for the space-group $\mathbb{S}$.

There is a direct one-to-one correspondence between the points of $^* \mathbf{k}$ and the orbit of $\mathbf{k}$. We can define the correspondence as this:

$$\mathbf{k} \Longleftrightarrow ^{(\mathbf{k})} \Delta, \quad R\mathbf{k} \Longleftrightarrow ^{(R\mathbf{k})} \Delta.$$

A key point. We may think of the orbit of $\mathbf{k}$ and the star of $\mathbf{k}$ as being the same, with $^* \mathbf{k}$ simply being a picture of the orbit within the Brillouin zone.

The area (or volume) of the Brillouin zone includes *all* the orbits of $\mathbb{T}$ for a given Bravais lattice. Each $\mathbf{k}$ corresponds to an Irrep $^{(\mathbf{k})} \Delta$. However, we must be careful here to count only those $\mathbf{k}$ -points that actually belong to the Brillouin zone. This includes *all* points *within* the Brillouin zone; it is the boundaries that require care. We follow the convention

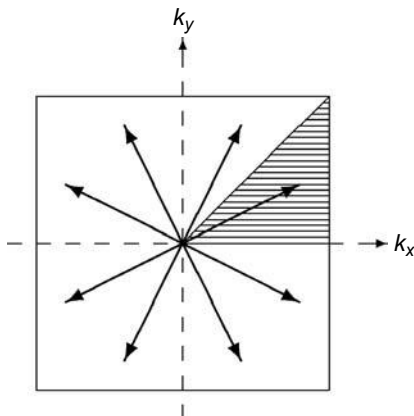


Fig. 11.2. Brillouin zone for a square net. Starting with any of the $\mathbf{k}$ -vectors, the other seven are generated by the point-group operations of C_{4v} to form $^*\mathbf{k}$. The shaded region is the *irreducible zone*

that only points on the sides (or faces) of the Brillouin zone that intersect the positive k_x or k_y axes belong to the zone. Thus, in Figure 11.2, $\mathbf{k}$ -points on the top side and right-hand side of the square are counted; but, $\mathbf{k}$ -points on the bottom side and left-hand side differ from the former by a $\mathbf{G}$ vector and must not be counted. This conforms with the restriction imposed by (11.20).

In practice, it may be convenient to consider the Brillouin zone to include all its sides, in which case it is only necessary to keep in mind that $\mathbf{k}$ -vectors that terminate on opposite side of the Brillouin zone are actually equivalent.

The triangular region in Figure 11.2 shows an *irreducible zone*, also called a *basic zone*. An irreducible zone is the smallest section of the full Brillouin zone that is bounded by symmetry lines of the Bravais lattice to which the Brillouin zone is attached and such that *every* point $\mathbf{k}'$ of the full Brillouin zone can be obtained from a $\mathbf{k}$ -point within the irreducible zone by means of a point-group operation $\mathbf{k}' = R\mathbf{k}$, where $R \in \mathcal{P}_B$, the holohedry group. One can think of the relationship geometrically by visually noting that the full Brillouin zone can be constructed by operating on the irreducible zone with all the holohedry point-group operations. Each $\mathbf{k}$ -point within the irreducible zone depicts an Irrep representative of a distinct orbit, or star.

The rest of the Brillouin zone in Figure 11.2, consisting of the seven remaining triangular irreducible regions, belongs to the seven conjugate Irreps of $\mathbb{S}_{\mathbf{k}}$. The remaining Irreps can all be generated by conjugation because $\mathbb{S}_{\mathbf{k}}$ is a normal subgroup of $\mathbb{S}$. All this can be discussed either in terms of the star of $\mathbf{k}$ or in terms of conjugation. The star of $\mathbf{k}$ presents a nice picture of the connection between conjugate Irreps.

In the more general case, where there is a basis of more than one atom and the symmetry is reduced, the zone to which one representative $\mathbf{k}$ of each $^*\mathbf{k}$ belongs is called the *representation zone*. We will find it to be larger than the irreducible zone but such that only one point of the star of $\mathbf{k}$ belongs to each representation zone.

Next, we identify the little-group of the second kind $\mathcal{L}^{II} \left({}^{(\mathbf{k})}\Delta \right)$ of the Irrep ${}^{(\mathbf{k})}\Delta$, or simply $\mathcal{L}^{II}(\mathbf{k})$, as the maximal set of space-group elements $(R|\mathbf{w})$ that generate conjugate Irreps equivalent to $\mathbf{k}$, as a matter of fact, identical to ${}^{(\mathbf{k})}\Delta$. This group is called the little-group of $\mathbf{k}$ and represented as $\mathbb{S}_{\mathbf{k}}$. Thus:

$$\mathcal{L}^{II}(\mathbf{k}) \iff \mathbb{S}_{\mathbf{k}}.$$

The little-group of $\mathbf{k}$, $\mathbb{S}_{\mathbf{k}}$, consists of the set of space-group elements $(R|\tau(R) + \mathbf{t})$ whose *rotations* R leave $\mathbf{k}$ invariant:

$$\mathbb{S}_{\mathbf{k}} = \{ (R|\tau + \mathbf{t}) \} \text{ such that } R\mathbf{k} = \mathbf{k} + \mathbf{G} \equiv \mathbf{k}, \quad (11.22)$$

where $\mathbf{G}$ is a reciprocal lattice vector.

Clearly, the set of space-group elements $(R|\tau + \mathbf{t})$ that satisfy (11.22) must be infinite, since there is an infinite number of translations. However, it is also obvious that $\mathbb{T}$ is a normal subgroup of $\mathbb{S}_{\mathbf{k}}$; and we may express $\mathbb{S}_{\mathbf{k}}$ in terms of left cosets of $\mathbb{T}$ as

$$\mathbb{S}_{\mathbf{k}} = \sum_{i=1}^{q_{\mathbf{k}}} (R_{i\mathbf{k}}|\tau_{i\mathbf{k}}) \mathbb{T}, \quad (11.23)$$

where $q_{\mathbf{k}}$ is the index of $\mathbb{T}$ in $\mathbb{S}_{\mathbf{k}}$ and the extra subscript $\mathbf{k}$ on $R_{i\mathbf{k}}$ is to emphasize that the rotations are restricted to those that leave $\mathbf{k}$ invariant. Equation (11.23) and the invariance of $\mathbb{T}$ in $\mathbb{S}_{\mathbf{k}}$, define the little-group of the first kind as:

The little-group of the first kind, $\mathcal{L}^I(\mathbf{k}) \equiv \mathbb{G}_{\mathbf{k}}$, is the factor group

$$\mathcal{L}^I(\mathbf{k}) \equiv \mathbb{G}_{\mathbf{k}} = \frac{\mathbb{S}_{\mathbf{k}}}{\mathbb{T}} \quad (11.24)$$

with coset representative elements $(R_{i\mathbf{k}}|\tau_{i\mathbf{k}})$.

$\mathbb{S}_{\mathbf{k}}$ is also the subgroup of elements of $\mathbb{S}$ that leave Irreps ${}^{(\mathbf{k})}\Delta(E|\mathbf{t})$ of $\mathbb{T}$ invariant under conjugation. We can construct $\mathbb{S}$ from left cosets of $\mathbb{S}_{\mathbf{k}}$ as

$$\mathbb{S} = \sum_{i=1}^{n_{\mathbf{k}}} (R_i|\tau_i) \mathbb{S}_{\mathbf{k}} \quad \left\{ \begin{array}{l} (R_1|\tau_1) = (E|\mathbf{0}), \\ (R_i|\tau_i) \notin \mathbb{S}_{\mathbf{k}}, \quad i \neq 1, \end{array} \right. \quad (11.25)$$

where $n_{\mathbf{k}}$ is the index of $\mathbb{S}_{\mathbf{k}}$ in $\mathbb{S}$

$$n_{\mathbf{k}} = \frac{s}{s_{\mathbf{k}}}.$$

We find that the set of point-group operations $R_{i\mathbf{k}}$ satisfy the group postulates, and form the *group of the $\mathbf{k}$ -vector* denoted by $\mathcal{P}_{\mathbf{k}}$. Thus:

Table 11.1. *Point group notation (left-hand side) and the corresponding space-group notation (right-hand side).*

$\mathcal{G}$	:	$(\mu)\Gamma$	$\Longleftrightarrow$	$\mathbb{S}$	:	$(\mu, \mathbf{k})\Gamma$	$\mathcal{N}$	:	$(\mu)\Delta$	$\Longleftrightarrow$	$\mathbb{T}$	:	$(\mathbf{k})\Delta$
$\mathcal{L}_{\mu}^{II}$	:	$(\mu)\Lambda$	$\Longleftrightarrow$	$\mathbb{S}_{\mathbf{k}}$	:	$(\mu, \mathbf{k})\Lambda$	$\mathcal{L}_{\mu}^I$	:	$(\alpha)\Omega$	$\Longleftrightarrow$	$\mathbb{G}_{\mathbf{k}}$	:	$(\alpha, \mathbf{k})\Omega$
$\mathcal{K}$			$\Longleftrightarrow$	$\mathbb{T}_{\mathbf{k}}$			$\mathcal{Q}$	:	$(\alpha)\Sigma$	$\Longleftrightarrow$	$\mathbb{Q}_{\mathbf{k}}$	:	$(\alpha, \mathbf{k})\Sigma$

The point-group of the $\mathbf{k}$ -vector, $\mathcal{P}_{\mathbf{k}}$, is the set of all point-group operations R that leave $\mathbf{k}$ invariant, which we label $R_{\mathbf{k}}$. It forms a group known as the *point-group of the $\mathbf{k}$ -vector*, which we denote by $\mathcal{P}_{\mathbf{k}}$, and which is isomorphic with the factor-group $\mathbb{Q}_{\mathbf{k}}$.

$$\mathcal{P}_{\mathbf{k}} = \{R_{\mathbf{k}}\} \quad \text{such that} \quad R_{\mathbf{k}}\mathbf{k} = \mathbf{k} + \mathbf{G} \equiv \mathbf{k}. \quad (11.26)$$

We can determine $\mathcal{P}_{\mathbf{k}}$ by setting to zero all translations, τ and $\mathbf{t}$, in $\mathbb{S}_{\mathbf{k}}$ as defined by (11.22). It is a subgroup of the crystallographic point-group, $\mathcal{P}$.

Although the little-group $\mathcal{L}^I(\mathbf{k}) \equiv \mathbb{Q}_{\mathbf{k}}$ is isomorphic with $\mathcal{P}_{\mathbf{k}}$, the point-group of $\mathbf{k}$, it differs from $\mathcal{P}_{\mathbf{k}}$ only in that it may require a factor system, a kind of phase factor, as will be explained later.

We conclude this section with Table 11.1 that relates the terminology and notation used for point-groups to that used for space-groups. It will be helpful in the next section, where we discuss the procedure for inducing Irreps of space-groups.

A note on symmetry and degeneracy Although our interest here is in developing the methods of inducing Irreps of space-groups, it is useful to comment briefly on what we can anticipate in future applications. We will be interested in such matters as the degeneracies that can occur, say, in the electronic energy for particular $\mathbf{k}$ -states. These states are described by Bloch functions. We now know that because of translational symmetry, every translation operation that takes a crystal into itself will simply multiply the Bloch function by a phase factor and there will be no change in state. Thus, only those symmetry operations that are not pure translations but which leave $\mathbf{k}$ invariant (to within a reciprocal lattice vector $\mathbf{G}$) can lead to true degeneracies. This is precisely those operations belonging to the little-group of the $\mathbf{k}$ vector.

11.1.5 Rectangular Brillouin zone

The example of $^*\mathbf{k}$ in Figure 11.3 has a high degree of symmetry, which fits in with the natural notion of a star. Such a high degree of symmetry is, however, not the general rule.

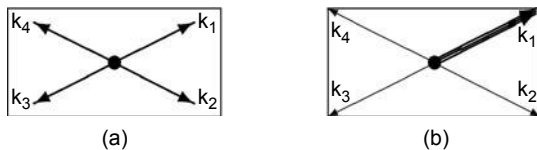


Fig. 11.3. The star of $\mathbf{k}$ for a rectangular Brillouin zone. (a) The $\mathbf{k}$ -vector $\mathbf{k}_1$ is transformed into the *inequivalent* states $\mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4$ by the point-group operators σ_x, C_2, σ_y . The star of $\mathbf{k}$ consists of all four vectors. (b) The $\mathbf{k}$ -vector $\mathbf{k}_1$ is transformed into the *equivalent* states $\mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4$. The three equivalent vectors $\mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4$ are drawn with thin lines. They no longer belong to the star of $\mathbf{k}$. Strictly speaking, they do not belong to the Brillouin zone, as they do not satisfy the restrictions imposed by (11.25). The star of $\mathbf{k}$ is just $\mathbf{k}_1$ itself.

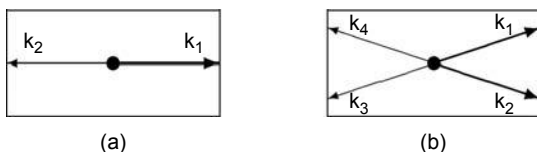


Fig. 11.4. Operations $R\mathbf{k}_1$ as an aid in determining the little-group of the wavevector. (a) $C_2\mathbf{k}_1$ gives $\mathbf{k}_2$, which is equivalent to $\mathbf{k}_1$ by a reciprocal lattice vector translation. The reflection operation σ_y also takes $\mathbf{k}_1$ into $\mathbf{k}_2 \equiv \mathbf{k}_1$, whereas σ_x takes $\mathbf{k}_1$ into itself. Thus the small group of the wavevector for a symmorphic crystal is $\mathbb{S}_{\mathbf{k}} = \{(E|\mathbf{t}), (C_2|\mathbf{t}), (\sigma_x|\mathbf{t}), (\sigma_y|\mathbf{t})\}$. (b) The same set of point-group operations just used gives only two equivalent $\mathbf{k}$ -vectors when operating on $\mathbf{k}_1$, namely $\mathbf{k}_1$ and $\mathbf{k}_4$, which are generated by E and σ_y . Thus the little-group of the wavevector is $\mathbb{S}_{\mathbf{k}} = \{(E|\mathbf{t}), (\sigma_x|\mathbf{t})\}$.

Figure 11.3(a) is an example of $^*\mathbf{k}$ for the Brillouin zone of a two-dimensional rectangular crystal. The vector $\mathbf{k}_1$ is transformed into the mutually inequivalent $\mathbf{k}$ -vectors $\mathbf{k}_2, \mathbf{k}_3$, and $\mathbf{k}_4$ by the point-group symmetry operations. The star still has a relatively high degree of symmetry. However, when the $\mathbf{k}$ -vectors are extended to reach the corners of the Brillouin zone, as illustrated in Figure 11.3(b), all the $\mathbf{k}$ -vectors are then connected by reciprocal lattice vectors and are equivalent. The star of $\mathbf{k}$ then consists of $\mathbf{k}_1$ alone; the star has lost its original symmetry.

Pictures of the set of operations $R\mathbf{k}$ are also useful for determining the group of the wavevector $\mathbb{S}_{\mathbf{k}}$. Unlike the case of $^*\mathbf{k}$, however, where we determined the set of mutually *inequivalent* $\mathbf{k}$ -vectors, here we want the set of *equivalent* $\mathbf{k}$ -vectors. For this purpose, consider Figure 11.4.

We have been dealing with symmorphic space-groups in the last few examples, but suppose the space-group is nonsymmorphic, as in the two-dimensional example of Figure 11.4.

As we found in Chapter 10, there are only four nonsymmorphic space-groups in two dimensions, and the *only* nonsymmorphic operation allowed is a glide with reflection across a line in the plane, labeled g in International notation.

The origin of the unit cell is chosen such that all point-group operators in the Seitz space-group operator refer to point-group operations about the same origin, as discussed

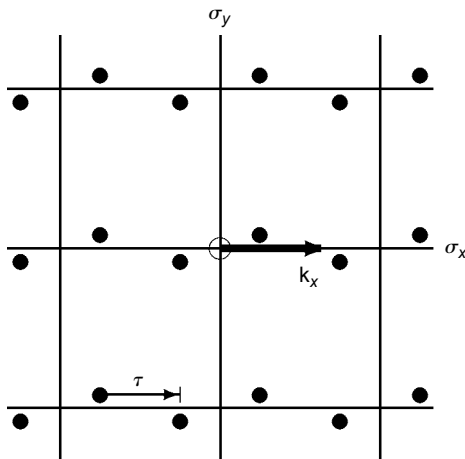


Fig. 11.5. A two-dimensional square crystal with lattice constants $\mathbf{a}$ and a fractional glide translation $\tau = \mathbf{a}/2$. The wavevector $\mathbf{k}$ is taken to be along the x -axis of the crystal. It is along the $\Gamma - X$ axis of the Brillouin zone (Figure 11.7), which is *attached* to the direct lattice and shares the same origin.

earlier. This is necessary in order that the point-group operators actually form a group, which would not be the case otherwise.

We have one little-group left to introduce: the little-group of the first kind, $\mathcal{L}_{\mathbf{k}}^I$. It is a natural outcome of the decomposition of the space-group, $\mathbb{S}$.

Decomposition of the space-group

The space-group $\mathbb{S}$ can be decomposed into cosets based on $\mathbb{S}_{\mathbf{k}}$, the little-group of $\mathbf{k}$, which is a subgroup of $\mathbb{S}$. We obtain

$$\mathbb{S} = \sum_{i=1}^{n_{\mathbf{k}}} (R_i | \tau_i) \mathbb{S}_{\mathbf{k}}, \quad \text{where } (R_i | \tau_i) \notin \mathbb{S}_{\mathbf{k}}, \quad (11.27)$$

except, of course,

$$(R_1 | \tau_1) = (E | \mathbf{0}) \in \mathbb{S}_{\mathbf{k}},$$

That is, $(E | \mathbf{0})$ must be both a coset representative and an element of $\mathbb{S}_{\mathbf{k}}$ in order that both $\mathbb{S}$ and $\mathbb{S}_{\mathbf{k}}$ be groups.

Example 11.1

Figure 11.5 shows a two-dimensional square crystal with a fractional glide translation $\tau = \mathbf{a}/2$. The wavevector $\mathbf{k}$ is taken to be along the x -axis of the crystal. For this case, $\mathbb{S}_{\mathbf{k}} = \{(E | \mathbf{t}), (\sigma_x | \tau + \mathbf{t})\}$, the elements whose *rotations* leave $\mathbf{k}$ invariant. The coset representatives that enter into (11.27) are $\{(E | \mathbf{0}), (C_2 | \mathbf{0})\}$. (We could have chosen $(\sigma_y | \tau)$ as a coset representative, but it produces the same coset $\{(\sigma_y | \tau), (C_2 | \mathbf{0})\}$ as does $(C_2 | \mathbf{0})$.)

We will find in later sections that the group of the wavevector, $\mathbb{S}_{\mathbf{k}}$, is the heart of the matter. It contains $\mathbb{T}$ as a normal subgroup. Thus we can decompose $\mathbb{S}_{\mathbf{k}}$ into cosets with respect to $\mathbb{T}$ as

$$\mathbb{S}_{\mathbf{k}} = \sum_{i=1}^{g_{\mathbf{k}}} (R_{i\mathbf{k}} | \tau_{i\mathbf{k}}) \mathbb{T}, \quad (11.28)$$

where $g_{\mathbf{k}}$ is the order of $\mathbb{S}_{\mathbf{k}}$ and the extra subscript $\mathbf{k}$ on $R_{i\mathbf{k}}$ is to emphasize that the rotations are restricted to those that leave $\mathbf{k}$ invariant.

Example 11.2.

For Figure 11.5, with $\mathbb{S}_{\mathbf{k}} = \{(E | \mathbf{t}), (\sigma_x | \tau + \mathbf{t})\}$, the coset representatives that enter into (11.28) are the elements of $\mathbb{S}_{\mathbf{k}}$ containing only nonprimitive translations, namely, $(E | 0)$ and $(\sigma_x | \tau)$. Thus

$$\mathbb{S}_{\mathbf{k}} = \{(E | 0) + (\sigma_x | \tau)\} \mathbb{T}.$$

11.2 Induction of Irreps of space-groups

Now that we are equipped with all the essential components of the method of induction as outlined in Chapter 9, we proceed with the construction of the space-group Irreps $^{(\mu, \star \mathbf{k})} \Gamma$ [12, 13, 30, 31]. We first induce $^{(\mu, \mathbf{k})} \Omega$, the Irreps of $\mathbb{S}_{\mathbf{k}}$. From these induced Irreps we choose the *allowable* Irreps, which we denote by $^{(\mu, \mathbf{k})} \Omega_A$, where the subscript A signifies that the Irrep is *allowable*.

The allowable induced Irreps $^{(\mu, \mathbf{k})} \Omega_A$ of $\mathbb{S}_{\mathbf{k}}$ are those that subduce a multiple of $^{(\mathbf{k})} \Delta$ on $\mathbb{T}$ such that

$$^{(\mu, \mathbf{k})} \Omega_A (E | \mathbf{t}) = \exp(-i \mathbf{k} \cdot \mathbf{t}) \mathbb{I}, \quad (11.29)$$

where $\mathbb{I}$ is the unit matrix of dimension $l_{\mu, \mathbf{k}}$ of $^{(\mu, \mathbf{k})} \Omega_A$.

To each $^{(\mu, \mathbf{k})} \Omega_A$ of $\mathbb{S}_{\mathbf{k}}$ corresponds one $^{(\mu, \mathbf{k})} \Gamma$ of $\mathbb{S}$. We induce each $^{(\mu, \mathbf{k})} \Gamma$ from $^{(\mu, \mathbf{k})} \Omega_A$ as follows:

- (i) We decompose $\mathbb{S}$ into cosets of $\mathbb{S}_{\mathbf{k}}$ as

$$\mathbb{S} = \{(R_1 | \tau_1) \mathbb{S}_{\mathbf{k}}, (R_2 | \tau_2) \mathbb{S}_{\mathbf{k}}, \dots, (R_{n_{\mathbf{k}}} | \tau_{n_{\mathbf{k}}}) \mathbb{S}_{\mathbf{k}}\}, \quad (11.30)$$

where $n_{\mathbf{k}}$ is the index of $\mathbb{S}_{\mathbf{k}}$ in $\mathbb{S}$, $(R_1 | \tau_1) = (E | \mathbf{0})$ and $(R_i | \tau_i) \notin \mathbb{S}_{\mathbf{k}}$, for $i \neq 1$.

As we showed in Chapter 9, we can induce a Rep of the covering group $\mathbb{S}$ from a Rep of its subgroup $\mathbb{S}_{\mathbf{k}}$ by means of the *ground representation*, which we denote by

$$^{(\mathbf{k})} \mathcal{Z} (R | \tau + \mathbf{t}) \quad (11.31)$$

whose dimension is $n_{\mathbf{k}}$. Its elements are given by

$$^{(\mathbf{k})} \mathcal{Z}_{ij} (R | \mathbf{w}) = \begin{cases} 1, & \text{if } (R_i | \tau_i)^{-1} (R | \mathbf{w}) (R_j | \tau_j) \in \mathbb{S}_{\mathbf{k}} \\ 0, & \text{otherwise,} \end{cases} \quad (11.32)$$

where $\mathbf{w} = \tau + \mathbf{t}$. Here, we omit the hat over the operators, but implicitly identify all the group operators as function operators because the ground representation is induced by operating on cosets, which are treated as functions. (See Section 9.2.2.)

- (ii) The induced Irrep $^{(\mu, \star \mathbf{k})} \Gamma$ then has dimension $l_{\mu, \mathbf{k}} \cdot n_{\mathbf{k}}$, and has the block form

$$^{(\mu, \star \mathbf{k})} \Gamma_{ij} (R | \mathbf{w}) = {}^{(\mu, \mathbf{k})} \Omega_A \left[(R_i | \tau_i)^{-1} (R | \mathbf{w}) (R_j | \tau_j) \right] {}^{(\mathbf{k})} \mathcal{Z}_{ij} (R | \mathbf{w}), \quad (11.33)$$

which, in the absence of translations, can be written in shorthand notation as

$$\Gamma_{ij} (R) = \Omega_A (R_i^{-1} R R_j) \mathcal{Z}_{ij} (R).$$

- (iii) The problem is now reduced to that of finding the Irreps of $\mathbb{S}_{\mathbf{k}}$, which is taken up in the next section.

11.2.1 The method of the little-group of the first kind: projective Irreps and multiplier factor systems

The little-group of the first kind, $\mathbb{G}_{\mathbf{k}}$, comprises the coset representatives of $\mathbb{S}_{\mathbf{k}}$ with respect to $\mathbb{T}$, (11.23). The coset representatives obey the multiplication rule for Seitz operators:

$$\begin{aligned} (R_{i\mathbf{k}} | \tau_{i\mathbf{k}}) (R_{j\mathbf{k}} | \tau_{j\mathbf{k}}) &= (R_{i\mathbf{k}} R_{j\mathbf{k}} | \tau_{i\mathbf{k}} + R_{i\mathbf{k}} \tau_{j\mathbf{k}}) \\ &= (R_{i\mathbf{k}} R_{j\mathbf{k}} | \tau_{i\mathbf{k}} + R_{i\mathbf{k}} \tau_{j\mathbf{k}} + \tau_{k\mathbf{k}} - \tau_{k\mathbf{k}}) \\ &= (R_{k\mathbf{k}} | \tau_{k\mathbf{k}} + \mathbf{t}_{ij}) \\ &= (E | \mathbf{t}_{ij}) (R_{k\mathbf{k}} | \tau_{k\mathbf{k}}), \end{aligned} \quad (11.34)$$

where $R_i R_j = R_k$, and $\mathbf{t}_{ij}$ is a lattice translation operator

$$\mathbf{t}_{ij} = \tau_{i\mathbf{k}} + R_{i\mathbf{k}} \tau_{j\mathbf{k}} - \tau_{k\mathbf{k}}. \quad (11.35)$$

The third line of (11.34) shows that the product of two coset representatives $(R_{i\mathbf{k}} | \tau_{i\mathbf{k}})$ and $(R_{j\mathbf{k}} | \tau_{j\mathbf{k}})$ is not a coset representative $(R_{k\mathbf{k}} | \tau_{k\mathbf{k}})$, but another *element* of the coset, namely, $(R_{k\mathbf{k}} | \tau_{k\mathbf{k}} + \mathbf{t}_{ij})$.

For the sake of simplicity, we now adopt for the Irrep $^{(\mu, \mathbf{k})} \Lambda (R_{i\mathbf{k}} | \tau_{i\mathbf{k}})$ the abbreviated notation

$$^{(\mu, \mathbf{k})} \Lambda (R_{i\mathbf{k}}) \equiv {}^{(\mu, \mathbf{k})} \Lambda (R_{i\mathbf{k}} | \tau_{i\mathbf{k}}), \quad (11.36)$$

and rewrite the first and last terms of (11.34) as

$$^{(\mu, \mathbf{k})} \Lambda (R_{i\mathbf{k}}) {}^{(\mu, \mathbf{k})} \Lambda (R_{j\mathbf{k}}) = {}^{(\mathbf{k})} \Delta (E | \mathbf{t}_{ij}) {}^{(\mu, \mathbf{k})} \Lambda (R_{k\mathbf{k}}). \quad (11.37)$$

Next, we define a new Irrep

$$^{(\mu, \mathbf{k})} \tilde{\Lambda} (R_{i\mathbf{k}}) = \exp [i \mathbf{k} \cdot \tau_{i\mathbf{k}}] {}^{(\mu, \mathbf{k})} \Lambda (R_{i\mathbf{k}}); \quad \forall (R_{i\mathbf{k}} | \tau_{i\mathbf{k}}) \in \mathbb{S}_{\mathbf{k}}, \quad (11.38)$$

where $^{(\mu, \mathbf{k})} \tilde{\Lambda}(R_{i\mathbf{k}})$ satisfies the binary product law

$$\begin{aligned}
 ^{(\mu, \mathbf{k})} \tilde{\Lambda}(R_{i\mathbf{k}}) ^{(\mu, \mathbf{k})} \tilde{\Lambda}(R_{j\mathbf{k}}) &= \exp[i\mathbf{k} \cdot (\tau_{i\mathbf{k}} + \tau_{j\mathbf{k}})] ^{(\mu, \mathbf{k})} \Lambda(R_{i\mathbf{k}}) ^{(\mu, \mathbf{k})} \Lambda(R_{j\mathbf{k}}) \\
 &= \exp[i\mathbf{k} \cdot (\tau_{i\mathbf{k}} + \tau_{j\mathbf{k}})] ^{(\mathbf{k})} \Delta(E|\mathbf{t}_{ij}) ^{(\mu, \mathbf{k})} \Lambda(R_{k\mathbf{k}}) \\
 &= \exp[i\mathbf{k} \cdot (\tau_{i\mathbf{k}} + \tau_{j\mathbf{k}})] \\
 &\quad \times \exp[-i\mathbf{k} \cdot (\tau_{i\mathbf{k}} + R_{i\mathbf{k}}\tau_{j\mathbf{k}} - \tau_{k\mathbf{k}})] ^{(\mu, \mathbf{k})} \Lambda(R_{k\mathbf{k}}) \\
 &= \exp[-i\mathbf{G}_i \cdot (\tau_{j\mathbf{k}})] \exp[i\mathbf{k} \cdot \tau_{k\mathbf{k}}] ^{(\mu, \mathbf{k})} \Lambda(R_{k\mathbf{k}}) \\
 &= \exp[-i\mathbf{G}_i \cdot \tau_{j\mathbf{k}}] ^{(\mu, \mathbf{k})} \tilde{\Lambda}(R_{k\mathbf{k}}), \tag{11.39}
 \end{aligned}$$

where use has been made of Equations (11.34)–(11.38) together with $R_{j\mathbf{k}}^{-1}\mathbf{k} = \mathbf{k} + \mathbf{G}_i$, to give the final result. This definition ensures that the Irrep matrices $^{(\mu, \mathbf{k})} \tilde{\Lambda}(R)$ are the same for all members of a given coset $(R_{i\mathbf{k}}|\tau_{i\mathbf{k}}) \mathbb{T}$, and we establish a correspondence between $^{(\mu, \mathbf{k})} \tilde{\Lambda}(R)$ and the elements of $\mathbb{G}_{\mathbf{k}}$, so that they form an Irrep of $\mathbb{G}_{\mathbf{k}}$ with a multiplication rule

$$^{(\mu, \mathbf{k})} \tilde{\Lambda}(R_{i\mathbf{k}}) ^{(\mu, \mathbf{k})} \tilde{\Lambda}(R_{j\mathbf{k}}) = \exp[-i\mathbf{G}_i \cdot \tau_{j\mathbf{k}}] ^{(\mu, \mathbf{k})} \tilde{\Lambda}(R_{i\mathbf{k}}R_{j\mathbf{k}}). \tag{11.40}$$

The set $^{(\mu, \mathbf{k})} \tilde{\Lambda}$ together with a factor system

$$w(\mathbf{R}_i, \mathbf{R}_j) = \exp[-i\mathbf{G}_i \cdot \tau_j] \tag{11.41}$$

form a *projective* Irrep of the group $\mathbb{G}_{\mathbf{k}}$. The set $^{(\mu, \mathbf{k})} \tilde{\Lambda}$ by itself forms an Irrep of the isomorphic group $\mathcal{P}_{\mathbf{k}}$, which, being a point-group, has no translations, fractional or otherwise, and so the factor system reduces to unity. We now encounter two possibilities regarding the multiplier factor system:

- (i) All the multiplier factors $w(\mathbf{R}_i, \mathbf{R}_j) = 1$, and hence the Irreps of $\mathbb{G}_{\mathbf{k}}$ and $\mathcal{P}_{\mathbf{k}}$ coincide and we have that all the allowable Irreps of $\mathbb{S}_{\mathbf{k}}$ are of the form

$$^{(\mu, \mathbf{k})} \Omega_{\Lambda}(R_{\mathbf{k}}|\tau_{\mathbf{k}} + \mathbf{t}) = \exp[-i\mathbf{k} \cdot (\tau_{\mathbf{k}} + \mathbf{t})] ^{(\mu)} \Lambda(R_{\mathbf{k}}), \tag{11.42}$$

where $^{(\mu)} \Lambda(R_{\mathbf{k}})$ is the μ th Irrep of the point-group $\mathcal{P}_{\mathbf{k}}$ of dimension l_{μ} .

The factor system maps onto unity if one of the following conditions is fulfilled:

- (a) $\mathbf{k}$ lies inside the first Brillouin zone, and $R_{i\mathbf{k}}\mathbf{k} - \mathbf{k} = 0$;
- (b) $\mathbb{S}$ is a symmorphic space-group, then all $\tau_i = 0$;
- (c) $\mathbb{S}_{\mathbf{k}}$ is a symmorphic group.

- (ii) When $\mathbb{S}_{\mathbf{k}}$ is nonsymmorphic and $\mathbf{k}$ lies on the Brillouin zone boundary, the above conditions do not hold. In this situation, we must follow a slightly more complicated way to find the allowable Irreps of $\mathbb{S}_{\mathbf{k}}$. We need to use the method of kernel and quotient subgroups to construct the multiplier factors, and hence the projective Irreps.

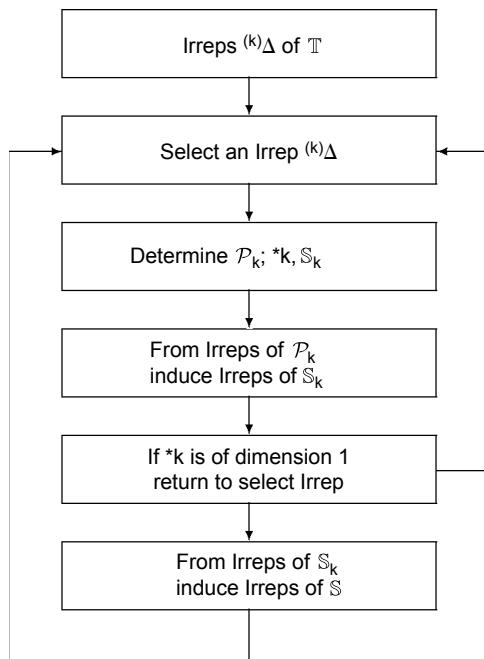


Fig. 11.6. Flow chart for inducing symmorphic space-group Irreps for *all* $\mathbf{k}$ -vectors and for inducing nonsymmorphic space-group Irreps *within* the Brillouin zone.

We will examine the first case, a symmorphic space-group, in the next section. The second case, using the method of the kernel and quotient subgroups will be taken up in Section 11.2.4.

11.2.2 Examples of symmorphic space-groups

The procedure we follow is laid out in the flow chart of Figure 11.6, which is taken from the flow chart of Figure 9.3 and modified to conform to the conventions used in solid state physics.

Comment on the flow chart of Figure 11.6 The little-group of the first kind is designated as G_k . It is isomorphic with $\mathcal{P}_k$, the point-group of the wavevector. These two groups differ only in that for G_k multiplication rules may require a factor system $\neq 1$. If the factor system is unity, as it is for $\mathbf{k}$ -values within the Brillouin zone, or for symmorphic groups, both $\mathcal{P}_k$ and G_k have identical Irreps. So, in Figure 11.6 and in this section, we use only $\mathcal{P}_k$.

The two-dimensional symmorphic space-group $p4mm$

The primitive unit cell of a two-dimensional square net is shown in Figure 11.7 along with its planes of symmetry, which are perpendicular to the plane of the square. The basis is taken to be a single point-like atom at each lattice point.

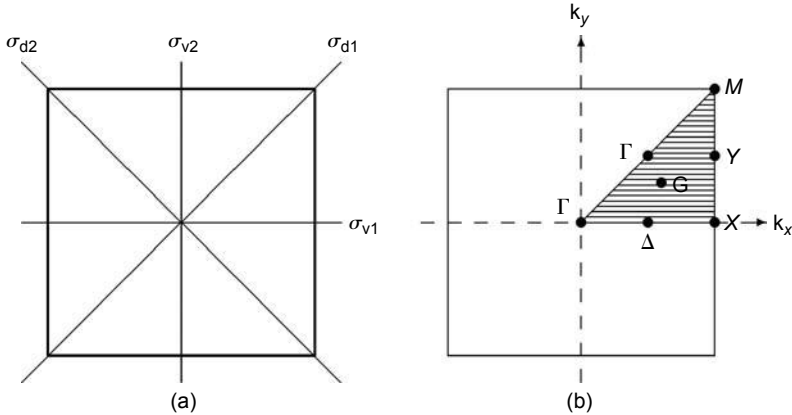


Fig. 11.7. (a) The unit cell of a two-dimensional Bravais net. Planes of symmetry that are perpendicular to the plane of the square unit cell are denoted by σ . (b) The hatched area is the irreducible Brillouin zone for a square net. The point G is a general $\mathbf{k}$ -point in the irreducible zone. The other symbols denote $\mathbf{k}$ -points or lines of special symmetry.

This space-group is characteristic of all (001) surfaces of monatomic metallic systems with cubic crystalline structure. For a monatomic basis the holohedry group is C_{4v} ($4mm$). The space-group has the following generators:

$$(C_4^+|\mathbf{0}), \quad (\sigma_v^1|\mathbf{0}), \quad (E|(a,0)), \quad (E|(0,a)).$$

The first Brillouin zone is a square. Its irreducible zone is $1/8$ of the full zone, as illustrated in Figure 11.7 by the hatched area. The irreducible zone is bounded by high-symmetry directions and lines, which are shown along with representative symmetry points described in standard notation.

We now determine the Irreps for the six symmetry points (or lines): $\bar{\Gamma}$, $\bar{\Delta}$, $\bar{\Sigma}$, $\bar{M}$, $\bar{X}$, and $\bar{Y}$. For each point we derive $S_{\mathbf{k}}$ and $\mathcal{P}_{\mathbf{k}}$; determine the Irreps of $\mathcal{P}_{\mathbf{k}}$; induce from these the allowable Irreps of $S_{\mathbf{k}}$; and, finally, induce the Irreps of S from those of $S_{\mathbf{k}}$. We give a rather complete description for the $\bar{\Gamma}$ -point and the $\bar{\Delta}$ -line. For the others we provide a concise outline.

The convention adopted in solid state physics is to designate the Irreps of $\mathcal{P}_{\mathbf{k}}$ according to the symbol used for the $\mathbf{k}$ -symmetry point or line. For example, the Irreps of $\mathcal{P}_{\mathbf{k}}$ of a $\mathbf{k}$ -vector along the symmetry line $\bar{\Delta}$ of Figure 11.7 are designated $^{(\bar{\Delta})}\Lambda$. This is *not* to be confused with our earlier use of Δ to denote an Irrep $^{(k)}\Delta$ of the translation group $\mathbb{T}_{\mathbf{k}}$.

Guided by the flow chart of Figure 11.6, we select an Irrep of $\mathbb{T}_{\mathbf{k}}$, the normal subgroup of the space-group S . We do this implicitly when we select a value for $\mathbf{k}$, since each $\mathbf{k}$ -point corresponds to an Irrep of the translation group. We begin with the Γ -point.

The $\bar{\Gamma}$ -point: $\mathbf{k} = 0$ The translation group $\mathbb{T}_{\mathbf{k}} = \mathbb{T}_{\bar{\Gamma}}$ has Irreps $\exp(i\mathbf{k} \cdot \mathbf{t}) = 1$, since $\mathbf{k} = 0$ at the $\bar{\Gamma}$ -point. For completeness, we note that *all* translation operations map onto unity in this case, so the kernel group, which is the set of translation operators that map

Table 11.2. The character table for the Irreps of $\mathcal{P}_{\bar{\Gamma}} = \mathcal{C}_{4v}$.

	E	C_2	$2C_4$	$2\sigma_v$	$2\sigma_d$
$^{(1)}\Lambda$	1	1	α	α	1
$^{(2)}\Lambda$	1	1	α	$-\alpha$	-1
$^{(3)}\Lambda$	1	1	$-\alpha$	α	-1
$^{(4)}\Lambda$	1	1	$-\alpha$	$-\alpha$	1
$^{(5)}\Lambda$	2	-2	0	0	0

onto unity, is the full translation group $\mathbb{T}$. The *point-group* of the wavevector is $\mathcal{P}_{\bar{\Gamma}} \equiv \mathcal{C}_{4v}$ ($4mm$), which is the full crystallographic point-group $\mathcal{P}$. The *little-group* of the wavevector $\mathbb{S}_{\bar{\Gamma}}$ is the full space-group, since *all* space-group operators acting on $\mathbf{k} = 0$ must leave $\mathbf{k}$ invariant. Finally, the orbit is of dimension 1, since there can be only one distinct coset for $\mathbf{k} = 0$. Put differently, the last conclusion follows from the one-to-one correspondence between the points of $^*\mathbf{k}$ and the orbit. Here, with $\mathbf{k} = 0$, the star has only one point. Thus, at the $\bar{\Gamma}$ -point we have

$$\begin{aligned}\mathbb{S}_{\bar{\Gamma}} &= \mathbb{S}, \\ \mathcal{P}_{\bar{\Gamma}} &= \mathcal{P}, \\ \mathbb{T}_{\bar{\Gamma}} &= \mathbb{T}.\end{aligned}\tag{11.43}$$

Given the Irreps of $\mathcal{C}_{4v} \equiv \mathcal{P}_{\bar{\Gamma}}$ in Table 11.2, with $\alpha = 1$, we can induce Irreps of $\mathbb{S}_{\bar{\Gamma}}$ from (11.42), which, because $\mathbf{k} = 0$, are Irreps of $\mathbb{S}$. Are they *allowable* Irreps of $\mathbb{S}$? Yes!

Each of the five Irreps of $\mathbb{S}_{\bar{\Gamma}}$ *subduces* an Irrep of $\mathbb{T}$,

$$(\bar{\Gamma}, \mu)\Gamma \downarrow \mathbb{T} = \mathbb{I}_{\mu},$$

with $\mathbb{I}_{\mu}$ a unit matrix with dimension l_{μ} , rendering all five *allowable* Irreps of $\mathbb{S}$ corresponding to $\mathbf{k} = \mathbf{0}$. Thus the $\bar{\Gamma}$ -point contributes four 1-dimensional Irreps and one 2-dimensional Irrep of $\mathbb{S}$.

The $\bar{\Delta}$ -line: $\mathbf{k} = (k, 0)$, $0 < k < \pi/a$ With the help of Figure 11.8, we find that, along the $\bar{\Delta}$ line, only the point-group operations E and σ_v^1 leave k_x invariant. Thus the point-group of the wavevector is $\mathcal{P}_{\bar{\Delta}} = \{E, \sigma_v^1\}$, with Irreps

	E	σ_v^1
$(\Delta, +)\Lambda$	1	1
$(\Delta, -)\Lambda$	1	-1

The Irreps Ω of $\mathbb{S}_{\bar{\Delta}}$ are induced from the Irreps Λ of $\mathcal{P}_{\bar{\Delta}}$ using (11.42). We obtain the one-dimensional Irreps

$$^{(\Delta, \pm)}\Omega_{\Lambda}(R_{\bar{\Delta}}|\mathbf{t}) = \exp(-ikm_x a)^{(\Delta, \pm)}\Lambda(R_{\bar{\Delta}}).\tag{11.44}$$

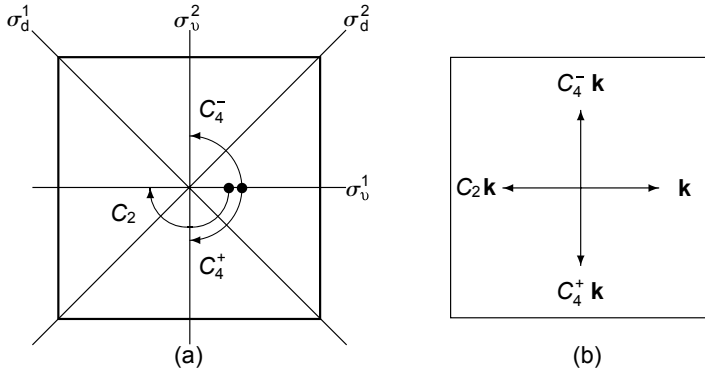


Fig. 11.8. (a) The unit cell of a two-dimensional square Bravais net with the point-group operations shown. (b) The star of $\mathbf{k}$ for the $\bar{\Delta}$ -line. (Refer to Figure 11.7.) The points of the star are labeled according to the coset representative that generates the point when operating on $\mathbf{k}$.

The various point-group operations shown in Figure 11.8 make up the point-group C_{4v} . We have already considered this group in some detail in Section 9.3.3. We can now make use of what was done there, particularly the group multiplication table for C_{4v} , Table 9.12. Note, though, as we consider the $\bar{\Delta}$ -line, that the subgroup and the coset representatives turn out to be just the reverse of what they were in the example from Chapter 9.

To induce the Irreps Γ for the space-group $\mathbb{S}$, we need to know the ground representation. We begin with $^*\mathbf{k}$. The star of $\mathbf{k}$ is found by operating on $\mathbf{k}$ with the elements of the point-group of the crystal, from which we find three other mutually inequivalent $\mathbf{k}$ values, making for a total of four inequivalent $\mathbf{k}$ -vectors. They are symmetrically located on the k_x and k_y axes with respect to the origin, as illustrated in Figure 11.8. The number of points, or prongs, on the star is the dimension of the orbit, so the orbit is of dimension 4, and thus the ground representation is four-dimensional. However, this method of determining $^*\mathbf{k}$ leads to redundancies; here, each point of the star is determined twice. For example, the prong of the star given by $C_4^- \mathbf{k}$ is also given by $\sigma_d^2 \mathbf{k}$.

A precise way to determine $^*\mathbf{k}$, although not necessarily a faster way, is to generate the points of the star by operating on $\mathbf{k}$ with the coset representatives $\{R_{cj}\} = \{E, C_2, C_4^+, C_4^-\}$, which we have chosen so as to constitute a group, C_4 . This emphasizes the direct one-to-one correspondence between the points of $^*\mathbf{k}$ and the conjugate Irreps generated with coset representatives.

The points of $^*\mathbf{k}$ can be labeled by $R_{cj}\mathbf{k}$, where R_{cj} is the coset representative that produces the point of the star when operating on $\mathbf{k}$. For example, in Figure 11.8, the point-group symmetry operator C_4^- shown in (a) produces the point of $^*\mathbf{k}$ denoted by $C_4^- \mathbf{k}$ in (b).

We first construct *modified* ground representation matrices, $\mathbf{M}^*(R)$, as an intermediate step in the construction of the ground representation $^{(\mathbf{k})}\mathcal{Z}_{ij}((R|\mathbf{0}))$ that we will use in (11.33). Since the ij th element of the modified ground representation is given by $R_{ci}^{-1}RR_{cj}$, we obtain

$$\begin{aligned}
\mathbf{M}^*(C_4^+) &= \begin{pmatrix} EC_4^+E & EC_4^+C_2 & EC_4^+C_4^+ & EC_4^+C_4^- \\ C_2C_4^+E & C_2C_4^+C_2 & C_2C_4^+C_4^+ & C_2C_4^+C_4^- \\ C_4^-C_4^+E & C_4^-C_4^+C_2 & C_4^-C_4^+C_4^+ & C_4^-C_4^+C_4^- \\ C_4^+C_4^+E & C_4^+C_4^+C_2 & C_4^+C_4^+C_4^+ & C_4^+C_4^+C_4^- \end{pmatrix} \\
&= \begin{pmatrix} C_4^+ \notin \mathcal{P}_{\bar{\Delta}} & C_4^- \notin \mathcal{P}_{\bar{\Delta}} & C_2 \notin \mathcal{P}_{\bar{\Delta}} & E \\ C_4^- \notin \mathcal{P}_{\bar{\Delta}} & C_4^+ \notin \mathcal{P}_{\bar{\Delta}} & E & C_2 \notin \mathcal{P}_{\bar{\Delta}} \\ E & C_2 \notin \mathcal{P}_{\bar{\Delta}} & C_4^+ \notin \mathcal{P}_{\bar{\Delta}} & C_4^- \notin \mathcal{P}_{\bar{\Delta}} \\ C_2 \notin \mathcal{P}_{\bar{\Delta}} & E & C_4^- \notin \mathcal{P}_{\bar{\Delta}} & C_4^+ \notin \mathcal{P}_{\bar{\Delta}} \end{pmatrix} \\
&= \begin{pmatrix} 0 & 0 & 0 & E \\ 0 & 0 & E & 0 \\ E & 0 & 0 & 0 \\ 0 & E & 0 & 0 \end{pmatrix}. \\
\mathbf{M}^*(\sigma_v^1) &= \begin{pmatrix} E\sigma_v^1E & E\sigma_v^1C_2 & E\sigma_v^1C_4^+ & E\sigma_v^1C_4^- \\ C_2\sigma_v^1E & C_2\sigma_v^1C_2 & C_2\sigma_v^1C_4^+ & C_2\sigma_v^1C_4^- \\ C_4^- \sigma_v^1E & C_4^- \sigma_v^1C_2 & C_4^- \sigma_v^1C_4^+ & C_4^- \sigma_v^1C_4^- \\ C_4^+ \sigma_v^1E & C_4^+ \sigma_v^1C_2 & C_4^+ \sigma_v^1C_4^+ & C_4^+ \sigma_v^1C_4^- \end{pmatrix} \\
&= \begin{pmatrix} \sigma_v^1 & \sigma_v^2 \notin \mathcal{P}_{\bar{\Delta}} & \sigma_d^2 \notin \mathcal{P}_{\bar{\Delta}} & \sigma_d^1 \notin \mathcal{P}_{\bar{\Delta}} \\ \sigma_v^2 \notin \mathcal{P}_{\bar{\Delta}} & \sigma_v^1 & \sigma_d^1 \notin \mathcal{P}_{\bar{\Delta}} & \sigma_d^2 \notin \mathcal{P}_{\bar{\Delta}} \\ \sigma_d^2 \notin \mathcal{P}_{\bar{\Delta}} & \sigma_d^1 \notin \mathcal{P}_{\bar{\Delta}} & \sigma_v^2 \notin \mathcal{P}_{\bar{\Delta}} & \sigma_v^1 \\ \sigma_d^1 \notin \mathcal{P}_{\bar{\Delta}} & \sigma_d^2 \notin \mathcal{P}_{\bar{\Delta}} & \sigma_v^1 & \sigma_v^2 \notin \mathcal{P}_{\bar{\Delta}} \end{pmatrix} \\
&= \begin{pmatrix} \sigma_v^1 & 0 & 0 & 0 \\ 0 & \sigma_v^1 & 0 & 0 \\ 0 & 0 & 0 & \sigma_v^1 \\ 0 & 0 & \sigma_v^1 & 0 \end{pmatrix}.
\end{aligned}$$

The matrix elements of $\mathbf{M}^*(R)$ are either 0 or E if $R \in \mathcal{C}_4 = \{E, C_2, C_4^+, C_4^-\}$ and are either 0 or σ_v^1 if $R \in \sigma_v^1\mathcal{C}_4 = \{\sigma_v^1, \sigma_v^2, \sigma_d^2, \sigma_d^1\}$.

The matrix elements of the ground representation $^{(\mathbf{k})}\mathcal{Z}_{ij}((R|\mathbf{0}))$ are obtained by substituting a 1 for each matrix element in $\mathbf{M}^*(R)$ for which $R \in \mathcal{P}_{\bar{\Delta}}$, and 0 otherwise. Thus, for example,

$$^{(\star\Delta)}\mathcal{Z}(\sigma_v^1|\mathbf{0}) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}. \quad (11.45)$$

There are a total of eight matrices similar to $^{(\star\Delta)}\mathcal{Z}(\sigma_v^1|\mathbf{0})$, one for each element of $\mathcal{C}_{4v}$.

Each point on the $\bar{\Delta}$ -line engenders two 4-dimensional Irreps of $\mathbb{S}$, a typical example of which, using (11.43), is

$$({}^*\Delta, +)\Gamma((\sigma_v^1|\mathbf{t})) = \begin{pmatrix} e^{-ikm_x a} & 0 & 0 & 0 \\ 0 & e^{-ikm_x a} & 0 & 0 \\ 0 & 0 & 0 & e^{-ikm_x a} \\ 0 & 0 & e^{-ikm_x a} & 0 \end{pmatrix}. \quad (11.46)$$

What we have just done is a standard method for inducing Irreps. It is equivalent to finding $({}^*\Delta, \pm)\Gamma(R|\mathbf{t})$ by replacing each matrix element $M_{ij}^*(R)$ of the modified ground representation with $M_{ij}^*(\Delta, \pm)\Omega(R|\mathbf{t})$. We can describe this as

$$({}^*\Delta, \pm)\Gamma_{ij}(R|\mathbf{t}) = M_{ij}^*\left((\Delta, \pm)\Omega(R|\mathbf{t})\right). \quad (11.47)$$

Applying this to the case of $\mathbf{M}^*(\sigma_v^1)$ we obtain

$$\begin{aligned} ({}^*\Delta, \pm)\Gamma((\sigma_v^1|\mathbf{t})) &= \begin{pmatrix} (\Delta, \pm)\Omega(\sigma_v^1|\mathbf{t}) & 0 & 0 & 0 \\ 0 & (\Delta, \pm)\Omega(\sigma_v^1|\mathbf{t}) & 0 & 0 \\ 0 & 0 & 0 & (\Delta, \pm)\Omega(\sigma_v^1|\mathbf{t}) \\ 0 & 0 & (\Delta, \pm)\Omega(\sigma_v^1|\mathbf{t}) & 0 \end{pmatrix} \\ &= \begin{pmatrix} e^{-ikm_x a (\pm)}\Lambda(\sigma_v^1) & 0 & 0 & 0 \\ 0 & e^{-ikm_x a (\pm)}\Lambda(\sigma_v^1) & 0 & 0 \\ 0 & 0 & 0 & e^{-ikm_x a (\pm)}\Lambda(\sigma_v^1) \\ 0 & 0 & e^{-ikm_x a (\pm)}\Lambda(\sigma_v^1) & 0 \end{pmatrix}, \end{aligned}$$

which, on substituting for $(+)\Lambda(\sigma_v^1)$ gives (11.46). This latter method may be conceptually simpler to implement.

The $\bar{\Sigma}$ -line: $\mathbf{k} = (k, k)$, $0 < k < \pi/a$ The $\bar{\Sigma}$ -line is similar in many respects to the $\bar{\Delta}$ -line. The steps for obtaining Irreps are outlined below.

(i) The point-group of the wavevector is $\mathcal{P}_{\bar{\Sigma}} = \{E, \sigma_d^1\}$, with Irreps

	E	σ_d^1
$(+)\Sigma$	1	1
$(-)\Sigma$	1	-1

(ii) Again the ground representation is four-dimensional. (See Figure 11.9 for the star of $\bar{\Sigma}$.) The four coset representatives are: E , C_2 , C_4^+ , C_4^- .

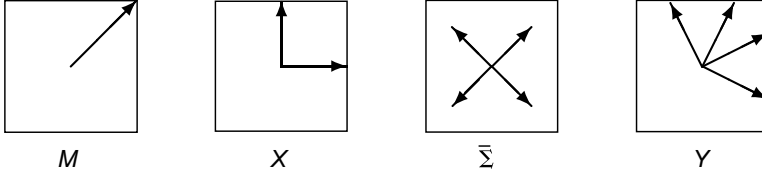


Fig. 11.9. The star of $\mathbf{k}$ for some symmetry points and lines in the Brillouin zone of a square net. Each star is labeled according to the convention of Figure 11.7.

Table 11.3. Irreps of C_{2v} , $\alpha = 1$.

	E	C_2	σ_v^1	σ_v^2
$(1)X$	1	α	α	1
$(2)X$	1	α	$-\alpha$	-1
$(3)X$	1	$-\alpha$	α	-1
$(4)X$	1	$-\alpha$	$-\alpha$	1

(iii) The induced Irreps of $S_{\bar{S}}$ are

$$({}^{\Sigma, \pm})\Omega_A (R_{\bar{S}}|\mathbf{t}) = \exp(-ik(m_x + m_y)a) ({}^{\pm})\Lambda (R_{\bar{S}}).$$

(iv) Each point on the $\bar{S}$ -line engenders two 4-dimensional Irreps of S .

The $\bar{X}$ -point: $\mathbf{k} = (\pi/a, 0)$

(i) The point-group of the wavevector is $\mathcal{P}_{\bar{X}} = C_{2v} = \{E, C_2, \sigma_v^1, \sigma_v^2\}$. Its Irreps are given in Table 11.3, with $\alpha = 1$.

(ii) The ground representation is two-dimensional with coset representatives E, σ_d , where σ_d may be either σ_d^1 or σ_d^2 . The matrix representatives are

$$({}^{*\mathbf{X}})\mathcal{Z}(R) = \begin{cases} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}, & R \in \mathcal{P}_{\bar{X}}, \\ \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, & R \notin \mathcal{P}_{\bar{X}}. \end{cases} \quad (11.48)$$

See Figure 11.9 for the star of $\bar{X}$.

(iii) The induced Irreps of $S_{\bar{X}}$ are

$$({}^{\mathbf{X}, \mu})\Omega_A (R_{\bar{X}}|\mathbf{t}) = \exp(-im_x\pi) ({}^{\mu})\Lambda (R_{\bar{X}}). \quad (11.49)$$

(iv) The $\bar{X}$ -point engenders four 2-dimensional Irreps of S .

E	C_2	C_4^+	C_4^-	σ_d^1	σ_d^2	σ_x	σ_y
$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$
$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$
$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$
$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

The $\bar{M}$ -point: $\mathbf{k} = (\pi/a, \pi/a)$

(i) The point-group of the wavevector is $\mathcal{P}_{\bar{M}} = C_{4v}$, and $\mathbb{S}_{\bar{M}} = \mathbb{S}$. The character table for the Irreps of $\mathcal{P}_{\bar{M}}$ is

	E	C_2	$2C_4$	$2\sigma_v$	$2\sigma_d$
$^{(1)}M$	1	1	1	1	1
$^{(2)}M$	1	1	1	-1	-1
$^{(3)}M$	1	1	-1	1	-1
$^{(4)}M$	1	1	-1	-1	1
$^{(5)}M$	2	-2	0	0	0

(ii) The ground representation is one-dimensional. See Figure 11.9 for the star of $\bar{M}$.

(iii) The induced Irreps of $\mathbb{S}_{\bar{M}}$ are

$$^{(\mathbf{M}, \mu)}\Omega_{\Lambda}(R_M|\mathbf{t}) = \exp(-i(m_x + m_y)\pi) {}^{(\mu)}\Lambda(R_{\bar{M}}). \quad (11.50)$$

(iv) The $\bar{M}$ -point engenders four 1-dimensional Irreps and one 2-dimensional Irrep of $\mathbb{S}$.

The $\bar{Y}$ -line: $\mathbf{k} = (\pi/a, k)$, $0 < k < \pi/a$

(i) The point-group of the wavevector, $\mathcal{P}_{\bar{Y}} = \{E, \sigma_v\}$, has Irreps

	E	σ_v
$^{(+)}Y$	1	1
$^{(-)}Y$	1	-1

(ii) The ground representation is four-dimensional: E , C_2 , C_4 , σ_d . See Figure 11.9 for the star of $\bar{Y}$.

Table 11.4. *The Irreps for space-groups of the square mesh for certain symmetry points and lines.*

Symmetry point/line	$\mathbf{k}$	$\mathcal{P}_{\mathbf{k}}$	Number of Irreps	Dimension of Irreps
$\bar{\Gamma}$	(0,0)	$\mathcal{C}_{4v}$	5	1,1,1,1,2
$\bar{M}$	$(\pi/a, \pi/a)$	$\mathcal{C}_{4v}$	5	1,1,1,1,2
$\bar{X}$	$(\pi/a, 0)$	$\mathcal{C}_{2v}$	4	2,2,2,2
$\bar{\Delta}$	$(k, 0)$	$\mathcal{C}_2$	2	4,4
$\bar{\Sigma}$	(k, k)	$\mathcal{C}_2$	2	4,4
$\bar{Y}$	$(\pi/a, k)$	$\mathcal{C}_2$	2	4,4

(iii) The induced Irreps of $\mathbb{S}_{\bar{Y}}$ are

$$({}^{\mathbf{Y}}, \pm) \Omega_{\mathbf{A}} (R_{\bar{Y}} | \mathbf{t}) = \exp(-i(m_x \pi + k m_y a)) ({}^{\pm}) Y(R_{\bar{Y}}).$$

(iv) Each point on the T -line engenders two 4-dimensional Irreps of $\mathbb{S}$.

A summary The results for the Irreps of the space-groups for a two-dimensional square net are summarized in Table 11.4.

A key point concerning the symmetry of Bravais lattices and Brillouin zones

What we have just done in this section can be somewhat deceptive. One might (incorrectly) infer that the symmetry we speak of in discussing the induction of Irreps is the symmetry of the Brillouin zone. It is not! The Brillouin zone has no intrinsic symmetry of its own. It is derived entirely from the symmetry of the Bravais lattice. This becomes apparent when one recognizes, for example, that a square Bravais net with a basis has the same square Brillouin zone as does a square Bravais net *without* a basis. That is because the Brillouin zone deals only with translational symmetry. None of the possible reduction in symmetry of the Bravais net provided by a basis carries over to the Brillouin zone. It is for this reason that we emphasize that one should always view the reciprocal lattice and Brillouin zones as attached to the actual Bravais lattice of real space.

We illustrate these points in the next section, where we consider a space-group with the square net and basis shown in Figure 11.10.

A two-dimensional crystal with a symmorphic space-group $p4$

Figure 11.10 shows the unit cell of a two-dimensional net with a basis. Note the reduced symmetry of the unit cell compared with that of Figure 11.7, because of the atomic basis assigned to each lattice point. As can be seen from Figure 11.10(a) the location of the basis is at (u, v) , $(-v, u)$, $(-u, -v)$, $(v, -u)$. Notice that the reflection planes are not symmetry elements of this crystal, since σ_x and σ_d do not restore the crystal to its original configuration. Hence, the symmetry group has the coset representatives: $(E|\mathbf{0})$, $(C_2|\mathbf{0})$, $(C_4|\mathbf{0})$, $(C_4^{-1}|\mathbf{0})$. The reduced symmetry results in a *representation* zone that is twice the volume of the irreducible zone of Figure 11.10.

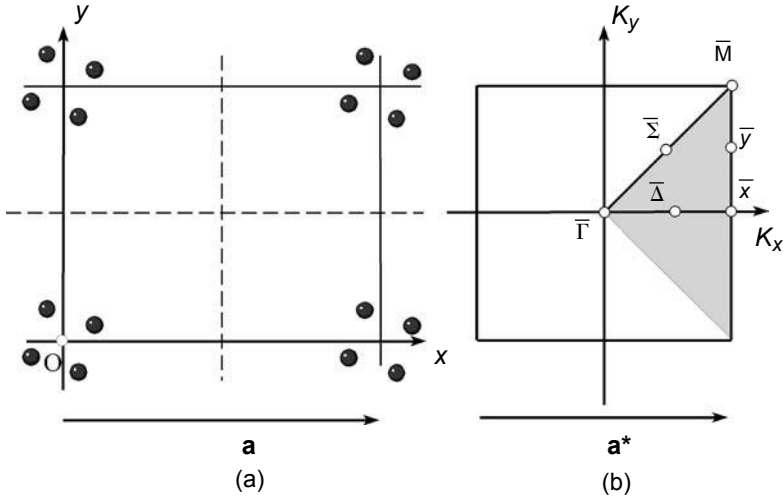


Fig. 11.10. (a) The unit cell of a two-dimensional square crystal with a basis of four atoms per net point. The space-group is symmorphic $P4$. (b) The Brillouin zone with reciprocal lattice vector $\mathbf{a}^*$.

The $\bar{\Gamma}$ -point: $\mathbf{k} = 0$ The point-group symmetry $P_{\bar{\Gamma}}$ in this case is C_4 (4).

Each of the four Irreps of $\mathbb{S}_{\bar{\Gamma}}$ *subduces* an Irrep of $\mathbb{T}$,

$$^{(\mu)}\Gamma \downarrow \mathbb{T} = \mathbb{I}_{\mu},$$

with $\mathbb{I}_{\mu}$ a unit matrix with dimension l_{μ} , rendering all four *allowable* Irreps of $\mathbb{S}$ corresponding to $\mathbf{k} = \mathbf{0}$. Thus the $\bar{\Gamma}$ -point contributes four one-dimensional Irreps of $\mathbb{S}$.

The $\bar{\Delta}$ -line: $\mathbf{k} = (k, 0)$, $0 < k < \pi/a$, and the **$\bar{\Sigma}$ -line:** $\mathbf{k} = (k, k)$, $0 < k < \pi/a$. The group of $\mathbf{k}$ is $\mathbb{S}_{\mathbf{k}} = E$ (1) in both cases and also at any point in the reduced zone. It clearly subduces an Irrep of $\mathbb{T}$ of the allowable type. Thus, the ground representation is four-dimensional, and induces a four-dimensional space-group Irrep, given by

$$\begin{aligned} ^{(\bar{\Delta})}\Omega_A(E|\mathbf{t}) &= \exp(-i(km_x a)), \\ ^{(\bar{\Sigma})}\Omega_A(E|\mathbf{t}) &= \exp(-i(k(m_x + m_y)a)), \\ ^{(\mathbf{k})}\Omega_A(E|\mathbf{t}) &= \exp(-i(\mathbf{k} \cdot \mathbf{t})). \end{aligned}$$

Table 11.5. *The character table for the Irreps of $\mathbb{S}_{\bar{\Gamma}} = C_4$.*

	E	C_2	C_4	C_4^{-1}
$^{(1)}\Gamma$	1	1	1	1
$^{(2)}\Gamma$	1	1	-1	-1
$^{(3)}\Gamma$	1	-1	i	$-i$
$^{(4)}\Gamma$	1	-1	$-i$	i

The $\bar{X}$ -point: $\mathbf{k} = (\pi/a, 0)$, **and the $\bar{M}$ -point:** $\mathbf{k} = (\pi/a, \pi/a)$ The little-group of $\bar{X}$ is $\mathbb{S}_{\bar{X}} = \{(E|\mathbf{t}), (C_2|\mathbf{t})\}$, and its two Irreps $^{(\pm)}\Omega$ are allowed. The ground representation is two-dimensional, and two 2-dimensional Irreps of P4 are induced.

The little-group of $\bar{M}$ is $\mathbb{S}_{\bar{M}} = \{(E|\mathbf{t}), (C_2|\mathbf{t}), (C_4^+|\mathbf{t}), (C_4^-|\mathbf{t})\} \equiv \mathbb{S}$, and has the four 1-dimensional Irreps of Table 11.5, which are allowed.

11.2.3 Program for constructing subgroups of the wavevectors

Input data

Example: *Fd3m* (diamond structure)

```

<< C:/book/programs/spgr/0h.txt
<< C:/book/programs/spgr/diamond.txt

NPGR=30  ⇔   (point-group number)
VV=SG227 ⇔   (space-group number)
Q  ⇔   (basic wavevectors)
Q={ {0,0,0}, {0,0,1/5}, {3/16,3/16,0}, {1/8,1/8,1/8} }
NQ={1,5,4,4} ⇔   (number of sampled wavevectors for basic vectors)
slnn=1;  ⇔   ()
NG=5  ⇔   (number of generators)
g=48  ⇔   (order of point-group)
NPER=8  ⇔   (number of permutation objects)
(* Point-group generators  $C_2$ ,  $U_x$ ,  $U_1^d$ ,  $C_3$ ,  $I$  *)

Rot  ⇔   (rotation matrix representation of generators)
Rot={ { {-1,0,0}, {0,-1,0}, {0,0,1} }, { {1,0,0}, {0,-1,0}, {0,0,-1} },
      { {0,1,0}, {1,0,0}, {0,0,-1} }, { {0,0,1}, {1,0,0}, {0,1,0} },
      { {-1,0,0}, {0,-1,0}, {0,0,-1} } }

PER  ⇔   (permutation representation of generators)
PER={ {3,4,1,2,7,8,5,6}, {6,5,8,7,2,1,4,3}, {7,6,5,8,3,2,1,4},
      {6,2,1,5,7,3,4,8}, {7,8,5,6,3,4,1,2} }

Non-primitive translations for space-group 227 generators:
SG227={ {0,0,0}, {0,0,0}, {1/4,1/4,1/4}, {0,0,0}, {1/4,1/4,1/4} }

```

We should note here some transformations from Cartesian to reciprocal lattice coordinates:

$$\mathbf{k}_G = \mathbf{RL}^T \cdot \mathbf{k}_C; \quad \mathbf{R}_G = \mathbf{RL}^T : \mathbf{R}_C : \mathbf{G}, \quad (11.51)$$

where subscripts C and G indicate Cartesian and reciprocal lattice coordinates, respectively. $\mathbf{RL}$ and $\mathbf{G}$ are matrices containing primitive and reciprocal bases, respectively.

Program

1. Construct coset representatives of the space-group

```
NONPRIM = SG227;
```

```
RECIP[RL, ND]; generate reciprocal lattice basis
```

```
Seitz[PER, NG, NONPRIM, NPER, g]; space-group coset Reps
```

2. Input wavevectors

```
iq = 0;
```

```
LQ = {};
```

```
Print["Number of wavevector directions = ", Length[Q]];
```

```
While[iq < Length[Q], Label[work];
```

```
    iq++; QQ = Q[[iq]]; Delta = {}; LQ = {}; gq = 0;
```

```
    Switch[QQ == {0, 0, 0}, True,
```

```
        Γ-point
```

```
            gq = g; LQ = {Range[g]};
```

```
            Do[AppendTo[Delta, 1], {i, 1, g}];
```

```
            Print["Group of the wavevector ", QQ,
```

```
                  " is the full point-group."];
```

```
            If[iq < Length[Q], Goto[work]]
```

```
        ];
```

```
Other q-directions
```

```
    Qrecip = Transpose[RL].QQ;
```

```
Qrecip is q in terms of reciprocal lattice basis
```

```
qn = 0;
```

```
While[qn < NQ[[iq]], qn++; SX = {};
```

```
    Qtest = qn*Qrecip; Qsame = qn*QQ;
```

```
    BZTST[Qtest, B, ND];
```

Test if the wavevector lies on the BZ boundary.

$WV = -1$ inside BZ, $WV=1$ outside BZ, $WV=0$ on BZ boundary.

```
Switch[And[WV ≤ 0, iq ≤ Length[Q]],
      True, SS = {0, 0, 0};
      ];
```

3. When Q is inside BZ or on its boundary, generate its point-group

```
Switch[Or[qn == 1, WV == 0], True,
      GKSYM[Qtest, GK, Gktab];
      Switch[WV < 0, True,
            Print["Wavevector ", Qsame, " inside BZ."];
            Switch[qn == 1, True,
                  Print["The Group of the Wavevector ",
                        Qsame, " of order ", gq, " is ", LQ];
                  Print["Its Multiplication Table is"];
                  Print[TableForm[mtab]];
                  ],
            False,
            Print["Wavevector ", Qsame, " on BZ boundary."];
            Switch[Or[NSYM == 0, SS == {0, 0, 0}],
                  True,
                  Print["The Group of the Wavevector ", Qsame,
                        " of order ", gq, " is symmorphic with
                        elements ", LQ];
                  Print["Its Multiplication Table is"];
                  Print[TableForm[mtab]];
                  ]
            If[iq < Length[Q], Goto[work]],
```

For nonsymmorphic S_Q we use the Herring group method.

```

GKSYM[Qtest_, GK_, Gktab_] :=
Module[{LQ, mtab},
  Do[
    XP= Rotg[i]·Qtest - Qtest;
    XM= Sum[Mod[XP[[k]],1],{k,3}];
    Switch[And[XM == 0, FreeQ[LQ,i]],
      True,
      gq++; SS += Tau[[i]];
      AppendTo[LQ,i]
    ],{i, 1, g}
  ]; GK = LQ; mtab = {};
  Do[
    AppendTo[mtab,0],{i, 1, gq*gq};
    ]; mtab = Partition[mtab,gq];
  Do[
    ix = LQ[[i]]; jx = LQ[[j]];
    kx = m[[1,ix,jx]];
    mtab[[i,j]]=Position[LQ, kx],
    {i, 1, gq},{j, 1, gq}
  ]; Gktab = mtab
]

```

11.2.4 Nonsymmorphic space-groups: Herring's method of kernel and quotient subgroups

When $\mathbf{k}$ lies on the Brillouin zone boundary and the crystal is nonsymmorphic, we must deal with the factor system of (11.40) and (11.41). It is then convenient to use Herring's method, which involves *kernel* and *quotient* subgroups [12, 13, 54].

Herring's method is depicted schematically in the flow chart of Figure 11.11. It is described in this section and an example is provided in the next section.

The kernel subgroup $\mathcal{K}$ of the translation group $\mathbb{T}$ is the set of all translations $(E|\mathbf{t}_{\mathbf{k}})$ that are mapped onto 1 by $^{(\mathbf{k})}\Delta$, and which satisfy the relation

$$\mathbf{k} \cdot \mathbf{t}_{\mathbf{k}} = 2n\pi, \quad (11.52)$$

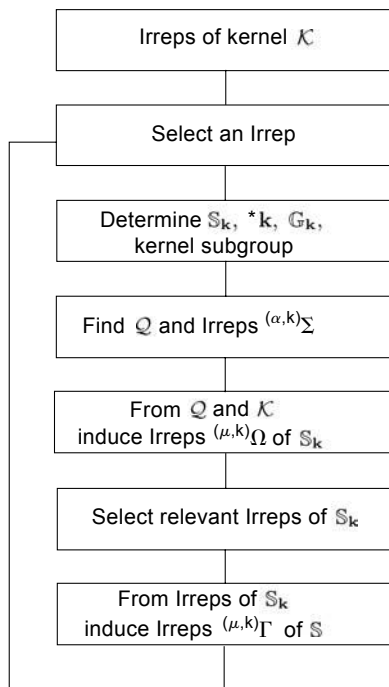


Fig. 11.11. Flow chart for inducing nonsymmorphic space-group Irreps on the Brillouin zone boundary.

where n is an integer. Thus the Irreps of $\mathcal{K}$ are given by

$$^{(\mathbf{k})}\Delta = \exp(-i\mathbf{k} \cdot \mathbf{t}_{\mathbf{k}}) = 1. \quad (11.53)$$

We designate this subgroup $\mathbb{T}_{\mathbf{k}}$.

Clearly, all $\mathbf{k}$ on the Brillouin zone boundary satisfy (11.52), but so do many points within the zone that bear a rational number to $\mathbf{G}$ vectors.

Example 11.3

Consider the one-dimensional case. For *some* k *within* the zone, where

$$\frac{-2\pi m}{Na} < k \leq \frac{2\pi m}{Na},$$

there may exist some translations $\mathbf{t}_{\mathbf{k}} = pa$ that also satisfy (11.52) for *some* integers p . These translations also belong to the set $(E|\mathbf{t}_{\mathbf{k}})$.

With the use of periodic boundary conditions, we require that

$$\mathbf{t}_{\mathbf{k}} < Na.$$

Thus

$$\mathbf{t}_{\mathbf{k}} = pa, \quad p < N.$$

With the help of (11.52) we find that

$$p = \frac{n}{m}N,$$

which requires $n < m$.

Let us take $N = 32$, for convenience. If we consider values of k corresponding to odd integers m , we find that no translations exist that satisfy (11.52). On the other hand, some even integers m do lead to translations that satisfy (11.52). Those that do are $m = 2, 4, 8, 16$, corresponding to $p = 16, 8, 4, 2$. These p values in turn lead to translations $t_k = \pm 2a, \pm 4a, \pm 8a, \pm 16a$.

The idea behind Herring's method is that any element $(E|\mathbf{t}_k) \in \mathbb{T}$ satisfying $\mathbf{k} \cdot \mathbf{t}_k = 2\pi n$, when combined with any element $(R|\tau + \mathbf{t}) \in \mathbb{S}_k$, namely, $(E|\mathbf{t}_k)(R|\tau + \mathbf{t})$ will be represented by the same matrix as the one that represents $(R|\tau + \mathbf{t})$. That is, the subgroup $\mathbb{T}_k$ acts as if it were the identity.

Although some interior points of the Brillouin zone satisfy (11.52) and (11.53), we shall restrict our use of Herring's method to $\mathbf{k}$ values on the zone boundary, where the factor system increases the complexity of our task of inducing Irreps. We already know how to deal with interior points.

Herring's little-group and its Irreps

The quotient group,

$$\mathcal{Q}_k = \frac{\mathbb{S}_k}{\mathbb{T}_k}, \quad (11.54)$$

which is also known as Herring's little-group, comprises the coset representatives in the coset decomposition of $\mathbb{S}_k$ with respect to $\mathbb{T}_k$:

$$\mathbb{S}_k = \{ \mathbb{T}_k, (E|\mathbf{s})\mathbb{T}_k, (R_k|\tau_k)\mathbb{T}_k, (R_k|\tau_k + \mathbf{s})\mathbb{T}_k, \dots \} \quad (11.55)$$

where $\mathbf{s}$ is a translation that does not satisfy (11.52) and thus $\mathbf{s} \notin \mathbb{T}_k$. That is

$$\exp(-i\mathbf{k} \cdot \mathbf{s}) \neq 1. \quad (11.56)$$

The quotient group $\mathcal{Q}_k$ is finite and of not too high order, but it is in general not isomorphic to any point subgroup of $\mathbb{P}$. Its multiplication table, however, can be easily constructed as follows: label each element $(R_k|\tau_k + \mathbf{s})$ of the abstract group with two indices i and s , where i is the index of the corresponding point-group $\mathcal{P}_k$ and

$$s = \exp[-i\mathbf{k} \cdot (\tau + \mathbf{s})] \quad (11.57)$$

is determined by the translational part of the coset representative. Then, for any product of two elements of $\mathcal{Q}_k$, the first index of the product is determined from the multiplication table of the point-group $\mathcal{P}_k$ and the second index is calculated from the Seitz multiplication rule and the above definition. Once the multiplication table has been constructed we use the computational methods outlined in earlier chapters to determine the corresponding Irreps.

Notice that for any pair of coset representatives,

$$(R_{i\mathbf{k}}|\tau_i + \mathbf{s}) \text{ and } (R_{j\mathbf{k}}|\tau_j + \mathbf{s}'),$$

the corresponding representations obey

$$^{(\mu, \mathbf{k})}\Omega\left((R_{i\mathbf{k}}|\tau_i + \mathbf{s})\right) ^{(\mu, \mathbf{k})}\Omega\left((R_{j\mathbf{k}}|\tau_j + \mathbf{s}')\right) = ^{(\mu, \mathbf{k})}\Omega\left((R_{l\mathbf{k}}|\tau_l)\right), \quad (11.58)$$

which follows from

$$(R_{i\mathbf{k}}|\tau_i + \mathbf{s}) (R_{j\mathbf{k}}|\tau_j + \mathbf{s}') = (R_{l\mathbf{k}}|\tau_l) (E|\mathbf{t}_{\mathbf{k}}); \quad (E|\mathbf{t}_{\mathbf{k}}) \in \mathbb{T}_{\mathbf{k}}. \quad (11.59)$$

The *allowable* Irreps of $\mathcal{Q}_{\mathbf{k}}$, denoted by $^{(\mu)}\Sigma_A$, are those satisfying the relation

$$^{(\mu)}\Sigma_A \left((E|\mathbf{s}) \otimes \mathbb{T}_{\mathbf{k}} \right) = \exp(-i\mathbf{k} \cdot \mathbf{s}) \mathbb{I}. \quad (11.60)$$

The construction of allowable Irreps

All allowable Irreps of $\mathbb{S}_{\mathbf{k}}$ can be formed from allowable Irreps of $\mathbb{S}_{\mathbf{k}}/\mathbb{T}_{\mathbf{k}}$ as follows:

(i) We write each $(R_{\mathbf{k}}|\tau_{\mathbf{k}} + \mathbf{t}) \in \mathbb{S}_{\mathbf{k}}$ as

$$(R_{\mathbf{k}}|\tau_{\mathbf{k}} + \mathbf{t}) = (E|\mathbf{t}_{\mathbf{k}}) (R_{\mathbf{k}}|\tau_{\mathbf{k}} + \mathbf{s}), \quad (11.61)$$

where $(R_{\mathbf{k}}|\tau_{\mathbf{k}} + \mathbf{s})$ is a coset representative in (11.55) and $(E|\mathbf{t}_{\mathbf{k}}) \in \mathbb{T}_{\mathbf{k}}$.

(ii) We construct an allowable Irrep of $\mathbb{S}_{\mathbf{k}}$ according to

$$\begin{aligned} ^{(\mu \mathbf{k})}\Gamma_A((R_{\mathbf{k}}|\tau + \mathbf{t})) &= ^{(\mu \mathbf{k})}\Sigma_A((R_{\mathbf{k}}|\tau + \mathbf{s} + \mathbf{t}_{\mathbf{k}})) \\ &= \exp(-i\mathbf{k} \cdot \mathbf{s}) ^{(\mu \mathbf{k})}\Sigma_A((R_{\mathbf{k}}|\tau + \mathbf{t}_{\mathbf{k}})) \\ &= \exp(-i\mathbf{k} \cdot \mathbf{t}) ^{(\mu \mathbf{k})}\Sigma_A((R_{\mathbf{k}}|\tau)). \end{aligned} \quad (11.62)$$

Program for generating the Herring group for nonsymmorphic $\mathbb{S}_{\mathbf{Q}}$, when $\mathbf{Q}$ is on BZ boundary

Nonsymmorphic group of $\mathbf{Q}$ on the BZ boundary

Generate the Herring group and its Irreps

```

Print["The Group of the Wavevector ", Qsame,
      " is Nonsymmorphic."];
Print[" Its Point Group is : ", LQ];
TQ ={};
Do[ix = LQ[[i]]; AppendTo[TQ,Tau[[ix]]],{i, 1, gq}];
FQ = Range[gq];
Print[TQ];

⇒ TQ will contain  $\tau$  and  $\mathbf{t} + \tau$ ,  $\mathbf{t} \notin \mathbb{T}_k$ ,
   associated with the elements of the Herring group.

⇒  $\mathbf{t}$  contains lattice translations not in  $\mathbb{T}_k$ .
⇒  $\mathbf{tr}$  contains the scalar products  $\mathbf{k} \cdot \mathbf{t}$ ,  $\mathbf{t} + \tau$ ,  $\mathbf{t} \in \mathbb{T}$ .

t = {{0, 0, 0}}; it = 0;
tr ={}; Print["Q = ",Qtest];
While[it < 3, it++;
  Switch[And[Mod[Qtest[[it]], 1] != 0,
    FreeQ[tr,Qtest[[it]]]],
    True, AppendTo[t, B.A[[it]]];
    AppendTo[tr, Qtest[[it]]];
    Do[
      is=LQ[[i]];
      rs=B.A[[it]]+Tau[[is]];
      AppendTo[TQ, rs];
      AppendTo[FQ,Length[TQ]],
      {i,1,gq}
    ]
  ]
];

gq = Length[TQ];
Print[" The Herring Factor Group Order = ", gq];
Print["Its point-group operations are:"];
Print["LQ = ", LQ];
Print["The Translation elements of the Herring group are "];
Print[TQ];

```

Generate multiplication table of Herring group

```

Do[mherring[i, j] = 0, {i, 1, gq}, {j, 1, gq}];
Do[
  is = LQ[[im]]; it = LQ[[in]];
  tt = G.Rot[is].Transpose[RL].TQ[[in]] + TQ[[im]];
  mel = m[[1, is, it]];
  Do[
    Switch[LQ[[ix]] == mel, True,
      MX = Qtest.(tt - TQ[[ix]]);
      Switch[Mod[MX, 1] == 0, True,
        mherring[im, in] = ix]
    ],
  {ix, 1, gq}
],
{im, 1, gq}, {in, 1, gq}
];
Multip = Array[mherring, {gq, gq}];
Print["Its Multiplication Table is"];
Print[TableForm[Multip]];

```

11.2.5 Examples of nonsymmorphic space-groups

The two-dimensional space-group $p2mg$

We consider here a two-dimensional system with space-group $p2mg$, as presented in Chapter 10. It has a rectangular Bravais net, with generating primitive vectors $\mathbf{a} \equiv (a, 0)$ and $\mathbf{b} \equiv (0, b)$, and an atomic basis of four atoms per lattice point. Its point-group is

$$\mathcal{P} = \mathcal{C}_{2v} = E, C_2, \sigma_x, \sigma_y,$$

and a space-group coset decomposition

$$\begin{aligned} \mathcal{S} &= (E|\mathbf{0})\mathbb{T} + (C_2|\mathbf{0})\mathbb{T} + (\sigma_x|\tau)\mathbb{T} + (\sigma_y|\tau)\mathbb{T}, \\ \tau &= \frac{a}{2}\mathbf{x} + \frac{b}{2}\mathbf{y}, \end{aligned} \quad (11.63)$$

with reflection planes coinciding with the x - and y -axes.

The Brillouin zone is shown in Figure 11.12, together with the generating reciprocal lattice vectors $\mathbf{a}^* = (2\pi/a, 0)$ and $\mathbf{b}^* = (0, 2\pi/b)$.

We consider the Irreps associated with the $\bar{X}$ -point.

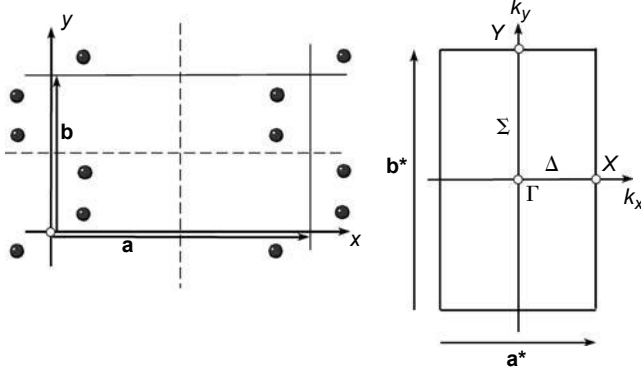


Fig. 11.12. (a) The unit cell of a two-dimensional rectangular crystal with a basis of four atoms per lattice point such that there is a fractional lattice translation $\tau = \frac{a}{2} \mathbf{x} + \frac{b}{2} \mathbf{y}$. The symmetry is $P2mg$. (b) The Brillouin zone with reciprocal lattice vectors $\mathbf{a}^*$ and $\mathbf{b}^*$.

The $\bar{X}$ -point: $\mathbf{k} = (\pi/a, 0)$

- (i) The star of $\mathbf{k}$ is

$$^*\mathbf{k}_{\bar{X}} = \{E\mathbf{k}_X = \mathbf{k}_X, C_2\mathbf{k}_X = -\mathbf{k}_X, \sigma_x\mathbf{k}_X = -\mathbf{k}_X, \sigma_y\mathbf{k}_X = \mathbf{k}_X\} \sim \mathbf{k}_X,$$

which implies a one-dimensional ground representation.

- (ii) The point-group of $\mathbf{k}_X$ is

$$\mathcal{P}_X = C_{2v}.$$

- (iii) Because $\mathcal{P}_X = C_{2v} = \mathcal{P}$, the coset expansion of $\mathcal{P}$ by $\mathcal{P}_X$ is

$$C_{2v} = EC_{2v},$$

thus the ground representation is one-dimensional and is labeled by $(E|\mathbf{0})$.

- (iv) The kernel subgroup $\mathbb{T}_{\mathbf{k}}$ of the translation group $\mathbb{T}$ contains translation elements of the form $\exp(-i\mathbf{k} \cdot \mathbf{t})$ that map onto unity. Thus, with $\mathbf{t} = m\mathbf{a} + n\mathbf{b}$, and $\mathbf{k}_X = (\pi/a, 0)$, only terms

$$\mathbf{k} \cdot \mathbf{t} = \frac{\pi}{a} ma = 2\pi n, \quad m \text{ even},$$

will map onto unity. The kernel group is then

$$\mathbb{T}_X = \{(E|m\mathbf{a}) + (E|n\mathbf{b})\}; \quad m \text{ even, and } \forall \text{ integers } n.$$

- (v) Decompose $\mathbb{T}$ into coset of $\mathbb{T}_{\mathbf{k}}$

$$\mathbb{T} = [(E|\mathbf{0}) + (E|\mathbf{a})] \mathbb{T}_{\mathbf{k}}. \quad (11.64)$$

Table 11.6. *Multiplication table for the quotient group, $\mathcal{Q}_X$, for the nonsymmorphic space-group $p2mg$. The vector $\mathbf{w} = \tau + \mathbf{a}$ is also a fractional vector corresponding to a term that does not map onto the kernel group.*

	$(E \mathbf{0})$	$(E \mathbf{a})$	$(C_2 \mathbf{0})$	$(C_2 \mathbf{a})$	$(\sigma_x \tau)$	$(\sigma_x \mathbf{w})$	$(\sigma_y \tau)$	$(\sigma_y \mathbf{w})$
$(E \mathbf{0})$	$(E \mathbf{0})$	$(E \mathbf{a})$	$(C_2 \mathbf{0})$	$(C_2 \mathbf{a})$	$(\sigma_x \tau)$	$(\sigma_x \mathbf{w})$	$(\sigma_y \tau)$	$(\sigma_y \mathbf{w})$
$(E \mathbf{a})$	$(E \mathbf{a})$	$(E \mathbf{0})$	$(C_2 \mathbf{a})$	$(C_2 \mathbf{0})$	$(\sigma_x \mathbf{w})$	$(\sigma_x \tau)$	$(\sigma_y \mathbf{w})$	$(\sigma_y \tau)$
$(C_2 \mathbf{0})$	$(C_2 \mathbf{0})$	$(C_2 \mathbf{a})$	$(E \mathbf{0})$	$(E \mathbf{a})$	$(\sigma_y \mathbf{w})$	$(\sigma_y \tau)$	$(\sigma_x \mathbf{w})$	$(\sigma_x \tau)$
$(C_2 \mathbf{a})$	$(C_2 \mathbf{a})$	$(C_2 \mathbf{0})$	$(E \mathbf{a})$	$(E \mathbf{0})$	$(\sigma_y \tau)$	$(\sigma_y \mathbf{w})$	$(\sigma_x \tau)$	$(\sigma_x \mathbf{w})$
$(\sigma_x \tau)$	$(\sigma_x \tau)$	$(\sigma_x \mathbf{w})$	$(\sigma_y \tau)$	$(\sigma_y \mathbf{w})$	$(E \mathbf{a})$	$(E \mathbf{0})$	$(C_2 \mathbf{a})$	$(C_2 \mathbf{0})$
$(\sigma_x \mathbf{w})$	$(\sigma_x \mathbf{w})$	$(\sigma_x \tau)$	$(\sigma_y \mathbf{w})$	$(\sigma_y \tau)$	$(E \mathbf{0})$	$(E \mathbf{a})$	$(C_2 \mathbf{0})$	$(C_2 \mathbf{a})$
$(\sigma_y \tau)$	$(\sigma_y \tau)$	$(\sigma_y \mathbf{w})$	$(\sigma_x \tau)$	$(\sigma_x \mathbf{w})$	$(C_2 \mathbf{0})$	$(C_2 \mathbf{a})$	$(E \mathbf{0})$	$(E \mathbf{a})$
$(\sigma_y \mathbf{w})$	$(\sigma_y \mathbf{w})$	$(\sigma_y \tau)$	$(\sigma_x \mathbf{w})$	$(\sigma_x \tau)$	$(C_2 \mathbf{a})$	$(C_2 \mathbf{0})$	$(E \mathbf{a})$	$(E \mathbf{0})$

(vi) The Herring factor group is then

$$\begin{aligned}
 \mathcal{Q}_X &= [(E|\mathbf{0}) + (E|\mathbf{a})] \cdot [(E|\mathbf{0}) + (C_2|\mathbf{0}) + (\sigma_x|\tau) + (\sigma_y|\tau)] \\
 &= (E|\mathbf{0}) + (C_2|\mathbf{0}) + (\sigma_x|\tau) + (\sigma_y|\tau) \\
 &\quad + (E|\mathbf{a}) + (C_2|\mathbf{a}) + (\sigma_x|\tau + \mathbf{a}) + (\sigma_y|\tau + \mathbf{a}).
 \end{aligned}$$

(vii) We now generate the multiplication table of $\mathcal{Q}_k$ by considering all pair combinations of elements belonging to the Herring factor group, for example

$$(E|\mathbf{a}) (\sigma_x|\tau) = (\sigma_x|\tau + \mathbf{a}) \equiv (\sigma_x|\mathbf{w}), \quad (11.65)$$

introduces a new translation vector $\mathbf{w} = \tau + \mathbf{a}$ as shown in Table 11.6.

The multiplications satisfy modulo $\mathbb{T}_X$, as we demonstrate for the case

$$(E|\mathbf{a}) (\sigma_x|\mathbf{w}) = (\sigma_x|\mathbf{w} + \mathbf{a}) = (\sigma_x|\tau + 2\mathbf{a}) = (\sigma_x|\tau), \quad (11.66)$$

where the last step follows because all terms with integer multiples of $2\mathbf{a}$ are contained in the kernel subgroup $\mathbb{T}_X$.

This group is isomorphic to $\mathcal{D}_4$, and has five classes, its character table is given in Table 11.7, where we use the notation $\mathbf{w} \equiv \tau \pm \mathbf{a}$.

We find that only Irrep $^{(5)}\Sigma$ satisfies (11.60), i.e.

$$^{(\mu)}\Sigma_A ((E|a) \mathbb{T}_X) = \exp(-i\pi) \mathbb{I}.$$

Table 11.7. The character table for the quotient group $\mathcal{Q}_X$, which is isomorphic to the point-group $\mathcal{D}_4$. The group elements are arranged in five classes.

	$(E \mathbf{0})$	$(E \mathbf{a})$	$(C_2 \mathbf{0})$	$(\sigma_x \tau)$	$(\sigma_y \tau)$
			$(C_2 \mathbf{a})$	$(\sigma_x \mathbf{w})$	$(\sigma_y \mathbf{w})$
$(1)\Sigma$	1	1	1	1	1
$(2)\Sigma$	1	1	1	-1	-1
$(3)\Sigma$	1	1	-1	1	-1
$(4)\Sigma$	1	1	-1	-1	1
$(5)\Sigma$	2	-2	0	0	0

We then induce an $(5,X)\Omega$ Irrep with representative matrices

$$\begin{aligned}
 (5,X)\Omega((E|\mathbf{0})) &= \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}, & (5,X)\Omega((E|\mathbf{a})) &= \begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix}, \\
 (5,X)\Omega((C_2|\mathbf{0})) &= \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, & (5,X)\Omega((C_2|\mathbf{a})) &= \begin{bmatrix} 0 & -1 \\ -1 & 0 \end{bmatrix}, \\
 (5,X)\Omega((\sigma_x|\tau)) &= \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix}, & (5,X)\Omega((\sigma_x|\mathbf{w})) &= \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix}, \\
 (5,X)\Omega((\sigma_y|\tau)) &= \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, & (5,X)\Omega((\sigma_y|\mathbf{w})) &= \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix}.
 \end{aligned} \tag{11.67}$$

Strictly speaking, it is sufficient to list the matrices for the four coset representatives of $\mathbb{S}$, which are the operations that do not contain $\mathbf{a}$, since, given them and the matrix for $(E|\mathbf{a})$, the rest follows.

Irreps of the 2D space-group $p4gm$

This group can be expressed as

$$\mathbb{C}_4 + (\sigma_x|\tau) \mathbb{C}_4,$$

where $\tau = (\frac{1}{2}\frac{1}{2})$. Its Irreps inside the BZ are identical to those of $p4mm$, and we only consider the X and M points here.

The $\bar{X}$ -point: $\mathbf{k}=(\pi/a, 0)$

$$\mathbb{P}_X = \{(E|00), (C_2|00), (\sigma_x|\tau), (\sigma_y|\tau)\},$$

$$\mathbb{T}_X = \{(E|ma\hat{\mathbf{x}}) + (E|na\hat{\mathbf{y}})\}; \quad m \text{ even, and } \forall \text{ integers } n,$$

$$\mathbb{T} = [(E|\mathbf{0}) + (E|a\hat{\mathbf{x}})] \mathbb{T}_{\mathbf{x}},$$

$$\begin{aligned}
\mathcal{Q}\mathbf{x} &= [(E|\mathbf{0}) + (E|a\hat{\mathbf{x}})] \otimes [(E|\mathbf{0}) + (C_2|\mathbf{0}) + (\sigma_x|\tau) + (\sigma_y|\tau)] \\
&= (E|\mathbf{0}) + (C_2|\mathbf{0}) + (\sigma_x|\tau) + (\sigma_y|\tau) \\
&\quad + (E|a\hat{\mathbf{x}}) + (C_2|a\hat{\mathbf{x}}) + (\sigma_x|\tau + a\hat{\mathbf{x}}) + (\sigma_y|\tau + a\hat{\mathbf{x}}). \tag{11.68}
\end{aligned}$$

The ground-Rep is given in (11.48), and the allowable Irrep in (11.67). The $^*X$ Irrep of $p4gm$ is four-dimensional and is given by:

E	C_2	C_4^+	C_4^-
$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}$
σ_x	σ_y	σ_d^1	σ_d^2
$\begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix}$

$$\text{Irreps of the space-group } P\frac{4_2}{nmn} (\mathcal{D}_{4h}^{14})$$

As was detailed in Chapter 10, the space-group $P\frac{4_2}{nmn} (\mathcal{D}_{4h}^{14})$ comprises the left cosets

$$\begin{aligned}
&(E|\mathbf{0}), (C_2|\mathbf{0}), (C_4|\tau), (C_4^{-1}|\tau), (I|\mathbf{0}), (\sigma_h|\mathbf{0}), (S_4|\tau), (S_4^{-1}|\tau), \\
&(U_x|\tau), (U_y|\tau), (U_1^d|\mathbf{0}), (U_2^d|\mathbf{0}), (\sigma_d|\mathbf{0}), (\sigma_d|\mathbf{0}), (\sigma_x|\tau), (\sigma_y|\tau),
\end{aligned}$$

where $\tau = (\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3)/2$. The nonprimitive vector τ corresponds to an origin taken at the center of the unit cell, namely $(1/2, 1/2, 1/2)$. The corresponding point-group $\mathcal{P}$ is $\mathcal{D}_{4h}$.

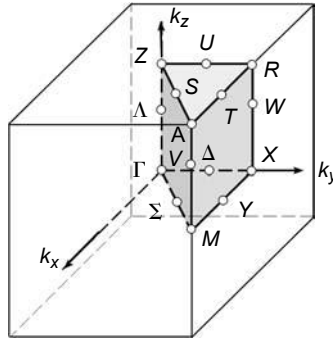


Fig. 11.13. Brillouin zone of the primitive tetragonal Bravais lattice.

Table 11.8. Irreps of $\mathcal{D}_{4h}$.

		E	C_2	$2C_4$	$2U$	$2U^d$	I	σ_h	$2S_4$	2σ	$2\sigma_d$
A_{1g}	$(1)\Gamma^+$	1	1	α	α	1	1	1	α	α	1
B_{1g}	$(2)\Gamma^+$	1	1	$-\alpha$	α	-1	1	1	$-\alpha$	α	-1
A_{2g}	$(3)\Gamma^+$	1	1	α	$-\alpha$	-1	1	1	α	$-\alpha$	-1
B_{2g}	$(4)\Gamma^+$	1	1	$-\alpha$	$-\alpha$	1	1	1	$-\alpha$	$-\alpha$	1
E_g	$(5)\Gamma^+$	2	-2	0	0	0	2	-2	0	0	0
A_{1u}	$(1)\Gamma^-$	1	1	α	α	1	-1	-1	$-\alpha$	$-\alpha$	-1
B_{1u}	$(2)\Gamma^-$	1	1	$-\alpha$	α	-1	-1	-1	α	$-\alpha$	1
A_{2u}	$(3)\Gamma^-$	1	1	α	$-\alpha$	-1	-1	-1	$-\alpha$	α	1
B_{2u}	$(4)\Gamma^-$	1	1	$-\alpha$	$-\alpha$	1	-1	-1	$-\alpha$	α	-1
E_u	$(5)\Gamma^-$	2	-2	0	0	0	-2	2	0	0	0

For points inside the Brillouin zone, Figure 11.13, the Irreps of $\mathbb{S}_{\mathbf{k}}$ are identical to those of $\mathcal{P}_{\mathbf{k}}$, since, as we have demonstrated earlier, the multiplier system comprises ones.

The Γ -point: $\mathbf{k} = (0, 0, 0)$

$\mathcal{P}_{\mathbf{k}}$	$^*\mathbf{k}$	$\mathbb{T}$ Irreps	Ground Rep	Allowable Irreps
$\mathcal{D}_{4h}$	$(0,0,0)$	1	1	10 Irreps (Table 11.8)

The Λ -line: $\mathbf{k} = (0, 0, k)$

$\mathcal{P}_{\mathbf{k}}$	$^*\mathbf{k}$	$\mathbb{T}$ Irreps	Ground Rep	Allowable Irreps
$\mathcal{C}_{4v}$: $E, 2C_4, C_2$,	$(0, 0, \pm k)$	$\exp(ikm_z c)$	$\mathcal{P}_{\mathbf{k}} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	5 Irreps
$2\sigma_v, 2\sigma_d$		$\exp(-ikm_z c)$	$I\mathcal{P}_{\mathbf{k}} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	(Table 11.9)

Table 11.9. Irreps of Λ -line, $(\alpha = \exp(ik\pi))$.

Δ	E	C_2	σ	σ_d	C_4
Λ_1	1	1	α	1	α
Λ_2	1	1	α	-1	$-\alpha$
Λ_3	1	1	$-\alpha$	1	$-\alpha$
Λ_4	1	1	$-\alpha$	-1	α
Λ_5	2	-2	0	0	0

The Δ -line: $\mathbf{k} = (0, k, 0)$

$\mathcal{P}_{\mathbf{k}}$	$^*\mathbf{k}$	$\mathbb{T}$ Irreps	Ground Rep	Allowable Irreps
$\mathcal{C}_{2v} : E, C_{2y}$	$(\pm k, 0, 0)$	$\exp(ikm_x a), \exp(ikm_y a)$	$(4 \times 4),$	4 Irreps
$(y) \quad \sigma_x, \sigma_z$	$(0, \pm k, 0)$	$\exp(-ikm_x a), \exp(-ikm_y a)$	Table 11.10	Table 11.11

Table 11.10. *Ground representation.*

$E, \sigma_z = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$	$C_{2z}, I = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}$	$C_{2\bar{x}\bar{y}}, \sigma_{\bar{x}\bar{y}} = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$
$C_{2xy}, \sigma_{xy} = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}$	$C_4, S_4^{-1} = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$	$C_4^{-1}, S_4 = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \end{pmatrix}$
$C_{2x}, \sigma_x = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$	$C_{2y}, \sigma_y = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}$	

The Σ -line: $\mathbf{k} = (k, k, 0)$

$\mathcal{P}_{\mathbf{k}}$	$^*\mathbf{k}$	$\mathbb{T}$ Irreps	Ground Rep	Allowable Irreps
$\mathcal{C}_{2v} : E, C_{2d}$	$(\pm k, \pm k, 0)$	$\exp(ikm^+ a), \exp(ikm^- a)$	$(4 \times 4),$	4
$(xy) \quad \sigma_d, \sigma_z$		$\exp(-ikm^+ a), \exp(-ikm^- a)$	Table 11.10	Table 11.11

The M-point: $\mathbf{k} = \left(\frac{\pi}{a}, \frac{\pi}{a}, 0\right)$

Table 11.11. *Irreps of Δ and Σ directions $\alpha = \exp(ik\pi)$.*

Δ	E	U	σ	σ_h	Σ	E	U_d	σ_d	σ_h
Δ_1	1	α	α	1	Σ_1	1	1	1	1
Δ_2	1	α	$-\alpha$	-1	Σ_2	1	-1	-1	1
Δ_3	1	$-\alpha$	α	-1	Σ_3	1	-1	1	-1
Δ_4	$-\alpha$	$-\alpha$	1	1	Σ_4	1	1	-1	-1

$\mathcal{P}_{\mathbf{k}}$	$^*\mathbf{k}$	$\mathbb{T}$ Irreps	Ground Rep	Allowable Irreps
$\mathcal{D}_{4h}$	$\left(\frac{\pi}{a}, \frac{\pi}{a}, 0\right)$	$\exp(im^+ \pi)$	1	10, Table 11.8

Table 11.12. Character table for the M point.

M	E	C_2	$2\sigma_d$	$2U^d$	$2C_4$	$2U$	σ_h	I	2σ	$2S_4$
$M_1^\pm$	1	1	± 1	1	i	i	± 1	± 1	$\pm i$	$\pm i$
$M_2^\pm$	1	1	∓ 1	-1	$-i$	i	± 1	± 1	$\pm i$	$\mp i$
$M_3^\pm$	1	1	∓ 1	-1	i	$-i$	± 1	± 1	$\mp i$	$\pm i$
$M_4^\pm$	1	1	± 1	1	$-i$	$-i$	± 1	± 1	$\mp i$	$\mp i$
$M_5^\pm$	2	-2	0	0	0	0	∓ 2	± 2	0	0

The kernel subgroup of $\mathbb{T}$ is defined as

$$\begin{aligned}\mathbb{T}_M &= \{(E|\mathbf{t}); \quad \mathbf{t} = (m_x, m_y, m_z), \quad m_x + m_y = 2n\} \\ &= \{(E|\mathbf{t}); \quad \mathbf{t} = (m, 2n - m, m_z), \quad \forall m, n, m_z \text{ integers}\} \\ \mathcal{T}_M &= \frac{\mathbb{T}}{\mathbb{T}_M} = \left\{ (E|\mathbf{0}) \oplus (E|a(\hat{\mathbf{x}} + \hat{\mathbf{y}})) \right\}.\end{aligned}$$

The $\mathbf{X} \left(0, \frac{\pi}{a}, 0\right)$ and $\mathbf{R} \left(0, \frac{\pi}{a}, \frac{\pi}{c}\right)$ points

$\mathcal{P}_{\mathbf{k}}$	$\mathbf{k}$	$\mathbb{T}$ Irreps	Ground Rep	Allowable Irreps	
$\mathcal{D}_{2h}$	$\mathbf{X}$	$\left(0, \frac{\pi}{a}, 0\right)$	$\exp \left[i m_y \pi\right]$	$\mathcal{P}_{\mathbf{k}}=\left(\begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array}\right)$ 2 Irreps Table 11.13	
		$\left(\frac{\pi}{a}, 0, 0\right)$	$\exp \left[i m_x \pi\right]$		
	$\mathbf{R}$	$\left(\frac{\pi}{a}, 0, \frac{\pi}{c}\right)$	$\exp \left[i\left(m_x+m_z\right) \pi\right]$		$I \mathcal{P}_{\mathbf{k}}=\left(\begin{array}{cc} 0 & 1 \\ 1 & 0 \end{array}\right)$
		$\left(0, \frac{\pi}{a}, \frac{\pi}{c}\right)$	$\exp \left[i\left(m_y+m_z\right) \pi\right]$		

 Table 11.13. Small Irreps of X and R points.

X	E	σ_h	$2U$	C_2	I	$2\sigma_v$
R	E	I	$2U$	C_2	σ_h	$2\sigma_v$
1	1^-	2	-2	0	0	0
2	1^+	2	2	0	0	0

The kernel subgroup of $\mathbb{T}$ is defined as

$$\mathbb{T}_X = \{(E|\mathbf{t}) \Rightarrow \mathbf{t} = (m_x, 2n, m_z)\}, \quad \mathcal{T}_X = \frac{\mathbb{T}}{\mathbb{T}_X} = \left\{ (E|\mathbf{0}) \oplus (E|a\hat{\mathbf{y}}) \right\},$$

$$\mathbb{T}_R = \left\{ (E|\mathbf{t}); \Rightarrow \mathbf{t} = (m_x, m_y, m_z) \right\}, \begin{cases} m_x + m_y = 2n \\ \text{or} \\ (m_x, 2n - m, m), \forall m, n, m_x \text{ integers} \end{cases}$$

$$\mathcal{T}_R = \frac{\mathbb{T}}{\mathbb{T}_R} = \left\{ (E|\mathbf{0}) \oplus (E|a\hat{\mathbf{y}}) \right\}.$$

At the X -point the Herring quotient group $2m \otimes \left\{ (E|\mathbf{0}) \oplus (E|a\hat{\mathbf{y}}) \right\}$ is isomorphic to the point-group $4/mmm$, with the mapping

$(E \mathbf{0}) \rightarrow E$	$(U_x \tau) \rightarrow \sigma_1^d$	$(I \mathbf{0}) \rightarrow \sigma_x$	$(\sigma_x \tau) \rightarrow C_4^+$
$(E a\hat{\mathbf{y}}) \rightarrow C_2$	$(U_x \tau + a\hat{\mathbf{y}}) \rightarrow \sigma_2^d$	$(I a\hat{\mathbf{y}}) \rightarrow \sigma_y$	$(\sigma_x \tau + a\hat{\mathbf{y}}) \rightarrow C_4^-$
$(C_2 \mathbf{0}) \rightarrow U_x$	$(U_y \tau) \rightarrow S_4^+$	$(\sigma_h \mathbf{0}) \rightarrow I$	$(\sigma_y \tau) \rightarrow U_1^d$
$(C_2 a\hat{\mathbf{y}}) \rightarrow U_y$	$(U_y \tau + a\hat{\mathbf{y}}) \rightarrow S_4^-$	$(\sigma_h a\hat{\mathbf{y}}) \rightarrow \sigma_h$	$(\sigma_y \tau + a\hat{\mathbf{y}}) \rightarrow U_2^d$

The $\mathbf{Z} \left(0, 0, \frac{\pi}{c}\right)$ and $\mathbf{A} \left(\frac{\pi}{a}, \frac{\pi}{a}, \frac{\pi}{c}\right)$ points

$\mathcal{P}_{\mathbf{k}}$	$^*\mathbf{k}$	$\mathbb{T}$ Irreps	Ground Rep	Allowable Irreps
$\mathcal{D}_{4h}$	$\mathbf{Z} \left(0, 0, \frac{\pi}{c}\right)$	$\exp(im_z\pi)$	1	4 Irreps
	$\mathbf{A} \left(\frac{\pi}{a}, \frac{\pi}{a}, \frac{\pi}{c}\right)$	$\exp(im^+\pi)$		Table 11.14

Table 11.14. Character table for the Z -point.

Z	E	C_2	$2\sigma_d$	U_1^d	U_2^d	$2C_4$	$2U$	σ_h	I	2σ	$2S_4$
Z_1	2	2	2	0	0	0	0	0	0	0	0
Z_2	2	2	-2	0	0	0	0	0	0	0	0
Z_3	2	-2	0	2	-2	0	0	0	0	0	0
Z_4	2	-2	0	-2	2	0	0	0	0	0	0

The kernel subgroup of $\mathbb{T}$ is defined as

$$\mathbb{T}_Z = \left\{ (E|\mathbf{t}) \Rightarrow \mathbf{t} = (m_x, m_y, 2n) \right\}, \quad \mathcal{T}_Z = \frac{\mathbb{T}}{\mathbb{T}_Z} = \left\{ (E|\mathbf{0}) \oplus (E|c\hat{\mathbf{z}}) \right\}$$

$$\mathbb{T}_A = \left\{ (E|\mathbf{t}) \Rightarrow \mathbf{t} = (m_x, m_y, m_z) \right\}, \quad (m_x + m_y + m_z = 2nl, m, 2n - l - m),$$

$$\forall l, m, n \text{ integers.}$$

$$\mathcal{T}_A = \frac{\mathbb{T}}{\mathbb{T}_A} = \left\{ (E|\mathbf{0}) \oplus (E|c\hat{\mathbf{z}}) \right\}.$$

Exercises

- 11.1 Show that the action of a space-group operation $(R|\mathbf{w})$ on a plane-wave $\exp(i\mathbf{k} \cdot \mathbf{r})$, leads to

$$(R|\mathbf{w}) \exp(i\mathbf{k} \cdot \mathbf{r}) = \exp(iR\mathbf{k} \cdot (\mathbf{r} - \mathbf{w})).$$

- 11.2 The choice of coset representatives is not unique. Show that if we replace the coset representative C_4^- by σ_d^2 we find, for example,

$$\mathbf{M}^*(C_4^+) = \begin{pmatrix} 0 & 0 & 0 & \sigma_v^1 \\ 0 & 0 & E & 0 \\ E & 0 & 0 & 0 \\ 0 & \sigma_v^1 & 0 & 0 \end{pmatrix}.$$

Because we have used nonstandard coset representatives that do not form a group, the modified ground representation contains a mix of matrix elements from $\mathcal{P}_\Delta$. Nonetheless, the set of matrices obtained, $\mathbf{M}^*(R)$, still obey the group multiplication table for $\mathcal{C}_{4v}$.

- 11.3 Show that $\mathbb{T}_{\mathbf{k}}$ is a normal subgroup of $\mathbb{S}_{\mathbf{k}}$ and of $\mathbb{T}$.

- 11.4 Consider the two-dimensional square net; show that:

- (i) The translation subgroup of the wavevector $\mathbb{T}_{\bar{\Delta}}$ is a subset of all translation vectors $(m_x a, m_y a) \in \mathbb{T}$ that satisfy the condition

$$\mathbb{T}_{\bar{\Delta}} \equiv \{(E|(m_1 a, m_2 a))\}; \quad m_1 a k = 2n\pi, \text{ and } \forall m_2,$$

with cosets of $\mathbb{S}_{\bar{\Delta}}$

$$\mathbb{T}_{\bar{\Delta}}, (E|(ma, 0))\mathbb{T}_{\bar{\Delta}}, (\sigma_v|(ma, 0))\mathbb{T}_{\bar{\Delta}}; \quad m \neq m_1$$

which form the quotient group $\mathcal{Q}_{\bar{\Delta}}$.

- (ii) The translation subgroup of the wavevector $\mathbb{T}_{\Sigma}$ is the subgroup

$$\mathbb{T}_{\Sigma} \equiv \{(E|(m_1 a, m_2 a))\}; \quad (m_1 + m_2)ak = 2n\pi,$$

with cosets of $\mathbb{S}_{\Sigma}$

$$\mathbb{T}_{\Sigma}, (E|(ma, m' a))\mathbb{T}_{\Sigma}, (\sigma_d|(ma, m' a))\mathbb{T}_{\Sigma}; \quad m + m' a \neq m_1 + m_2,$$

which form the quotient group $\mathcal{Q}_{\Sigma}$.

- (iii) The translation subgroup of the wavevector $\mathbb{T}_M$ is the subgroup

$$\begin{aligned} \mathbb{T}_M &\equiv \{(E|(m_1 a, m_2 a))\}; \quad m_1 + m_2 \text{ even,} \\ &= \{(E|\mathbf{t}_e)\}, \end{aligned}$$

with cosets of $\mathbb{G}_M$

$$(R_{i\mathbf{k}}|(0, 0))\mathbb{T}_M, (R_{i\mathbf{k}}|(a, 0))\mathbb{T}_M, (R_{i\mathbf{k}}|(0, a))\mathbb{T}_M$$

which form the quotient group $\mathcal{Q}_M$.

- 11.5 Consider the two-dimensional space-group $p4mm$ presented in Section 11.2.2. Determine:

- (i) the two 4-dimensional Irreps for the Σ -line;
(ii) the 2-dimensional Irrep for the M -point.

11.6 Consider the 2D symmorphic space-group $p6mm$.

- (i) Determine its reciprocal lattice basis and determine the relative orientation of its Brillouin zone to its Wigner–Seitz cell.
- (ii) For wavevectors at $\bar{\Gamma}$, $\bar{\Delta}$, $\bar{\Sigma}$, M , and K , determine:
 - (a) the star of the wavevector;
 - (b) the wavevector point-subgroup;
 - (c) the corresponding point-subgroup Irreps;
 - (d) the corresponding ground Rep.

11.7 Repeat part (b) of the previous problem for the space-group $Pd3m$, and the symmetry points Γ , Δ , Λ , Σ , X , L , W , and K .

11.8 Use Herring’s method to obtain the Irreps of the rutile structure, $P\frac{4_2}{m}\frac{2_1}{n}\frac{2}{m}$, at the X -point.

11.9 Consider the space-group $P23(T^1)$. Determine the star of $\mathbf{k}_\Gamma$ and $\mathbf{k}_M$, their ground Reps and the Irreps of their little-groups.

11.10 Show that (11.29) can be generalized for the case of the more general space-group operator $(R|t)$.

11.11 Given two vectors, $\mathbf{k}$ and $\mathbf{t}$, and a rotation operator R with inverse R^{-1} , show that the angle between the vectors $R\mathbf{k}$ and $\mathbf{t}$ equals the angle between the vectors $\mathbf{k}$ and $R^{-1}\mathbf{t}$. Thus

$$\mathbf{k} \cdot R^{-1}\mathbf{t} = R\mathbf{k} \cdot \mathbf{t}.$$

11.12 Show that in two dimensions the glide and a two-fold screw axis are identical.

11.13 Find the elements of the point-group $\mathcal{P}$ for the two-dimensional nonsymmorphic crystal of Figure 11.5. Show that the elements of $\mathcal{P}$ actually form a group. Show that the point-group is not a subgroup of the space-group because of the existence of a glide plane.

11.14 Find the elements of the little-group of the wavevector, $\mathbb{S}_\mathbf{k}$, for the nonsymmorphic crystal of Figure 11.5, for each of the $\mathbf{k}$ -values (labeled by Γ , Δ , ...) in Figure 11.7(b).

11.15 Find the elements of the point-group, $\mathcal{P}_\mathbf{k}$, for the nonsymmorphic crystal of Figure 11.5, for each of the $\mathbf{k}$ -values (labeled by Γ , Δ , ...) in Figure 11.7(b).

11.16 Consider the space-groups associated with the f.c.c. lattice.

- (i) Determine the stars of $\mathbf{k}$ at the X , L , W points on the surface of the BZ.
- (ii) The diamond structure belongs to the space-group $Fd3m$. Use Herring’s method to obtain the corresponding Irreps at the above points.
- (iii) Repeat the problem for the hcp structure at the BZ surface points M , K , A .

12

Time-reversal symmetry: color groups and the Onsager relations

12.1 Introduction

Another important symmetry operation which has not so far been discussed and which cannot be directly represented by a matrix in $\mathcal{E}(n)$ Euclidean space is *time-reversal*. This operation, contrary to its historical label, and as we will demonstrate in this chapter, actually reverses the direction of motion of a dynamical system, i.e. the directions of momenta, angular momenta, and currents. A good starting point to explore the root of time-reversal symmetry is Newton's second law. Here we find that, because only the second time derivative is present, application of the time-inversion operation, i.e. $t \rightarrow -t$, reveals the symmetry that both $\mathbf{x}(t)$ and $\mathbf{x}(-t)$ are solutions to

$$m \frac{d^2 \mathbf{x}(t)}{dt^2} = -\nabla V(\mathbf{x}(t)).$$

It is rather important, pedagogically, to interpret this result in terms of the motions that may ensue. Thus, if the particle motion follows the trajectory $\mathbf{x}(t)$, and at some time t_0 we stop it, and restart the motion with the initial conditions $\mathbf{x}_{\text{initial}} = \mathbf{x}(t_0)$, $v_{\text{initial}} = -d\mathbf{x}(t)/dt|_{t_0}$, then the particle will retrace the original trajectory, but with time moving forward, i.e. for $t > 0$! We have effectively reversed the motion.

We can elaborate further on this situation within the framework of Hamiltonian dynamics. Here, if we consider a trajectory solution of Hamilton's equations, namely, $\mathbf{x}(t)$, $\mathbf{p}(t)$, the extension of time-reversal symmetry, implies that $\mathbf{x}(-t)$ and $-\mathbf{p}(-t)$ form another solution. For this condition to be satisfied the Hamiltonian has to be an even function of $\mathbf{p}$,

$$\mathcal{H}(\mathbf{x}, -\mathbf{p}) = \mathcal{H}(\mathbf{x}, \mathbf{p}). \quad (12.1)$$

12.2 The time-reversal operator in quantum mechanics

In order to explore the application of time-reversal symmetry within the framework of quantum mechanics, we examine how a *time-reversed* state, i.e. a state that has been operated on by a time-reversal operator Θ , evolves in time. We follow the argument of J. J. Sakurai [55], and we start with a state ket $|\phi\rangle$, representing a physical system, say at $t = 0$. We know that the time evolution of $|\phi\rangle$ is determined with the aid of the Hamiltonian $\mathcal{H}$ of the system that $|\phi\rangle$ describes. We can express the forward propagation

of this state ket in time, say to $t = \delta t$, according to the relation

$$|\phi; 0 \rightarrow \delta t\rangle = \left(\mathbb{I} - \frac{i\mathcal{H}}{\hbar} \delta t \right) |\phi\rangle. \quad (12.2)$$

To explore the manifestations of time-reversal symmetry, we adopt two time paths that should lead to the same final state if such symmetry is to be satisfied. In the first, we apply the time-reversal operator Θ at $t = 0$, and then allow the system to evolve to δt ; we obtain

$$\left(\mathbb{I} - \frac{i\mathcal{H}}{\hbar} \delta t \right) \Theta |\phi\rangle. \quad (12.3)$$

In the second, we pick the state ket at $t = -\delta t$, and then reverse its momenta and angular momenta, namely

$$\Theta |\phi; -\delta t\rangle = \Theta \left(\mathbb{I} - \frac{i\mathcal{H}}{\hbar} (-\delta t) \right) |\phi\rangle. \quad (12.4)$$

This means that

$$\left(\mathbb{I} - \frac{i\mathcal{H}}{\hbar} \delta t \right) \Theta |\phi\rangle = \Theta \left(\mathbb{I} - \frac{i\mathcal{H}}{\hbar} (-\delta t) \right) |\phi\rangle. \quad (12.5)$$

which, in turn, implies that

$$(-i\mathcal{H}) \Theta |\text{any!}\rangle = \Theta (i\mathcal{H}) |\text{any!}\rangle. \quad (12.6)$$

We now demonstrate that the presence of the *is* in (12.6) is essential to the validity of this relation and by extension to time-reversal symmetry. We bolster this argument with a *reductio ad absurdum* approach, that is, by writing

$$-\mathcal{H} \Theta = \Theta \mathcal{H}, \quad (12.7)$$

we can examine the physical consequence of removing the *is* in (12.6). We notice that (12.7) would imply that an eigenstate $|n\rangle$, with energy eigenvalue E_n , obeys the relation

$$\mathcal{H} \Theta |n\rangle = -\Theta \mathcal{H} |n\rangle = (-E_n) \Theta |n\rangle, \quad (12.8)$$

which is clearly violated when we consider the case of a free particle whose energy spectrum is non-negative, $0 \leq E < +\infty$.

The preceding argument strongly suggests that if time-reversal is to be a bona fide symmetry, we are not allowed to cancel the *is* in (12.6). To explore the significance of the *is* further, we consider the structure of the Schrödinger equation and its conjugation, namely,

$$\mathcal{H} \Psi(\mathbf{x}, t) = i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{x}, t) \Rightarrow \mathcal{H} \Psi^*(\mathbf{x}, t) = -i\hbar \frac{\partial}{\partial t} \Psi^*(\mathbf{x}, t), \quad (12.9)$$

where we used the fact that (12.1) implies that

$$\mathcal{H}(\mathbf{x}, i\hbar \nabla) = \mathcal{H}(\mathbf{x}, -i\hbar \nabla), \quad (12.10)$$

since $\mathbf{p} = i\hbar \nabla$. By applying time-inversion to the conjugated equation, it can be rewritten in the form

$$\mathcal{H} \Psi^*(\mathbf{x}, -t) = i\hbar \frac{\partial}{\partial t} \Psi^*(\mathbf{x}, -t), \quad (12.11)$$

which demonstrates that if $\Psi(\mathbf{x}, t)$ is a wavefunction that satisfies the Schrödinger equation, then $\Psi^*(\mathbf{x}, -t)$ must be a degenerate solution. Thus we conjecture that:

Time-reversal must involve both complex conjugation and time-inversion operations.

12.2.1 The conjugation operator and time-reversal

We may write this compound operation in the form

$$\Theta = U \mathcal{K}_0, \quad (12.12)$$

where U is a unitary operator, to be determined later, and $\mathcal{K}_0$ is the conjugation operator. Θ is known as Wigner's *time-reversal* operator; it uses time-inversion symmetry of the problem to obtain a new solution in which the directions of all momenta, as well as currents, as we show below, are reversed.

We define the effect of $\mathcal{K}_0$ as

$$\begin{aligned} \mathcal{K}_0 \Psi(\mathbf{x}) &= \Psi^*(\mathbf{x}), \\ \mathcal{K}_0 i\hbar \nabla \Psi(\mathbf{x}) &= -i\hbar \nabla \mathcal{K}_0 \Psi(\mathbf{x}) = -i\hbar \nabla \Psi^*(\mathbf{x}), \\ \mathcal{K}_0 \mathcal{H} \Psi(\mathbf{x}) &= \mathcal{H} \mathcal{K}_0 \Psi(\mathbf{x}) = \mathcal{H} \Psi^*(\mathbf{x}). \end{aligned} \quad (12.13)$$

Equation (12.13) shows that $\mathcal{K}_0$ satisfies the relations,

$$\mathcal{K}_0^2 = \mathbb{I} \quad \text{or} \quad \mathcal{K}_0^{-1} = \mathcal{K}_0. \quad (12.14)$$

Properties of the time-reversal operator

The time-reversal operator Θ has two properties that set it apart from other quantum mechanical operators:

(i) It is *antilinear*

$$\begin{aligned} \Theta (a \Psi + b \Phi) &= U \mathcal{K}_0 (a \Psi + b \Phi) \\ &= a^* U \mathcal{K}_0 \Psi + b^* U \mathcal{K}_0 \Phi \\ &= a^* \Theta \Psi + b^* \Theta \Phi. \end{aligned} \quad (12.15)$$

(ii) It is *antiunitary*

$$\begin{aligned} (\Theta \Psi, \Theta \Phi) &= (U \mathcal{K}_0 \Psi, U \mathcal{K}_0 \Phi) \\ &= (\Phi, \Psi) \\ &= (\Psi, \Phi)^*. \end{aligned} \quad (12.16)$$

To demonstrate how the second line of (12.16) was obtained, we expand the time-reversed states in terms of a basis set, as

$$\begin{aligned}
 |\tilde{\Psi}\rangle &= \Theta |\Psi\rangle = U\mathcal{K}_0 \sum_{\alpha} \langle\alpha|\Psi\rangle |\alpha\rangle = \sum_{\alpha} \langle\alpha|\Psi\rangle^* U |\alpha\rangle \\
 &= \sum_{\alpha} \langle\Psi|\alpha\rangle U |\alpha\rangle \rightarrow \langle\tilde{\Psi}| = \sum_{\alpha} \langle\alpha|\Psi\rangle \langle\alpha| U^{\dagger}, \\
 |\tilde{\Phi}\rangle &= \Theta |\Phi\rangle = U\mathcal{K}_0 \sum_{\alpha} \langle\alpha|\Phi\rangle |\alpha\rangle \\
 &= \sum_{\alpha} \langle\Phi|\alpha\rangle U |\alpha\rangle, \\
 \langle\tilde{\Psi}|\Phi\rangle &= \sum_{\alpha\alpha'} \langle\Phi|\alpha\rangle \langle\alpha'|\Psi\rangle \langle\alpha'| U^{\dagger} U |\alpha\rangle \\
 &= \langle\Phi|\Psi\rangle.
 \end{aligned}$$

- (iii) The elements of a point- or space-group, associated with a physical system, *commute with the time-reversal operator*,

$$\Theta R = R \Theta, \quad (12.17)$$

and, therefore, *have real representations*. We demonstrate this property for a spinless system as follows: We write the system's state wavefunction as

$$\psi(\mathbf{r}) = \psi_{\Re}(\mathbf{r}) + i \psi_{\Im}(\mathbf{r}), \quad (12.18)$$

where $\psi_{\Re}(\mathbf{r})$ and $\psi_{\Im}(\mathbf{r})$ are real functions. Operating on this wavefunction by ΘR and by $R \Theta$, we obtain

$$\begin{aligned}
 \Theta R \psi(\mathbf{r}) &= \Theta \psi(R^{-1}\mathbf{r}) = (\psi_{\Re}(R^{-1}\mathbf{r}) + i \psi_{\Im}(R^{-1}\mathbf{r}))^* \\
 R \Theta \psi(\mathbf{r}) &= \psi_{\Re}(R^{-1}\mathbf{r}) - i \psi_{\Im}(R^{-1}\mathbf{r}),
 \end{aligned} \quad (12.19)$$

The two results of (12.19) are equal, since R is an orthogonal matrix, and, hence, real. The case of a spin-1/2 system will be considered below.

12.2.2 Transformation of operators and wavefunctions under time-reversal

Here, we study the effect of Θ on operators and wavefunctions by considering a matrix element $\langle\psi|\mathcal{O}|\phi\rangle$ where $\mathcal{O}$ is an operator and $|\psi\rangle, |\phi\rangle$ are two state kets of a physical system. Following Sakurai's approach we define

$$|\zeta\rangle = \mathcal{O}^{\dagger}|\psi\rangle.$$

We can write the matrix element as

$$\begin{aligned}
 \langle\psi|\mathcal{O}|\phi\rangle &= \langle\zeta|\phi\rangle = \langle\tilde{\phi}|\tilde{\zeta}\rangle \\
 &= \langle\tilde{\phi}|\Theta \mathcal{O}^{\dagger}|\psi\rangle
 \end{aligned}$$

$$\begin{aligned}
&= \langle \tilde{\phi} | \Theta \mathcal{O}^\dagger \Theta^{-1} \Theta | \psi \rangle \\
&= \langle \tilde{\phi} | \Theta \mathcal{O}^\dagger \Theta^{-1} | \tilde{\psi} \rangle,
\end{aligned} \tag{12.20}$$

where $|\tilde{\phi}\rangle$ is the time-reversed state corresponding to the state $|\phi\rangle$. For a Hermitian observable $\mathcal{A}$, we obtain

$$\langle \psi | \mathcal{A} | \phi \rangle = \langle \tilde{\phi} | \Theta \mathcal{A} \Theta^{-1} | \tilde{\psi} \rangle. \tag{12.21}$$

Note: We have followed Sakurai's advice of employing kets, rather than bras, when operating with the antiunitary time-reversal operator, namely,

$$\langle \beta | \Theta | \phi \rangle \Rightarrow (\langle \beta |) \cdot (\Theta | \phi \rangle).$$

Equation (12.21) shows how a Hermitian operator transforms under time-reversal. As we have seen above, vector operators may either maintain or reverse their directions under time-reversal, and we may write, in general

$$\Theta \mathcal{A} \Theta^{-1} = \pm \mathcal{A}, \tag{12.22}$$

where the operator $\mathcal{A}$ is said to be even, (+), or odd, (−), under time-reversal. Substituting (12.22) in (12.21) we obtain

$$\langle \psi | \mathcal{A} | \phi \rangle = \pm \langle \tilde{\psi} | \mathcal{A} | \tilde{\phi} \rangle^*. \tag{12.23}$$

With this matrix element relation we now explore the symmetries of quantum operators and wavefunctions under time-reversal.

(i) **Expectation values** The expectation value of $\mathcal{A}$ is expressed as

$$\langle \phi | \mathcal{A} | \phi \rangle = \pm \langle \tilde{\phi} | \mathcal{A} | \tilde{\phi} \rangle^*. \tag{12.24}$$

(ii) **The momentum operator** The expectation value of the momentum in the time-reversed state should be of opposite sign to that in the original state, namely,

$$\langle \phi | \hat{\mathbf{p}} | \phi \rangle = - \langle \tilde{\phi} | \hat{\mathbf{p}} | \tilde{\phi} \rangle^* \Rightarrow \Theta \hat{\mathbf{p}} \Theta^{-1} = - \hat{\mathbf{p}}, \tag{12.25}$$

where $\hat{\mathbf{p}}$ is the momentum operator. This implies

$$\begin{aligned}
\hat{\mathbf{p}} \Theta | \mathbf{p} \rangle &= - \Theta \hat{\mathbf{p}} \Theta^{-1} \Theta | \mathbf{p} \rangle \\
&= (-\mathbf{p}) \Theta | \mathbf{p} \rangle = (-\mathbf{p}) | -\mathbf{p} \rangle
\end{aligned} \tag{12.26}$$

where $|\mathbf{p}\rangle$ is a momentum eigenket.

(iii) **The position operator** We also find that the requirement

$$\langle \phi | \hat{\mathbf{x}} | \phi \rangle = \langle \tilde{\phi} | \hat{\mathbf{x}} | \tilde{\phi} \rangle^* \Rightarrow \Theta \hat{\mathbf{x}} \Theta^{-1} = \hat{\mathbf{x}}, \tag{12.27}$$

leads to

$$\Theta | \mathbf{x} \rangle = | \mathbf{x} \rangle \quad (\text{up to a phase factor}). \tag{12.28}$$

- (iv) **The fundamental commutation relation** We now check the invariance of the fundamental commutation relation under time-reversal,

$$\begin{aligned}\Theta [x_i, p_j] \Theta^{-1} \Theta |\rangle &= \Theta i\hbar \delta_{ij} |\rangle, \\ [x_i, (-p_j)] \Theta |\rangle &= -i\hbar \delta_{ij} \Theta |\rangle, \\ \text{or,} \\ [x_i, (p_j)] \Theta |\rangle &= i\hbar \delta_{ij} \Theta |\rangle.\end{aligned}\tag{12.29}$$

We should note that the antiunitary character of the time-reversal operation Θ preserved the fundamental commutation relation.

- (v) **The wavefunction in the absence of spin** The wavefunction $\phi(\mathbf{x}) \equiv \langle \mathbf{x} | \phi \rangle$ of a spinless particle appears naturally in the position representation of a state $|\phi\rangle$ as

$$|\phi\rangle = \int d^3x |\mathbf{x}\rangle \langle \mathbf{x} | \phi \rangle.\tag{12.30}$$

When we operate on $|\phi\rangle$ by the time-reversal operator, we obtain

$$\begin{aligned}\Theta |\phi\rangle &= \int d^3x \Theta |\mathbf{x}\rangle \langle \mathbf{x} | \phi \rangle^* \\ &= \int d^3x |\mathbf{x}\rangle \langle \mathbf{x} | \phi \rangle^*\end{aligned}\tag{12.31}$$

and recover the rule

$$\Psi(\mathbf{x}) \xrightarrow{\Theta} \Psi^*(\mathbf{x}).\tag{12.32}$$

12.2.3 Time-reversal and spin-1/2 systems

The angular momentum operator

Similarly, we find that the angular momentum commutation relation,

$$[\hat{J}_i, \hat{J}_j] = i\hbar \epsilon_{ijk} \hat{J}_k,\tag{12.33}$$

is preserved if the angular momentum operator is odd under time-reversal, namely

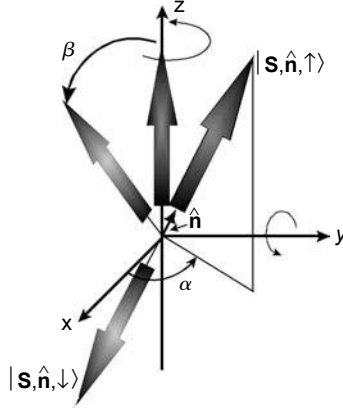
$$\Theta \hat{\mathbf{J}} \Theta^{-1} = -\hat{\mathbf{J}},\tag{12.34}$$

which also conforms with the case of orbital angular momentum where $\mathbf{J} \equiv \mathbf{L} = \mathbf{x} \times \mathbf{p}$.

We now reverse the argument followed above and write

$$\Theta \hat{\mathbf{J}} \Theta^{-1} = -\hat{\mathbf{J}} \Rightarrow \langle \phi | \hat{\mathbf{J}} | \phi \rangle = -\langle \tilde{\phi} | \hat{\mathbf{J}} | \tilde{\phi} \rangle^*,\tag{12.35}$$

$$\begin{aligned}\hat{\mathbf{J}} \Theta |\mathbf{J}\rangle &= -\Theta \hat{\mathbf{J}} \Theta^{-1} \Theta |\mathbf{J}\rangle \\ &= (-\mathbf{J}) \Theta |\mathbf{J}\rangle = (-\mathbf{J}) |-\mathbf{J}\rangle.\end{aligned}\tag{12.36}$$

Fig. 12.1. Construction of the ket $|\mathbf{S} \cdot \hat{\mathbf{n}}; \uparrow\rangle$.*The general spin-1/2 eigenket*

The general eigenvalue problem of a spin-1/2 particle can be expressed as

$$\left(\widehat{\mathbf{S} \cdot \hat{\mathbf{n}}}\right) |\mathbf{S} \cdot \hat{\mathbf{n}}; \uparrow\rangle = \frac{\hbar}{2} |\mathbf{S} \cdot \hat{\mathbf{n}}; \uparrow\rangle, \quad (12.37)$$

where $\hat{\mathbf{n}}$ is an arbitrary axis of quantization, with polar and azimuthal angles β and α , respectively. The eigenket $|\mathbf{S} \cdot \hat{\mathbf{n}}; \uparrow\rangle$ can be constructed, as shown in Figure 12.1, by applying two successive rotations to the state $|\hat{\mathbf{z}}; \uparrow\rangle$: first, by a rotation of an angle β about the y -axis, followed by an angle α about the z -axis, which we write as

$$|\mathbf{S} \cdot \hat{\mathbf{n}}; \uparrow\rangle = e^{-i\hat{S}_z\alpha/\hbar} e^{-i\hat{S}_y\beta/\hbar} |\uparrow\rangle. \quad (12.38)$$

The representation of Θ

Using (12.35), we find that when we apply time-reversal to $|\mathbf{S} \cdot \hat{\mathbf{n}}; \uparrow\rangle$, we get

$$\Theta |\mathbf{S} \cdot \hat{\mathbf{n}}; \uparrow\rangle = e^{i\theta} |\mathbf{S} \cdot \hat{\mathbf{n}}; \downarrow\rangle, \quad (12.39)$$

where θ is a phase angle to be determined. Alternatively, if we use (12.38) and the fact that

$$\Theta e^{-i\hat{S}_z\alpha/\hbar} \Theta^{-1} = e^{-i\hat{S}_z\alpha/\hbar}$$

we obtain

$$\Theta |\mathbf{S} \cdot \hat{\mathbf{n}}; \uparrow\rangle = e^{-i\hat{S}_z\alpha/\hbar} e^{-i\hat{S}_y\beta/\hbar} \Theta |\uparrow\rangle = e^{[i\theta]} |\mathbf{S} \cdot \hat{\mathbf{n}}; \downarrow\rangle. \quad (12.40)$$

We find from Figure 12.1 that

$$|\mathbf{S} \cdot \hat{\mathbf{n}}; \downarrow\rangle = e^{-i\hat{S}_z\alpha/\hbar} e^{-i\hat{S}_y(\pi+\beta)/\hbar} |\uparrow\rangle. \quad (12.41)$$

Substituting (12.41) in (12.40), we get

$$e^{-i\hat{S}_z\alpha/\hbar} e^{-i\hat{S}_y\beta/\hbar} \Theta |\uparrow\rangle = e^{[i\theta]} e^{-i\hat{S}_z\alpha/\hbar} e^{-i\hat{S}_y(\pi+\beta)/\hbar} |\uparrow\rangle, \quad (12.42)$$

Writing $\Theta = U\mathcal{K}_0$ and using the fact that $\mathcal{K}_0|\uparrow\rangle = |\uparrow\rangle$ we obtain the relation

$$\Theta = e^{[i\theta]} \left(e^{-i\pi/2} \right)^{2S_y/\hbar} \mathcal{K}_0 = -ie^{[i\theta]} \left(\frac{2S_y}{\hbar} \right) \mathcal{K}_0, \quad (12.43)$$

where we used the Pauli matrix representation $\frac{S_y}{\hbar} = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$.

Action of Θ

To determine the effect of Θ on a general ket $(\alpha|\uparrow\rangle + \beta|\downarrow\rangle)$ we write

$$\begin{aligned} \Theta(\alpha|\uparrow\rangle + \beta|\downarrow\rangle) &= e^{[i\theta]} e^{-i\pi S_y/\hbar} \mathcal{K}_0(\alpha|\uparrow\rangle + \beta|\downarrow\rangle) \\ &= e^{[i\theta]} \alpha^* |\downarrow\rangle - e^{[i\theta]} \beta^* |\uparrow\rangle \\ \Theta^2(\alpha|\uparrow\rangle + \beta|\downarrow\rangle) &= -(\alpha|\uparrow\rangle + \beta|\downarrow\rangle) \end{aligned} \quad (12.44)$$

so that

$$\Theta^2 = -\mathbb{I}, \quad (12.45)$$

for any spin orientation. This result is true, irrespective of the choice of the phase θ !

We can generalize (12.43) for any angular momentum $\mathbf{J}$ and write

$$\Theta = e^{[i\theta]} e^{-i\pi J_y/\hbar} \mathcal{K}_0. \quad (12.46)$$

If a system comprises n spin-1/2 particles, then

$$\mathbf{J} = \sum_{r=1}^n \mathbf{S}_r,$$

and Θ becomes

$$\Theta = e^{[in\theta]} \left(\prod e^{-i\pi(S_y)_r/\hbar} \right) \mathcal{K}_0. \quad (12.47)$$

Expanding an arbitrary state $|\phi\rangle = \sum_{j,m} |jm\rangle \langle jm | \phi \rangle$ and operating by Θ^2 we get

$$\begin{aligned} \Theta \left(\Theta \sum_{j,m} |jm\rangle \langle jm | \phi \rangle \right) &= \Theta \left(e^{[i\theta]} \sum_{j,m} e^{-i\pi J_y/\hbar} |jm\rangle \langle jm | \phi \rangle^* \right) \\ &= e^{-2i\pi J_y/\hbar} \sum_{j,m} |jm\rangle \langle jm | \phi \rangle; \end{aligned} \quad (12.48)$$

since $e^{-2i\pi J_y/\hbar}$ corresponds to a 2π rotation about the y -axis we find that

$$e^{-2i\pi J_y/\hbar} |jm\rangle = (-1)^{2j} |jm\rangle, \quad (12.49)$$

and we obtain for integer j

$$\mathcal{D}(\Theta^2) = \begin{cases} -\mathbb{I}, & j \text{ half-integer,} \\ +\mathbb{I}, & j \text{ integer.} \end{cases} \quad (12.50)$$

Alternatively, we may write

$$\Theta^2 = \lambda E \quad (12.51)$$

$$\text{where } \lambda = \begin{cases} 1, & \text{integer spin,} \\ -1, & \text{half-integer spin.} \end{cases}$$

Choice of the phase θ

To establish a convenient convention for the phase θ we consider the case of the position representation of an eigenket of the orbital angular momentum $|l, m\rangle$, namely, the spherical harmonics $Y_l^m(\mathbf{r})$

$$\Theta Y_l^m(\mathbf{r}) \rightarrow Y_l^{m*}(\mathbf{r}) = (-1)^m Y_l^{-m}(\mathbf{r}),$$

or

$$\Theta |l, m\rangle = (-1)^m |l, -m\rangle. \quad (12.52)$$

It is then convenient to generalize this convention to include half-integer angular momenta by choosing $\theta = \pi/2$, and writing

$$\Theta |j, m\rangle = i^{2m} |j, -m\rangle. \quad (12.53)$$

Commutation of Θ with symmetry operations associated with spin-1/2 systems

We consider the action of ΘR and $R \Theta$ on a spinor $\begin{bmatrix} \phi_1 \\ \phi_2 \end{bmatrix}$

$$\begin{aligned} \Theta R \begin{bmatrix} \phi_1(\mathbf{r}) \\ \phi_2(\mathbf{r}) \end{bmatrix} &= (iJ_y \mathcal{K}_0) \begin{bmatrix} \phi_1(R^{-1}\mathbf{r}) \\ \phi_2(R^{-1}\mathbf{r}) \end{bmatrix} {}^{(1/2)}\Gamma(R) \\ &= (iJ_y) {}^{(1/2)}\Gamma^*(R) \begin{bmatrix} \phi_1^*(R^{-1}\mathbf{r}) \\ \phi_2^*(R^{-1}\mathbf{r}) \end{bmatrix}, \\ R \Theta \begin{bmatrix} \phi_1(\mathbf{r}) \\ \phi_2(\mathbf{r}) \end{bmatrix} &= R (iJ_y \mathcal{K}_0) \begin{bmatrix} \phi_1(R^{-1}\mathbf{r}) \\ \phi_2(R^{-1}\mathbf{r}) \end{bmatrix} \end{aligned}$$

$$\begin{aligned}
&= R \begin{pmatrix} iJ_y \end{pmatrix} \begin{bmatrix} \phi_1^*(R^{-1}\mathbf{r}) \\ \phi_2^*(R^{-1}\mathbf{r}) \end{bmatrix} \\
&= {}^{(1/2)}\Gamma(R) \begin{pmatrix} iJ_y \end{pmatrix} \begin{bmatrix} \phi_1^*(R^{-1}\mathbf{r}) \\ \phi_2^*(R^{-1}\mathbf{r}) \end{bmatrix}.
\end{aligned} \tag{12.54}$$

However, since ${}^{(1/2)}\Gamma(R)$ has the form $\begin{bmatrix} a & b \\ -b^* & a^* \end{bmatrix}$, it satisfies the equality

$${}^{(1/2)}\Gamma^*(R) = (iJ_y)^{-1} {}^{(1/2)}\Gamma(R) (iJ_y) \tag{12.55}$$

and we obtain

$$\Theta^{-1} R \Theta = R. \tag{12.56}$$

12.2.4 Time-reversal in external fields

We consider here the case of a system represented by the Hamiltonian $\mathcal{H}(\mathbf{p}, \mathbf{r})$, which satisfies time-reversal invariance, i.e. under the transformation $\mathbf{p} \rightarrow -\mathbf{p}$. When the system is placed in external electromagnetic fields described by the vector and scalar potentials $\mathbf{A}$ and Φ , respectively, the new Hamiltonian $\mathcal{H}^I(\mathbf{p}, \mathbf{r})$ is given by writing

$$\mathcal{H}^I(\mathbf{p}, \mathbf{r}) = \mathcal{H}\left(\mathbf{p} - \frac{e\mathbf{A}}{c}, \mathbf{r}\right) + e\Phi. \tag{12.57}$$

$\mathcal{H}^I$ will be invariant under time-reversal operation only when the motion of the sources of the field are simultaneously reversed. Since the currents produced by a set of charges whose motion is reversed obey the relations

$$\begin{aligned}
\tilde{\mathbf{J}}(\mathbf{r}, t) &= -\mathbf{J}(\mathbf{r}, -t), \\
\tilde{\rho}(\mathbf{r}, t) &= \rho(\mathbf{r}, -t),
\end{aligned} \tag{12.58}$$

they will give rise to time-reversed fields and potentials obeying

$$\tilde{\mathbf{A}}(\mathbf{r}, t) = -\mathbf{A}(\mathbf{r}, -t), \quad \tilde{\Phi}(\mathbf{r}, t) = \Phi(\mathbf{r}, -t), \tag{12.59}$$

effectively reversing $\mathbf{A}$, but not Φ . The corresponding fields transform as

$$\tilde{\mathbf{E}}(\mathbf{r}, t) = \mathbf{E}(\mathbf{r}, -t), \quad \tilde{\mathbf{H}}(\mathbf{r}, t) = -\mathbf{H}(\mathbf{r}, -t), \tag{12.60}$$

under time-reversal. The time-reversed Hamiltonian is then obtained as

$$\tilde{\mathcal{H}}(\mathbf{H}, t) = \Theta \mathcal{H}(\mathbf{H}, -t) \Theta^{-1} = \mathcal{H}(\tilde{\mathbf{H}}, -t) \tag{12.61}$$

and the time-reversed wavefunction is given by

$$\tilde{\Psi}(\tilde{\mathbf{H}}, t) = \Theta \Psi(\mathbf{H}, -t), \tag{12.62}$$

which is a solution of the magnetic field-reversed problem.

12.3 Spin-1/2 and double-groups

In Chapter 10 we presented a detailed account of the Irreps of the elements of $\mathcal{O}(3)$ in terms of the eigenfunctions, with integer eigenvalues, of the angular momentum operator $\mathbf{J}$, which was shown to be the generator of infinitesimal rotations in Euclidean space. Here, we derive the Irreps engendered by the eigenfunctions of odd half-integer eigenvalues [13, 56, 57].

12.3.1 Representations of rotation operators for spin angular momentum $\frac{1}{2}$

Let us now consider a particle of spin 1/2, and define, with respect to a z -axis, two eigenstate kets $|+\rangle$, $|-\rangle$, with $J_z \equiv S_z = \pm 1/2$, where we set $\hbar = 1$. We can expand any state ket $|\alpha\rangle$ in terms of these eigenkets as

$$|\alpha\rangle = |+\rangle \langle +|\alpha\rangle + |-\rangle \langle -|\alpha\rangle. \quad (12.63)$$

We now examine the effect of the rotation operator $R(\hat{\mathbf{z}}, \phi) \equiv \exp(-i\hat{S}_z \phi)$ on this state,

$$e^{-i\hat{S}_z \phi} |\alpha\rangle = e^{-i\frac{\phi}{2}} |+\rangle \langle +|\alpha\rangle + e^{i\frac{\phi}{2}} |-\rangle \langle -|\alpha\rangle. \quad (12.64)$$

When we set the rotation angle $\phi = 2\pi$, we find that

$$R(\hat{\mathbf{z}}, 2\pi) |\alpha\rangle = -|\alpha\rangle \quad ! \quad (12.65)$$

We would need to rotate by an angle of 4π to get back to the original ket. Consequently, we conclude that this group of representative matrices of rotation operators has *twice as many elements as that of the $SO(3)$ group*. Consider rotations by 2π and 4π , respectively. In $SO(3)$ the corresponding operators map into the identity, and are both represented by a 3×3 unit matrix; however, in the group of spin-1/2 rotation operators, the 2π rotation is represented by a $-1 \times (2 \times 2)$ identity matrix.

Manipulations of spin rotations are most conveniently handled in the two-component spinor formalism. To this end, we introduce column vectors, or spinors, to represent the $|+\rangle$, $|-\rangle$, such that

$$\begin{aligned} |+\rangle &= \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \chi_+, & |-\rangle &= \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \chi_-, \\ \langle +| &= \begin{pmatrix} 1 & 0 \end{pmatrix} = \chi_+^\dagger, & \langle -| &= \begin{pmatrix} 0 & 1 \end{pmatrix} = \chi_-^\dagger, \\ |\alpha\rangle &= \begin{pmatrix} \langle +|\alpha\rangle \\ \langle -|\alpha\rangle \end{pmatrix}, & \langle \alpha| &= \begin{pmatrix} \langle +|\alpha\rangle & \langle -|\alpha\rangle \end{pmatrix}, \end{aligned} \quad (12.66)$$

where the column vectors are referred to as *two-component spinors*. The spin angular momentum operators can be expressed in terms of the eigenkets as

$$\begin{aligned} S_x &= \left(\frac{\hbar}{2}\right) \begin{bmatrix} |+\rangle \langle -| + |-\rangle \langle +| \\ -|+\rangle \langle -| + |-\rangle \langle +| \end{bmatrix}, \\ S_y &= \left(\frac{i\hbar}{2}\right) \begin{bmatrix} -|+\rangle \langle -| + |-\rangle \langle +| \\ |+\rangle \langle -| - |-\rangle \langle +| \end{bmatrix}, \\ S_z &= \left(\frac{\hbar}{2}\right) \begin{bmatrix} |+\rangle \langle +| - |-\rangle \langle -| \end{bmatrix}. \end{aligned} \quad (12.67)$$

When expressed in terms of the two-component spinors, we get

$$S_i = \left(\frac{i}{2} \right) \sigma_i, \quad i = 1, 2, 3, \quad (12.68)$$

where σ_i denotes the three Pauli matrices

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad (12.69)$$

which have the properties

$$\sigma_i^2 = \mathbb{I}, \quad (12.70)$$

$$\sigma_i \sigma_j + \sigma_j \sigma_i = \mathbf{0} \quad \text{for } i \neq j. \quad (12.71)$$

Equations (12.70) and (12.71) are equivalent to the anticommutator relations

$$\{\sigma_i, \sigma_j\} = 2\delta_{ij} \mathbb{I}, \quad (12.72)$$

Thus the Pauli matrices, and consequently the spin-1/2 angular momenta, satisfy both the anticommutator relations (12.72) as well as the angular momentum commutator relations

$$[\sigma_i, \sigma_j] = 2i\varepsilon_{ijk} \sigma_k. \quad (12.73)$$

We also note that

$$\sigma_i^\dagger = \sigma_i, \quad (12.74)$$

$$\det(\sigma_i) = -1, \quad (12.75)$$

$$\text{Tr}(\sigma_i) = 0. \quad (12.76)$$

We should stress at this point that the matrices σ_i are actually components of a vector $\sigma \equiv (\sigma_1, \sigma_2, \sigma_3)$. Consequently we may define its scalar product with a general vector $\mathbf{r} \equiv (x_1, x_2, x_3)$ as

$$\begin{aligned} \sigma \cdot \mathbf{r} &= \sum_i \sigma_i x_i \\ &= \begin{pmatrix} x_3 & x_1 - ix_2 \\ x_1 + ix_2 & -x_3 \end{pmatrix}. \end{aligned} \quad (12.77)$$

We also introduce the identity

$$\begin{aligned} (\sigma \cdot \mathbf{u})(\sigma \cdot \mathbf{v}) &= \sum_i \sigma_i u_i \sum_j \sigma_j v_j \\ &= \sum_{i,j} \left(\frac{1}{2} \{\sigma_i, \sigma_j\} + \frac{1}{2} [\sigma_i, \sigma_j] \right) u_i v_j \\ &= \sum_{i,j} (\delta_{ij} + i\varepsilon_{ijk} \sigma_k) u_i v_j \\ &= \mathbf{u} \cdot \mathbf{v} + \sigma \cdot (\mathbf{u} \times \mathbf{v}). \end{aligned} \quad (12.78)$$

For the case $\mathbf{u} = \mathbf{v}$, we get $(\sigma \cdot \mathbf{u})^2 = \mathbb{I} |\mathbf{u}|^2$.

Rotations in the two-component formalism

We are now ready to study the 2×2 matrix representation of the rotation operators $R(\phi)$. Writing

$$\exp(-i\mathbf{S} \cdot \phi) = \exp\left(\frac{-i\boldsymbol{\sigma} \cdot \phi}{2}\right), \quad (12.79)$$

and using the fact that

$$(\boldsymbol{\sigma} \cdot \hat{\phi})^n = \begin{cases} \mathbb{I} & \text{for } n \text{ even,} \\ \boldsymbol{\sigma} \cdot \hat{\phi} & \text{for } n \text{ odd,} \end{cases} \quad (12.80)$$

we get

$$\begin{aligned} \exp\left(\frac{-i\boldsymbol{\sigma} \cdot \hat{\phi} \phi}{2}\right) &= \left[\mathbb{I} - \frac{(\boldsymbol{\sigma} \cdot \hat{\phi})^2}{2!} \left(\frac{\phi}{2}\right)^2 + \frac{(\boldsymbol{\sigma} \cdot \hat{\phi})^4}{4!} \left(\frac{\phi}{2}\right)^4 - \dots \right] \\ &\quad - i \left[(\boldsymbol{\sigma} \cdot \hat{\phi}) \left(\frac{\phi}{2}\right) - \frac{(\boldsymbol{\sigma} \cdot \hat{\phi})^3}{3!} \left(\frac{\phi}{2}\right)^3 + \dots \right] \\ &= \mathbb{I} \cos\left(\frac{\phi}{2}\right) - i (\boldsymbol{\sigma} \cdot \hat{\phi}) \sin\left(\frac{\phi}{2}\right) \\ &= \begin{pmatrix} \cos\left(\frac{\phi}{2}\right) - i\hat{\phi}_z \sin\left(\frac{\phi}{2}\right) & (-i\hat{\phi}_x - \hat{\phi}_y) \sin\left(\frac{\phi}{2}\right) \\ (-i\hat{\phi}_x + \hat{\phi}_y) \sin\left(\frac{\phi}{2}\right) & \cos\left(\frac{\phi}{2}\right) + i\hat{\phi}_z \sin\left(\frac{\phi}{2}\right) \end{pmatrix}. \end{aligned} \quad (12.81)$$

Clearly, (12.81) is *unitary and unimodular*, i.e. its determinant is 1. We can write the most general unitary unimodular 2×2 matrix as

$$U(a, b) = \begin{pmatrix} a & b \\ -b^* & a^* \end{pmatrix} \quad (12.82)$$

with a and b complex numbers satisfying the unimodular condition

$$|a|^2 + |b|^2 = 1, \quad (12.83)$$

which also fulfill the unitarity condition. We notice that the components of the rotation matrix representation (12.81) satisfy the condition of (12.82). Consequently, we can say that every unimodular unitary 2×2 matrix represents a rotation. The set of all 2×2 unitary unimodular matrices form a group known as $SU(2)$, the special unitary group. It also constitutes an isomorphic representation of the group of rotation operators of spin-1/2 particles.

12.3.2 Double-groups

It is now clear that there exists a $2 \rightarrow 1$ homomorphism in mapping $SU(2) \rightarrow \mathcal{SO}(3)$. We find that both $U(a, b)$ and $U(-a, -b)$ matrices map into a single 3×3 matrix in $\mathcal{SO}(3)$. As we should have expected, this homomorphism is still manifest when we consider

Table 12.1. Values of $^{(j)}\chi$ for point-group operations ($n = 0, 1, 2, \dots$).

	E	$\bar{E}$	C_3		$\bar{C}_3$	C_2	C_4		$\bar{C}_4$
$\mathfrak{D}^{(j)}$	$(2j+1)$	$-(2j+1)$	1	$(j = 1/2 + 3n)$	-1		$\sqrt{2}$	$(j = 1/2 + 4n)$	$-\sqrt{2}$
			-1	$(j = 3/2 + 3n)$	1	0	0	$(j = 3/2 + 2n)$	0
			0	$(j = 5/2 + 3n)$	0		$-\sqrt{2}$	$(j = 5/2 + 4n)$	$\sqrt{2}$

the symmetry of spin-1/2 systems under discrete point-groups which are subgroups of $\mathcal{O}(3) = \mathcal{SO}(3) \otimes \{E, I\}$. This situation is clearly present when the system Hamiltonian explicitly contains spin operators. In such cases the appropriate symmetry group of the Hamiltonian is a discrete subgroup of $SU(2) \otimes \{E, I\}$, which we represent by $\mathfrak{DG}$, where $\mathcal{G}$ is the symmetry point-group of the Hamiltonian in the absence of spin. In order to distinguish between the two types of point-groups we term $\mathfrak{DG}$ a *double-group*, while $\mathcal{G}$ is called a *single-group*.

The construction of Irreps of double-groups is best approached by introducing a simple recipe in terms of the Irreps of $\mathcal{O}(3)$. We know from Chapter 10 that in Irrep $^{(j)}\Gamma$ the character of the operator $(R(\phi))$ is given by

$$^{(j)}\chi(\phi) = \frac{\sin((j + 1/2)\phi)}{\sin(\phi/2)}, \quad (12.84)$$

for both proper and improper rotations, since the angular momentum is an axial vector. For the rotation $R(\phi + 2\pi)$ becomes

$$^{(j)}\chi(\phi + 2\pi) = \frac{\sin((j + 1/2)(\phi + 2\pi))}{\sin(\phi/2 + \pi)} = (-1)^{2j} {}^{(j)}\chi(\phi). \quad (12.85)$$

We note that for half-integer j

$$\begin{aligned} {}^{(j)}\chi(\phi + 2\pi) &= - {}^{(j)}\chi(\phi), \\ \chi(\phi + 4\pi) &= {}^{(j)}\chi(\phi), \end{aligned} \quad (12.86)$$

so that the Irrep is *double-valued*. We introduce a new operator $\bar{E} \equiv R(2\pi)$, such that $\bar{E}^2 = E$, and define the elements of the double-group as

$$R, \bar{R} = \bar{E} R = R \bar{E}. \quad (12.87)$$

The matrix Irrep for $j = 1/2$ is given in terms of the angular vector $\phi = \phi \hat{\phi}$, where $\hat{\phi}$ is a unit vector, as

$$\mathfrak{D}^{(1/2)}(\phi) = \begin{pmatrix} \cos(\frac{\phi}{2}) - i\hat{\phi}_z \sin(\frac{\phi}{2}) & (-i\hat{\phi}_x - \hat{\phi}_y) \sin(\frac{\phi}{2}) \\ (-i\hat{\phi}_x + \hat{\phi}_y) \sin(\frac{\phi}{2}) & \cos(\frac{\phi}{2}) + i\hat{\phi}_z \sin(\frac{\phi}{2}) \end{pmatrix}.$$

Table 12.2 gives the matrix representatives for some point-group operations, together with their square products which are useful for determining the properties of corepresentations in Section 12.5.

Table 12.2. Some $SU(2)$ representative matrices, $\varepsilon = \exp[2\pi i/12]$.

R	$\mathcal{D}^{(1/2)}(R)$	R^2	R	$\mathcal{D}^{(1/2)}(R)$	R^2
C_{2y}	$\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$	$\bar{E}$	C_{2z}	$\begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix}$	$\bar{E}$
C_{2x}	$\begin{pmatrix} 0 & -i \\ -i & 0 \end{pmatrix}$	$\bar{E}$	C_{2a}	$\frac{1}{\sqrt{2}} \begin{pmatrix} 0 & -1+i \\ 1+i & 0 \end{pmatrix}$	$\bar{E}$
C_{2b}	$\frac{1}{\sqrt{2}} \begin{pmatrix} 0 & -1-i \\ 1-i & 0 \end{pmatrix}$	$\bar{E}$	C_{2c}	$\frac{1}{\sqrt{2}} \begin{pmatrix} -i & i \\ i & i \end{pmatrix}$	$\bar{E}$
C_{2d}	$\frac{1}{\sqrt{2}} \begin{pmatrix} -i & -1 \\ 1 & i \end{pmatrix}$	$\bar{E}$	C_{2e}	$\frac{1}{\sqrt{2}} \begin{pmatrix} -i & -i \\ -i & i \end{pmatrix}$	$\bar{E}$
C_{2f}	$\frac{1}{\sqrt{2}} \begin{pmatrix} i & -1 \\ 1 & -i \end{pmatrix}$	$\bar{E}$	C_{31}^+	$\frac{1}{2} \begin{pmatrix} 1+i & 1-i \\ -1-i & 1-i \end{pmatrix}$	$\bar{C}_{31}^-$
C_{32}^+	$\frac{1}{2} \begin{pmatrix} 1+i & -1+i \\ 1+i & 1-i \end{pmatrix}$	$\bar{C}_{32}^-$	C_{33}^+	$\frac{1}{2} \begin{pmatrix} 1-i & -1-i \\ 1-i & 1+i \end{pmatrix}$	$\bar{C}_{33}^-$
C_{34}^+	$\frac{1}{2} \begin{pmatrix} 1-i & 1+i \\ -1+i & 1+i \end{pmatrix}$	$\bar{C}_{34}^-$	C_{31}^-	$\frac{1}{2} \begin{pmatrix} 1-i & -1+i \\ 1+i & 1+i \end{pmatrix}$	$\bar{C}_{31}^+$
C_{32}^-	$\frac{1}{2} \begin{pmatrix} 1-i & 1-i \\ -1+i & 1+i \end{pmatrix}$	$\bar{C}_{32}^+$	C_{33}^-	$\frac{1}{2} \begin{pmatrix} 1+i & 1+i \\ -1+i & 1-i \end{pmatrix}$	$\bar{C}_{33}^+$
C_{34}^-	$\frac{1}{2} \begin{pmatrix} 1+i & -1-i \\ 1-i & 1-i \end{pmatrix}$	$\bar{C}_{34}^+$	C_{3z}^+	$\begin{pmatrix} \varepsilon^2 & 0 \\ 0 & \varepsilon^{*2} \end{pmatrix}$	$\bar{C}_3^-$
C_{3z}^-	$\begin{pmatrix} \varepsilon^{*2} & 0 \\ 0 & \varepsilon^2 \end{pmatrix}$	$\bar{C}_3^+$	C_{6z}^+	$\begin{pmatrix} \varepsilon & 0 \\ 0 & \varepsilon^* \end{pmatrix}$	C_3^+
C_{6z}^-	$\begin{pmatrix} \varepsilon^* & 0 \\ 0 & \varepsilon \end{pmatrix}$	C_3^-	C_{4x}^+	$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 & -i \\ -i & 1 \end{pmatrix}$	$\bar{C}_{2x}$
C_{4y}^+	$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}$	C_{2y}	C_{4z}^+	$\frac{1}{\sqrt{2}} \begin{pmatrix} 1+i & 0 \\ 0 & 1-i \end{pmatrix}$	C_{2z}
C_{4x}^-	$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 & i \\ i & 1 \end{pmatrix}$	C_{2x}	C_{4y}^-	$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix}$	$\bar{C}_{2y}$
C_{4z}^-	$\frac{1}{\sqrt{2}} \begin{pmatrix} 1-i & 0 \\ 0 & 1+i \end{pmatrix}$	$\bar{C}_{2z}$			

Some examples of double-group operators

- (i) An
- n
- fold rotation
- C_n
- satisfies

$$C_n^n = \overline{E}, \quad C_n^{2n} = E, \quad (12.88)$$

which shows that $C_n^{-1} = \overline{E} C_n^{n-1}$.

- (ii) The inversion operator
- $\mathfrak{I}$
- commutes with all the rotation operators in
- $\mathfrak{DG}$
- , hence,

$$\mathfrak{I}^2 = E.$$

Consequently, the corresponding matrix representative of $\mathfrak{I}$ can be written as

$$\mathcal{D}(\mathfrak{I}) = \lambda \mathbb{I}, \quad \lambda = \pm 1, \quad (12.89)$$

so that when it operates on the spin states $|+\rangle$ and $|-\rangle$ we obtain

$$\mathfrak{I} |\pm\rangle = \lambda |\pm\rangle.$$

Physical observables involve quantities in the form

$$\mathfrak{I} \langle \psi_i(\mathbf{r}) | \alpha | \psi_j(\mathbf{r}) | \beta \rangle = \lambda^2 \langle (\mathfrak{I} \psi_i(\mathbf{r})) | \alpha | (\mathfrak{I} \psi_j(\mathbf{r})) | \beta \rangle,$$

where $|\alpha\rangle, |\beta\rangle$ are general spin states. This shows that they are independent of the value of λ . We can therefore choose $\lambda = 1$, and we obtain

$$\mathfrak{I} |\pm\rangle = + |\pm\rangle,$$

so that spinors have even parity.

- (iii) If we express a reflection operation
- σ
- as
- $\sigma = \mathfrak{I} C_2$
- , for some two-fold rotation
- C_2
- , we find that

$$\sigma^2 = C_2^2 = \overline{E}, \quad \sigma^{-1} = \overline{\sigma}. \quad (12.90)$$

- (iv) Expressing roto-reflections as
- $S_n = \mathfrak{I} C_2 C_n$
- , we find that

$$\begin{aligned} S_3 &= \mathfrak{I} C_2 C_3 = \mathfrak{I} C_6^5 = \mathfrak{I} \overline{C}_6^{-1}, \\ S_4 &= \mathfrak{I} C_4^3 = \mathfrak{I} \overline{C}_4^{-1}, \\ S_6 &= \mathfrak{I} C_6^4 = \mathfrak{I} \overline{C}_3^{-1}. \end{aligned} \quad (12.91)$$

Since $E, \overline{E}$ commute with all the elements of $\mathfrak{DG}$, the quotient subgroup

$$\mathcal{Q} = \frac{\mathfrak{DG}}{\{E, \overline{E}\}} \leftrightarrow \mathcal{G}$$

is a normal subgroup of $\mathfrak{DG}$, which is isomorphic to $\mathcal{G}$. Thus, we expect $\mathfrak{DG}$ to have Irreps with $\{E, \overline{E}\}$ as a kernel, such that

$$\Gamma(\overline{R}) = \mathbb{I} \times \Gamma(R) = \Gamma(R),$$

which allows us to engender an Irrep of $\mathfrak{DG}$ from every Irrep of $\mathcal{G}$. However, since $\mathfrak{DG}$, by definition, has more classes than $\mathcal{G}$, it has more Irreps. These Irreps will be called the extra Irreps of $\mathfrak{DG}$. Opechowski [56] has studied double groups extensively, and proposed several simplifying rules that help determine their number of classes and some of their extra Irreps:

Opechowski's rules

- (i) If a set of proper or improper rotations R through $2\pi/n$ form a class in the single-group, then the sets of double-group rotations, $R, \bar{R}$, form two separate classes.
- (ii) The case of $n = 2$ constitutes one exception to the rule of (i). This occurs when there is a another proper or improper π -rotation about an axis perpendicular to that of R ; in this case $R, \bar{R}$ belong to the same class of the double group.
- (iii) The characters of the extra Irreps must satisfy the relations

$$^{(\mu)}\chi(\bar{R}) = -^{(\mu)}\chi(R) \quad (12.92)$$

for every R in the double group. This implies that the characters of the exceptional case (ii) must vanish.

Example 12.1

As an example, we consider the double-group $\mathfrak{D}\mathcal{D}_4(\mathfrak{D}422)$, which has 16 elements. Using the rules of Opechowski, we find that, because C_2 is perpendicular to $2U_2, 2U_2^d, \bar{C}_2$ is in the same class as C_2 , similar arguments hold for the mutually perpendicular pairs U_2^1, U_2^2 and U_2^{d1}, U_2^{d2} . Hence, we have the seven classes:

$$\{E\}, \{\bar{E}\}, \{2C_4\}, \{2\bar{C}_4\}, \{C_2, \bar{C}_2\}, \{2U_2, 2\bar{U}_2\}, \{2U_2^d, 2\bar{U}_2^d\}.$$

We can engender the five Irreps $^{(1)}\Gamma$ – $^{(5)}\Gamma$ of $\mathfrak{D}\mathcal{D}_4$, given in Table 12.3, from the five Irreps of $\mathcal{D}_4$. It is easy in the present case to determine the characters of the extra Irreps:

- (i) Using the dimension sum rule, we find that the dimensions of each of the remaining three Irreps must be 2, since

$$1^2 + 1^2 + 1^2 + 1^2 + 2^2 + 2^2 + 2^2 = 16.$$

- (ii) The characters of all the two-fold rotations are 0, according to Opechowski's third rule.

Table 12.3. *Irreps of $\mathfrak{D}422$.*

		E	$\bar{E}$	$2C_4$	$2\bar{C}_4$	C_2 $\bar{C}_2$	$2U_2$ $2\bar{U}_2$	$2U_2^d$ $2\bar{U}_2^d$
$^{(1)}\Gamma$	A_1	1	1	1	1	1	1	1
$^{(2)}\Gamma$	A_2	1	1	1	1	1	–1	–1
$^{(3)}\Gamma$	B_1	1	1	–1	–1	1	1	–1
$^{(4)}\Gamma$	B_2	1	1	–1	–1	1	–1	1
$^{(5)}\Gamma$	E	2	2	0	0	–2	0	0
$^{(6)}\Gamma$	$\bar{E}_1$	2	–2	$\sqrt{2}$	$-\sqrt{2}$	0	0	0
$^{(7)}\Gamma$	$\bar{E}_2$	2	–2	$-\sqrt{2}$	$\sqrt{2}$	0	0	0

(iii) From the character orthogonality theorem we have

$$4 + 4 + 4 \times \chi^2(C_4) + 10 \times 0 = 16,$$

which yields

$$\chi(C_4) = \pm\sqrt{2},$$

from which we engender the two Irreps $^{(6)}\Gamma$ and $^{(7)}\Gamma$ of Table 12.3.

Example 12.2

$\mathfrak{D}23 (\mathfrak{DT})$

The double-group $\mathfrak{D}23 (\mathfrak{DT})$ has 24 elements:

$$E, \bar{E}, 3C_2, 3\bar{C}_2, 4C_3^+, 4\bar{C}_3^+, 4C_3^-, 4\bar{C}_3^-.$$

Applying Opechowski's rules we obtain the classes

$$\{E\}, \{\bar{E}\}, \{3C_2, 3\bar{C}_2\}, \{4C_3^+\}, \{4\bar{C}_3^+\}, \{4C_3^-\}, \{4\bar{C}_3^-\}.$$

Using the Irreps of 23, we obtain the single-valued Irreps A_1, B_1, B_2 , and T of Table 12.4.

We obtain the double-valued Irreps by taking the outer-products

$$\bar{E} = \mathcal{D}^{(1/2)} \otimes A_1,$$

$$^1\bar{F} = \mathcal{D}^{(1/2)} \otimes B_1,$$

$$^2\bar{F} = \mathcal{D}^{(1/2)} \otimes B_2,$$

obtained with the aid of Table 12.1, and displayed in Table 12.4.

Table 12.4. *Character table of 23 and $\mathfrak{D}23$.*

	E	$\bar{E}$	$3C_2$	$4C_3^+$	$4\bar{C}_3^+$	$4C_3^-$	$4\bar{C}_3^-$
	$3\bar{C}_2$						
A_1	1	1	1	1	1	1	1
B_1	1	1	1	ω	ω	ω^*	ω^*
B_2	1	1	1	ω^*	ω^*	ω	ω
T	3	3	-1	0	0	0	0
$\bar{E}$	2	-2	0	1	-1	1	-1
$^1\bar{F}$	2	-2	0	ω^*	$-\omega^*$	ω	$-\omega$
$^2\bar{F}$	2	-2	0	ω	$-\omega$	ω^*	$-\omega^*$

$$\omega = \exp(i2\pi/3)$$

Example 12.3

Extra Irreps of $\mathfrak{D}432$

According to the above listed criteria we obtain the class structure of Table 12.5 for the double group $\mathfrak{D}432$.

Here, we construct the extra Irreps using outer-products of the form

$$^{(\mu)}\Gamma(432) \otimes \mathcal{D}^{(1/2)},$$

and check for its reducibility via the character orthogonality theorem. We start with

$$\Gamma = {}^{(1)}\Gamma(432) \otimes \mathcal{D}^{(1/2)},$$

and using Table 12.1 we find that

$$\frac{1}{48} \sum_{R \in \mathfrak{D}432} |\chi(R)|^2 = 1,$$

thus, this Rep is irreducible, and we identify it as the two-dimensional Irrep ${}^{(6)}\Gamma$. Next, we check

$$\Gamma = {}^{(2)}\Gamma(432) \otimes \mathcal{D}^{(1/2)},$$

and similarly find that it is a second two-dimensional Irrep ${}^{(7)}\Gamma$. Finally, inspection of the remaining Irreps of 432, reveals that the four-dimensional Rep

$${}^{(8)}\Gamma = {}^{(3)}\Gamma \otimes \mathcal{D}^{(1/2)}$$

is the last Irrep of $\mathfrak{D}432$, since we have

$$\sum_{\alpha=1}^8 d_{\alpha}^2 = 48.$$

Table 12.5. *Classes of $\mathfrak{D}O$.*

$\mathcal{C}_1 :$	E													
$\mathcal{C}_2 :$	$\bar{E}$													
$\mathcal{C}_3 :$	$C_{2x},$	$C_{2y},$	$C_{2z},$	$\bar{C}_{2x},$	$\bar{C}_{2y},$	$\bar{C}_{2z}$								
$\mathcal{C}_4 :$	$C_{31}^-,$	$C_{32}^-,$	$C_{33}^-,$	$C_{34}^-,$	$C_{31}^+,$	$C_{32}^+,$	$C_{33}^+,$	$C_{34}^+,$						
$\mathcal{C}_5 :$	$\bar{C}_{31}^-,$	$\bar{C}_{32}^-,$	$\bar{C}_{33}^-,$	$\bar{C}_{34}^-,$	$\bar{C}_{31}^+,$	$\bar{C}_{32}^+,$	$\bar{C}_{33}^+,$	$\bar{C}_{34}^+,$						
$\mathcal{C}_6 :$	$C_{4x}^-,$	$C_{4y}^-,$	$C_{4z}^-,$	$C_{4x}^+,$	$C_{4y}^+,$	$C_{4z}^+,$								
$\mathcal{C}_7 :$	$\bar{C}_{4x}^-,$	$\bar{C}_{4y}^-,$	$\bar{C}_{4z}^-,$	$\bar{C}_{4x}^+,$	$\bar{C}_{4y}^+,$	$\bar{C}_{4z}^+,$								
$\mathcal{C}_8 :$	$U_{2a},$	$U_{2b},$	$U_{2c},$	$U_{2d},$	$U_{2e},$	$U_{2f},$	$\bar{U}_{2a},$	$\bar{U}_{2b},$	$\bar{U}_{2c}$	$\bar{U}_{2d},$	$\bar{U}_{2e},$	$\bar{U}_{2f}$		

The Irreps of $\mathfrak{D}432$ are listed in Table 12.6.

Table 12.6. Irreps of $\mathfrak{D}432$ ($\mathfrak{D}O$).

			C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
Γ_1	Γ_1	A_1	1	1	1	1	1	1	1	1
Γ_2	Γ_2	A_2	1	1	1	1	1	-1	-1	-1
Γ_3	Γ_{12}	E	2	2	2	-1	-1	0	0	0
Γ_4	Γ_{15}	T_1	3	3	-1	0	0	1	1	-1
Γ_5	Γ'_{25}	T_2	3	3	-1	0	0	-1	-1	1
Γ_6	$\bar{\Gamma}_{12}(1/2)$	$\bar{E}_{1/2}$	2	-2	0	1	-1	$\sqrt{2}$	$-\sqrt{2}$	0
Γ_7	$\bar{\Gamma}_{12}$	$\bar{E}$	2	-2	0	1	-1	$-\sqrt{2}$	$\sqrt{2}$	0
Γ_8	$\bar{\Gamma}_{3/2}$	$\bar{G}_{3/2}$	4	-4	0	-1	1	0	0	0

Table 12.7. The 32 double-point-groups.

Point-group	Generating elements	Defining relations
$1 (\mathcal{C}_1)$	$\bar{E}$	
$\bar{1} (\mathcal{C}_i)$	$\bar{E}, I$	$\bar{E}^2 = I^2 = E, \bar{E}I = I\bar{E}$
$2 (\mathcal{C}_2)$	C_{2z}	$C_{2z}^4 = E$
$m (\mathcal{C}_{1h})$	σ_z	$\sigma_z^4 = E$
$2/m (\mathcal{C}_{2h})$	σ_z, I	$\sigma_z^4 = I^2 = E, \sigma_z I = I\sigma_z$
$222 (\mathcal{D}_2)$	C_{2z}, C_{2y}	$C_{2z}^4 = C_{2y}^4 = E, C_{2z}^3 C_{2y} = C_{2y} C_{2z}$
$mm2 (\mathcal{C}_{2v})$	C_{2z}, σ_y	$C_{2z}^4 = \sigma_y^4 = E, C_{2z}^3 \sigma_y = \sigma_y C_{2z}$
$mmm (\mathcal{D}_{2h})$	C_{2z}, C_{2y}, I	$\mathcal{D}_2 \otimes C_i$
$4 (\mathcal{C}_4)$	C_4^+	$(C_4^+)^8 = E$
$\bar{4} (\mathcal{S}_4)$	S_4^-	$(S_4^-)^8 = E$
$4/m (\mathcal{C}_{4h})$	C_4^+, I	
$422 (\mathcal{D}_4)$	C_{4z}^+, C_{2x}	
$4mm (\mathcal{C}_{4v})$	C_{4z}^+, σ_x	
$\bar{4}2m (\mathcal{D}_{2d})$	S_{4z}^-, C_{2x}	
$4/mmm (\mathcal{D}_{4h})$	C_{4z}^+, C_{2x}, I	
$3 (\mathcal{C}_3)$	C_3^+	
$\bar{3} (\mathcal{C}_{3i})$	S_6^+, I	
$32 (\mathcal{D}_3)$	C_3^+, U_2'	
$3m (\mathcal{C}_{3v})$	C_{3z}^+, σ_1	
$\bar{3}m (\mathcal{D}_{3d})$	C_{3z}^+, U_1, I	

Table 12.7. (*cont.*)

Point-group	Generating elements	Defining relations
$6 (C_6)$	C_{6z}^+	
$\bar{6} (C_{3h})$	S_3^-	
$6/m (C_{6h})$	C_{6z}^+, I	
$622 (D_6)$	C_{6z}^+, U_1'	
$6mm (C_{6v})$	C_{6z}^+, σ_{d1}	
$\bar{6}2m (D_{3h})$	S_{3z}^-, U_1'	
$6/mmm (D_{2h})$	C_{6z}^+, U_1', I	
$23 (T)$	$C_{3z}^-, U_x, \bar{U}_y$	
$m3 (T_h)$	$C_{3z}^-, U_x, \bar{U}_y, I$	
$432 (O)$	$C_{4x}^+, \bar{C}_{31}^-, C_{2b}$	
$\bar{4}3m (T_d)$	$S_{4z}^-, \bar{C}_{31}^-, \sigma_{db}$	
$m3m (O_h)$	$C_{4z}^+, \bar{C}_{31}^-, C_{2b}, I$	

In the above examples it was easy, using Opechowski's rules and other general sum rules, to determine the characters of the extra Irreps. This may not be possible in the general case. To determine the extra Irreps, one might have to resort either to employing the Burnside/Dixon methods, or to finding a group isomorphic to $\mathfrak{DG}$ whose Irreps are known.

Table 12.7 gives a list of the 32 double-point-groups, together with their generating elements and relations.

12.4 Magnetic and color groups

Alternative presentations of the topics discussed in this section may be found in references [13, 15, 58, 59, 60, 61, 62, 64, 65, 66, 67, 68]. The description of geometrical symmetry by group theoretical methods reached maturity at the beginning of the twentieth century with the work of Federov, Schoenflies, and others. Wigner's seminal work in the 1930s demonstrated the power of applying group theory methodology to physical problems. Thence it triggered a myriad of applications in many physical systems. In 1951 Shubnikov proposed the idea of antisymmetry operations. In this context, in addition to the Cartesian coordinate transformations which form the basis of the Federov symmetry groups, Shubnikov introduced a new operation, which we denote $\mathcal{C}$ for chromos (color), which acts only on an extra degree of freedom (DOF) σ , defined at each crystallographic site. σ assumes two possible values, ± 1 , or two colors, black and white! – a dichromatic group. The effect of $\mathcal{C}$ is to switch the value of σ between $+1$ and -1 , or between black and white. Since $\mathcal{C}$ does not operate on Cartesian coordinates, it commutes with all the operations of the Federov groups. The combination of $\mathcal{C}$ with a Federov group then gives rise to the

dichromatic groups. The similarities between Shubnikov's operator and the application of time-reversal to permanent magnetic moments in magnetic crystals was immediately realized, i.e. in the case of magnetic crystals, replacing $\mathcal{C}$ by Θ would produce symmetry groups isomorphous to the Shubnikov groups. Recently, however, it has also been realized that many physical systems possess other internal DOFs that remain hidden to the simplistic description of geometric symmetries. We encounter many situations where, in order to maintain invariance under geometric operation in the presence of some DOF, it is necessary to accompany such an operation by, say, permutations among the possible values, or colors, the DOF may assume, which may be more than two! Such cases give rise to *polychromatic* groups. Again, the operator $\mathcal{C}$ commutes with all the geometric operators since color transformations do not affect geometrical ones. The interpretation of the Landau theory of continuous phase transitions in terms of the permutational color groups can be given as an example [69].

The theory of crystallographic color groups is still a relatively new group theoretical approach in the description of the structure and physical properties of crystals [66]. Many problems of solid state physics connected with the determination of the relationships between the symmetry group of the crystal, its subgroups, factor groups, and their representations can effectively be solved using the color-group theory and the corresponding tables of groups [70].

12.4.1 Classification of magnetic or Shubnikov groups

Shubnikov point-groups

For the moment, we restrict the internal degrees of freedom to just two: black and white (+ and −). Such is the case of spin-1/2 particles. A change of state of this internal property can be effected with the aid of the operator $\mathcal{C}$, which changes color or sign, i.e. black into white or vice versa, so that $\mathcal{C}^2 = E$. Furthermore, we may augment the set of ordinary symmetry groups by the inclusion of such an operator $\mathcal{C}$ according to the following classification:

- (i) **Color or Shubnikov groups of type I** These groups describe objects that are monochromatic, i.e. having a definite color, say white. The operator $\mathcal{C}$ is then excluded from such groups. In fact, they are identical to the geometric point-groups,

$$\mathcal{M}^I = \mathcal{G}. \quad (12.93)$$

Consequently, we have 32 monochromatic point-groups.

- (ii) **Color or Shubnikov groups of type II (the gray groups)** Systems with this symmetry type possess identical and overlapping distributions of two colors, say black and white, as shown in Figure 12.2, hence the name gray. Such groups may describe the symmetry of paramagnetic and diamagnetic systems where there are equal numbers of (+) and (−) spin states, and the application of the operator $\mathcal{C}$ will leave the system invariant. The corresponding symmetry group can be expressed as the coset sum

$$\begin{aligned} \mathcal{M}^{II} &= \mathcal{G} \oplus \mathcal{C}\mathcal{G}, \\ &= \mathcal{G} \otimes \{E, \mathcal{C}\}, \end{aligned} \quad (12.94)$$

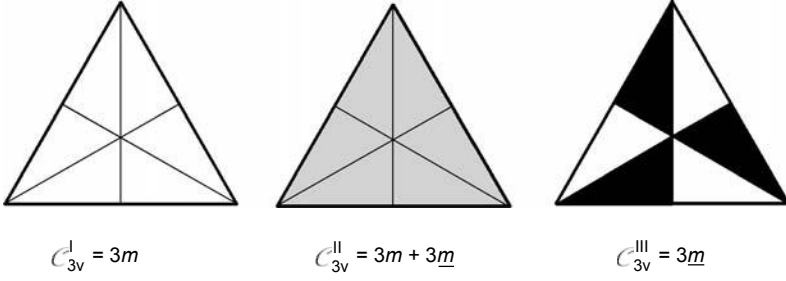


Fig. 12.2. Color point-groups of types I, II, and III, associated with C_{3v} .

where $\mathcal{G}$ is the geometric point-group associated with the atomic arrangement of the system. We find that $\mathcal{G}$ is an invariant subgroup of $\mathcal{M}^{\text{II}}$ with index 2, and that $\mathcal{C} \in \mathcal{M}^{\text{II}}$ and commutes with all the elements of $\mathcal{G}$.

Figure 12.2 shows the gray point-group C_{3v}^{II} with elements E , C_3 , C_3^{-1} , σ_1 , σ_2 , σ_3 , $\mathcal{C}$, $\mathcal{C}\sigma_1$, $\mathcal{C}\sigma_2$, $\mathcal{C}\sigma_3$.

- (iii) **Dichromatic or Shubnikov groups of type III** Groups that belong to this class do not contain $\mathcal{C}$ as a separate element, but include elements comprising products involving $\mathcal{C}$. To elucidate the role of such groups in describing the symmetry of physical systems, we consider the simple *dichromatic* equilateral triangle shown in Figure 12.2.

We first notice that $\mathcal{C}$ is not a symmetry operation of the colored triangle. Moreover, among the elements of $\mathcal{G} = C_{3v}$, we find that those of the subgroup C_3 leave the colored triangle invariant, while all the reflection operations do not. However, if we multiply these reflections by $\mathcal{C}$, the compound operation leaves the triangle invariant. Thus, the elements, E , C_3 , C_3^{-1} , $\mathcal{C}\sigma_1$, $\mathcal{C}\sigma_2$, $\mathcal{C}\sigma_3$, form a group $\mathcal{M}^{\text{III}} = C_{3v}^{\text{III}} \equiv 3\bar{m}$ with the same composition law as C_{3v} , which we call a color group. We notice that, in contrast to the gray group C_{3v}^{II} , C_{3v}^{III} does not have $\mathcal{C}$ as an element by itself, i.e. it does not have the product $\mathcal{C}E$. The structure of C_{3v}^{III} is typical of all color point-groups, and we may write

$$\mathcal{M}^{\text{III}} = \mathcal{N} \oplus \mathcal{C} (\mathcal{G} - \mathcal{N}) . \quad (12.95)$$

Alternatively, we can take any element A of $\mathcal{G} - \mathcal{N}$ and form the product $\mathcal{A} = \mathcal{C}A$, and rewrite (12.95) as

$$\mathcal{M}^{\text{III}} = \mathcal{N} \oplus \mathcal{A}\mathcal{N}, \quad (12.96)$$

and since $\mathcal{N}$ is a subgroup of $\mathcal{M}^{\text{III}}$ of index 2, it is a normal subgroup. In principle, we can take any ordinary point-group $\mathcal{G}$ of even order, determine all its subgroups of index 2, and construct from each a new color group! That is exactly what we did with C_{3v} , which is of order 6, and has only one subgroup of index 2, namely C_3 .

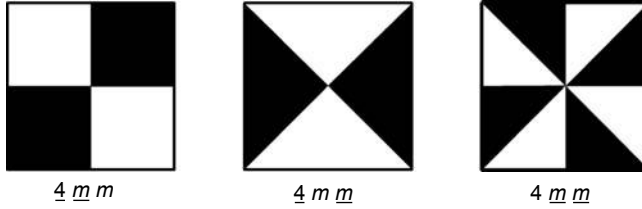


Fig. 12.3. Color point-groups of type III, associated with $C_{4v} = 4mm$.

As another example of this construction, let us consider C_{4v} , which is of order 8. It has two subgroups of index 2, C_4 and C_{2v} . The construction of the color groups gives

$$\begin{aligned} 4\bar{m}\bar{m} &= C_4 \oplus \mathcal{C}(\sigma_1, \sigma_2, \sigma_{d1}, \sigma_{d2}), \\ 4m\bar{m} &= C_{2v} \oplus \mathcal{C}(C_4, C_4^{-1}, \sigma_{d1}, \sigma_{d2}), \\ \bar{4}m\bar{m} &= C_{2v}^d \oplus \mathcal{C}(C_4, C_4^{-1}, \sigma_1, \sigma). \end{aligned} \quad (12.97)$$

The corresponding colored squares are shown in Figure 12.3. The number of subgroups of index 2 of a point-group $\mathcal{G}$ is given by

$$2^r - 1; \text{ where } r = \text{number of independent generators of } \mathcal{G} \quad (12.98)$$

This constitutes the maximum number of color groups that may be constructed from $\mathcal{G}$; however, the actual number is found by inspection of the different point-groups. In all, there are 58 dichromatic point-groups, as listed in Table 12.8.

Example 12.4

It is possible to identify the subgroups $\mathcal{N}$ of index 2 of a group $\mathcal{G}$ as being in one-to-one correspondence with the kernels of those one-dimensional Irreps which consist entirely of +1 and -1 (which occur in equal numbers). Hence, to obtain all magnetic groups of this type we need only search systematically through the character table for such Irreps. In the case of $C_{4v}(4mm)$ we have:

C_{4v}	E	C_2	$C_4^\pm$	σ_x, σ_y	σ_{da}, σ_{db}	$\mathcal{N}$	$\mathcal{M}$
A_2	1	1	1	-1	-1	C_4	$4\bar{m}\bar{m}$
B_1	1	1	-1	1	-1	C_{2v}	$\bar{4}m\bar{m}$
B_2	1	1	-1	-1	1	C_{2v}	$4m\bar{m}$

Table 12.8. *Magnetic (dichromatic) point-groups.*

	Inter- national	Shub- nikov	Schoenflies		Inter- national	Shub- nikov	Schoenflies
1	$\bar{1}$	$\bar{2}$	$C_i(C_1)$	30	$3\bar{2}$	$3 : \bar{2}$	$\mathcal{D}_3(C_3)$
2	$\underline{2}$	$\underline{2}$	$C_2(C_1)$	31	$3\bar{m}$	$3 \cdot \bar{m}$	$\mathcal{C}_{3v}(C_3)$
3	$\underline{m}$	$\underline{m}$	$C_s(C_1)$	32	$\bar{6}$	$3 : \bar{m}$	$\mathcal{C}_{3h}(C_3)$
4	$\underline{2}/\underline{m}$	$\underline{2} : \underline{m}$	$\mathcal{C}_{2h}(C_i)$	33	$\bar{3}$	$\bar{6}$	$\mathcal{C}_{3i}(C_3)$
5	$\underline{2}/\underline{m}$	$\underline{2} : \underline{m}$	$\mathcal{C}_{2h}(C_2)$	34	$\bar{3}\underline{m}$	$\bar{6}\underline{m}$	$\mathcal{D}_{3d}(C_{3i})$
6	$\underline{2}/\underline{m}$	$\underline{2} : \underline{m}$	$\mathcal{C}_{2h}(C_s)$	35	$\bar{3}\underline{m}$	$\bar{6}\underline{m}$	$\mathcal{D}_{3d}(\mathcal{D}_3)$
7	$\underline{2mm}$	$\underline{2} \cdot \underline{m}$	$\mathcal{C}_{2v}(C_2)$	36	$\bar{3}m$	$\bar{6} \cdot m$	$\mathcal{D}_{3d}(\mathcal{C}_{3v})$
8	$\underline{2mm}$	$\underline{2} \cdot m$	$\mathcal{C}_{2v}(C_s)$	37	$\bar{6}\underline{m}2$	$\underline{m} \cdot 3 : m$	$\mathcal{D}_{3h}(C_3)$
9	$\underline{222}$	$\underline{2} : \underline{2}$	$\mathcal{D}_2(C_2)$	38	$\bar{6}\underline{m}2$	$\underline{m} \cdot 3 : \underline{m}$	$\mathcal{D}_{3h}(\mathcal{D}_3)$
10	$\underline{mmm}$	$\underline{m} \cdot \underline{2} : m$	$\mathcal{D}_{2h}(C_{2h})$	39	$\bar{6}\underline{m}2$	$\underline{m} \cdot 3 : \underline{m}$	$\mathcal{D}_{3h}(C_{3v})$
11	$\underline{mmm}$	$\underline{m} \cdot \underline{2} : \underline{m}$	$\mathcal{D}_{2h}(\mathcal{D}_2)$	40	$\underline{6}$	$\underline{6}$	$\mathcal{C}_6(C_3)$
12	$\underline{mmm}$	$\underline{m} \cdot \underline{2} : \underline{m}$	$\mathcal{D}_{2h}(C_{2v})$	41	$\underline{6}2$	$\underline{6} : \underline{2}$	$\mathcal{D}_6(C_6)$
13	$\bar{4}$	$\underline{4}$	$\mathcal{C}_4(C_2)$	42	$\underline{6}2$	$\underline{6} : \underline{2}$	$\mathcal{D}_6(\mathcal{D}_3)$
14	$\bar{4}$	$\bar{4}$	$\mathcal{S}_4(C_2)$	43	$\underline{6mm}$	$\underline{6} \cdot \underline{m}$	$\mathcal{C}_{6v}(C_6)$
15	$\underline{4}/\underline{m}$	$\underline{4} : m$	$\mathcal{C}_{4h}(C_{2h})$	44	$\underline{6mm}$	$\underline{6} \cdot m$	$\mathcal{C}_{6v}(C_{3v})$
16	$\underline{4}/\underline{m}$	$\underline{4} : \underline{m}$	$\mathcal{C}_{4h}(C_4)$	45	$\underline{6}/\underline{m}$	$\underline{6} : \underline{m}$	$\mathcal{C}_{6h}(C_{3i})$
17	$\underline{4}/\underline{m}$	$\underline{4} : \underline{m}$	$\mathcal{C}_{4h}(\mathcal{S}_4)$	46	$\underline{6}/\underline{m}$	$\underline{6} : \underline{m}$	$\mathcal{C}_{6h}(C_6)$
18	$\underline{4}2$	$\underline{4} : \underline{2}$	$\mathcal{D}_4(C_4)$	47	$\underline{6}/\underline{m}$	$\underline{6} : m$	$\mathcal{C}_{6h}(C_{3h})$
19	$\underline{4}2$	$\underline{4} : \underline{2}$	$\mathcal{D}_4(\mathcal{D}_2)$	48	$\underline{6}/\underline{mmm}$	$\underline{m} \cdot \underline{6} : m$	$\mathcal{D}_{6h}(C_{6h})$
20	$\underline{4mm}$	$\underline{4} \cdot \underline{m}$	$\mathcal{C}_{4v}(C_4)$	49	$\underline{6}/\underline{mmm}$	$\underline{m} \cdot \underline{6} : \underline{m}$	$\mathcal{D}_{6h}(\mathcal{D}_{3d})$
21	$\underline{4mm}$	$\underline{4} \cdot m$	$\mathcal{C}_{4v}(C_{2v})$	50	$\underline{6}/\underline{mmm}$	$\underline{m} \cdot \underline{6} : \underline{m}$	$\mathcal{D}_{6h}(\mathcal{D}_6)$
22	$\bar{4}2\underline{m}$	$\bar{4} \cdot \underline{m}$	$\mathcal{D}_{2d}(\mathcal{S}_4)$	51	$\underline{6}/\underline{mmm}$	$\underline{m} \cdot \underline{6} : \underline{m}$	$\mathcal{D}_{6h}(C_{6v})$
23	$\bar{4}2\underline{m}$	$\bar{4} \cdot \underline{m}$	$\mathcal{D}_{2d}(\mathcal{D}_2)$	52	$\underline{6}/\underline{mmm}$	$\underline{m} \cdot \underline{6} : m$	$\mathcal{D}_{6h}(\mathcal{D}_{3h})$
24	$\bar{4}2m$	$\bar{4} \cdot m$	$\mathcal{D}_{2d}(C_{2v})$	53	$\underline{m}3$	$\bar{6}/2$	$\mathcal{I}_h(T)$
25	$\underline{4}/\underline{mmm}$	$\underline{m} \cdot \underline{4} : m$	$\mathcal{D}_{4h}(C_{4h})$	54	$\bar{4}3\underline{m}$	$3/\bar{4}$	$\mathcal{I}_d(T)$
26	$\underline{4}/\underline{mmm}$	$\underline{m} \cdot \underline{4} : m$	$\mathcal{D}_{4h}(\mathcal{D}_{2h})$	55	$\underline{4}3$	$3/\underline{4}$	$\mathcal{O}(T)$
27	$\underline{4}/\underline{mmm}$	$\underline{m} \cdot \underline{4} : \underline{m}$	$\mathcal{D}_{4h}(\mathcal{D}_4)$	56	$\underline{m}3\underline{m}$	$\bar{6}/\underline{4}$	$\mathcal{O}_h(\mathcal{I}_h)$
28	$\underline{4}/\underline{mmm}$	$\underline{m} \cdot \underline{4} : \underline{m}$	$\mathcal{D}_{4h}(C_{4v})$	57	$\underline{m}3\underline{m}$	$\bar{6}/4$	$\mathcal{O}_h(\mathcal{O})$
29	$\underline{4}/\underline{mmm}$	$\underline{m} \cdot \underline{4} : \underline{m}$	$\mathcal{D}_{4h}(\mathcal{D}_{2d})$	58	$\underline{m}3m$	$\bar{6}/\underline{4}$	$\mathcal{O}_h(\mathcal{I}_d)$

Dichromatic space-groups

Dichromatic space-groups have the form

$$\mathbb{M} = \mathbb{S} + \mathbb{C}R\mathbb{S}, \quad (12.99)$$

where $\mathbb{S}$ is a Fedorov group, and R cannot be chosen as the identity. In this case the group

$$\mathbb{S}' = \mathbb{S} + R\mathbb{S} \quad (12.100)$$

is also a Fedorov group, or a color group of type I. Groups of this type can be determined by taking a Fedorov group $\mathbb{S}'$ and exhausting all subgroups of index 2. There are 1191 such groups which are crystallographically distinguishable.

- (i) **Dichromatic Bravais lattices** The concept of color may equally be applied to translational symmetries as it is applied to point-group symmetries. In that sense we can construct dichromatic Bravais lattices by introducing a colored translation $\mathbb{C}\tau_0$, where τ_0 cannot be the identity. A dichromatic translation group $\mathbb{T}_c$ is then defined as

$$\mathbb{T}_c = \mathbb{T}_2 + \mathbb{C}\tau_0 \mathbb{T}_2, \quad (12.101)$$

where $\mathbb{T}_2$ is a subgroup of one of the ordinary, or monochromatic, 14 Bravais lattices $\mathbb{T}$, with index 2.

In two-dimensions, 5 extra dichromatic Bravais nets, displayed in Figure 12.4, can be constructed.

Equation (12.101) allows us to delineate the restrictions on τ_0 in three-dimensions. It can be shown, using the concepts of arithmetic classes, that any $\mathbb{T}$ has exactly seven subgroups of index 2, which are given in terms of its primitive vectors

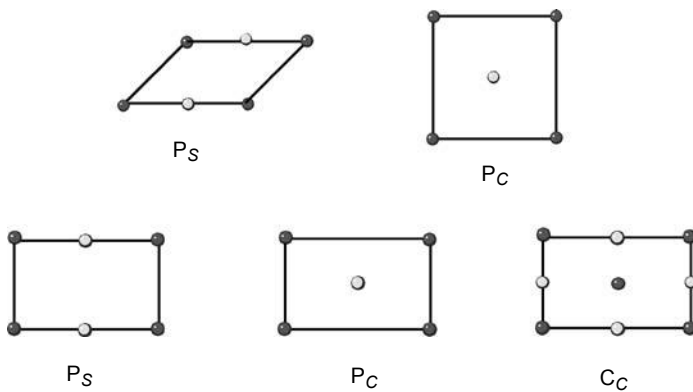


Fig. 12.4. Two-dimensional dichromatic Bravais nets.

$\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$, as:

$$\begin{aligned}
 \tau_0 = \mathbf{a}_1 & \rightarrow \begin{cases} 2\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3 \\ 2\mathbf{a}_1, \mathbf{a}_1 + \mathbf{a}_2, \mathbf{a}_3 \\ 2\mathbf{a}_1, \mathbf{a}_1 + \mathbf{a}_2, \mathbf{a}_1 + \mathbf{a}_3 \end{cases} \\
 \tau_0 = \mathbf{a}_2 & \rightarrow \begin{cases} \mathbf{a}_1, 2\mathbf{a}_2, \mathbf{a}_3 \\ 2\mathbf{a}_2, \mathbf{a}_2 + \mathbf{a}_3, \mathbf{a}_1 \end{cases} \\
 \tau_0 = \mathbf{a}_3 & \rightarrow \begin{cases} \mathbf{a}_1, \mathbf{a}_2, 2\mathbf{a}_3 \\ 2\mathbf{a}_3, \mathbf{a}_3 + \mathbf{a}_1, \mathbf{a}_2 \end{cases}
 \end{aligned} \tag{12.102}$$

With the aid of (12.102) and the concept of class equivalence, it is possible to construct 22 dichromatic Bravais classes, in addition to the 14 three-dimensional monochromatic Bravais classes.

A list of these dichromatic Bravais classes, together with the associated τ_0 is given in Table 12.9 and displayed in Figure 12.5.

Since a space-group comprises a combination of some Bravais lattice with a point subgroup of its holohedry, it is possible to construct dichromatic space-groups by combining either a dichromatic point-group with a monochromatic Bravais lattice or vice-versa.

Consequently, when classifying dichromatic space-groups, we should specify the color type of the associated Bravais lattice. This is effected by splitting dichromatic space-groups into two types:

- (a) **Type III** dichromatic space-groups involve combinations of monochromatic Bravais lattice/dichromatic point-group. We start with a subgroup $\mathbb{N}$ of index 2 in a Fedorov group $\mathbb{S}$, and construct the corresponding dichromatic space-group as

$$\mathbb{M}^{\text{III}} = \mathbb{N} + \mathbb{C}(\mathbb{S} - \mathbb{N}), \tag{12.103}$$

such that $(\mathbb{S} - \mathbb{N})$ does not contain pure translations. In such cases $\mathbb{S}$ and $\mathbb{M}^{\text{III}}$ are t-equal. There are 674 space-groups of this type.

- (b) **Type IV** dichromatic space-groups, are constructed by combining a dichromatic Bravais lattice with a given Fedorov space-group as

$$\mathbb{M}^{\text{IV}} = \mathbb{S} + \mathbb{C}\tau_0\mathbb{S}. \tag{12.104}$$

$\mathbb{M}^{\text{IV}}$ and $\mathbb{S}$ are k-equal. There are 517 type IV dichromatic space-groups.

Table 12.9. *The dichromatic Bravais lattices.*

Crystal system	Ordinary lattice	Dichromatic ^a lattice	τ_0
Triclinic	P	P_s	$\frac{1}{2}\mathbf{a}_i$
Monoclinic	P	P_b	$\frac{1}{2}\mathbf{a}_3$
		P_a	$\frac{1}{2}\mathbf{a}_2$
		P_C	$\frac{1}{2}[\mathbf{a}_2 + \mathbf{a}_3]$
		C_c	$\frac{1}{2}\mathbf{a}_1$
Orthorhombic	C	C_a	$\frac{1}{2}[\mathbf{a}_2 + \mathbf{a}_3]$
		$P_c (P_a)$	$\frac{1}{2}\mathbf{a}_3 (\frac{1}{2}\mathbf{a}_2)$
		$P_C (P_A)$	$\frac{1}{2}[\mathbf{a}_1 + \mathbf{a}_2] (\frac{1}{2}[\mathbf{a}_1 + \mathbf{a}_3])$
		P_I	$\frac{1}{2}(\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3)$
	C	C_c	$\frac{1}{2}\mathbf{a}_3$
		C_a	$\frac{1}{2}(\mathbf{a}_1 + \mathbf{a}_2)$
		C_A	$\frac{1}{2}(\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3)$
		A_a	$\frac{1}{2}\mathbf{a}_2$
	A	A_c	$\frac{1}{2}(\mathbf{a}_1 + \mathbf{a}_3)$
		A_C	$\frac{1}{2}(\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3)$
		F_s	$\frac{1}{2}(\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3)$
		I_c	$\frac{1}{2}(\mathbf{a}_1 + \mathbf{a}_2)$
Tetragonal	P	P_c	$\frac{1}{2}\mathbf{a}_3$
		P_C	$\frac{1}{2}(\mathbf{a}_1 + \mathbf{a}_2)$
		P_I	$\frac{1}{2}(\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3)$
		I	$\frac{1}{2}(\mathbf{a}_1 + \mathbf{a}_2)$
Trigonal	R	R_I	$\frac{1}{2}(\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3)$
Hexagonal	P	P_c	$\frac{1}{2}\mathbf{a}_3$
Cubic	P	P_I	$\frac{1}{2}(\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3)$
	F	F_s	$\frac{1}{2}(\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3)$
	I	—	—

^a The labeling of the dichromatic Bravais lattices follows the International notation, where the b -axis is taken as the two-fold axis: $b \rightarrow \mathbf{a}_3$, $c \rightarrow \mathbf{a}_1$, $a \rightarrow \mathbf{a}_2$. Lower-case subscripts reflect the axis of translation, while upper-case subscripts represent the centering face.

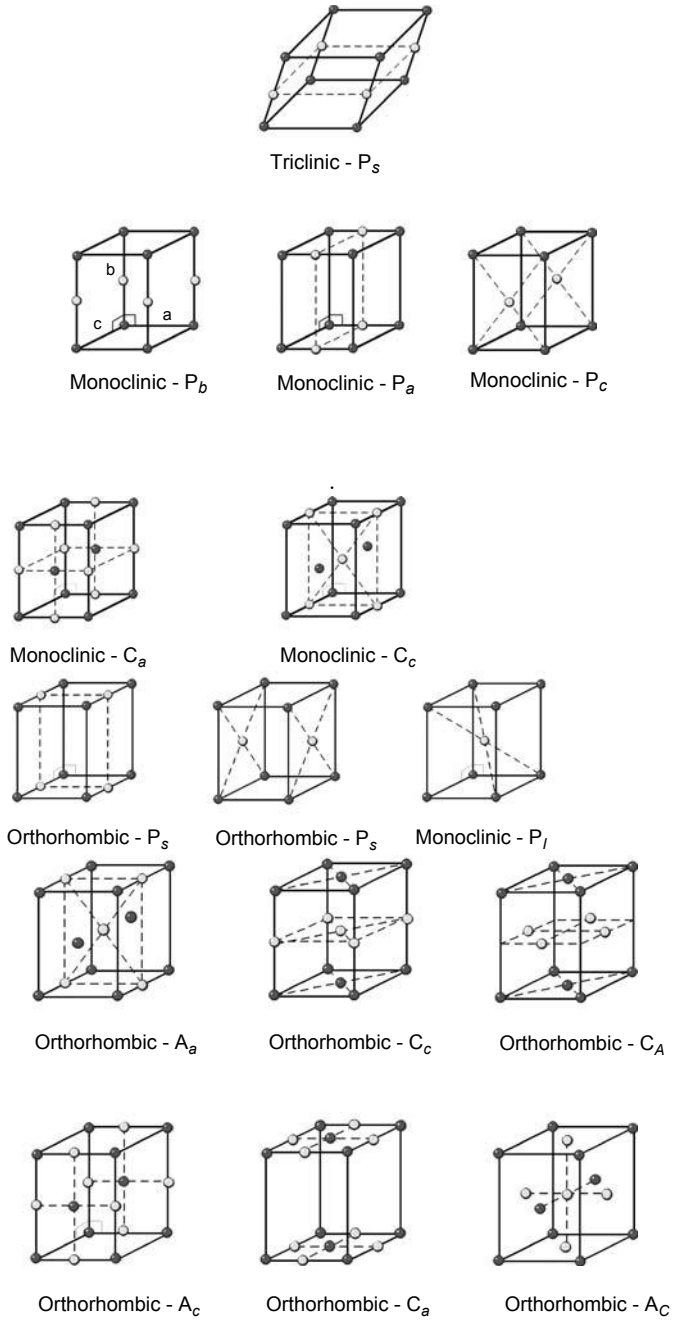
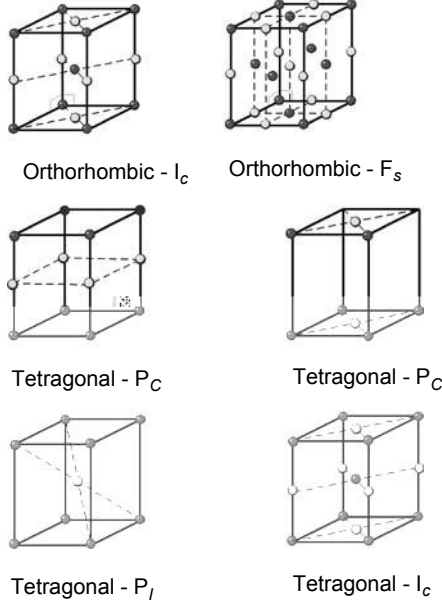


Fig. 12.5. Three-dimensional dichromatic Bravais lattices.



12.5. (cont.)

Example 12.5

Dichromatic space-groups associated with $P4_2/mnm$ ($\mathbb{D}_{4h}^{14}$)

- (i) **Dichromatic space-groups of type III** The monochromatic Bravais lattice of this system is a primitive tetragonal, and the coset representatives of the factor-group, isomorphic to the point-group $\mathcal{D}_{4h}$, are

$$\begin{aligned}
 &(E|\mathbf{0}), (C_4|\boldsymbol{\tau}), (C_4^{-1}|\boldsymbol{\tau}), (C_2|\mathbf{0}), (C_{2xy}|\mathbf{0}), (C_{2x\bar{y}}|\mathbf{0}), (C_{2x}|\boldsymbol{\tau}), (C_{2y}|\boldsymbol{\tau}), \\
 &(I|\mathbf{0}), \quad (\sigma_h|\mathbf{0}) = (C_2|\mathbf{0})(I|\mathbf{0}), \\
 &(S_4|\boldsymbol{\tau}) = (C_4^{-1}|\boldsymbol{\tau})(I|\mathbf{0}), \quad (S_4^{-1}|\boldsymbol{\tau}) = (C_4|\boldsymbol{\tau})(I|\mathbf{0}), \\
 &(\sigma_{xy}|\mathbf{0}) = (C_{2xy}|\mathbf{0})(I|\mathbf{0}), \quad (\sigma_{x\bar{y}}|\mathbf{0}) = (C_{2x\bar{y}}|\mathbf{0})(I|\mathbf{0}), \\
 &(\sigma_x|\boldsymbol{\tau}) = (C_{2x}|\boldsymbol{\tau})(I|\mathbf{0}), \quad (\sigma_y|\boldsymbol{\tau}) = (C_{2y}|\boldsymbol{\tau})(I|\mathbf{0}).
 \end{aligned}$$

Next, we construct the gray space-group associated with the Fedorov space-group $P4_2/mnm$, namely

$$P4_2/mnm\underline{1} = P4_2/mnm + \Theta P4_2/mnm.$$

	Nonunitary	Unitary

Nonmagnetic	$P 4_2/mnm\bar{1} \rightarrow P 4_2/mnm$
	$\downarrow \qquad \qquad \downarrow$
Magnetic	$P \underline{4}_2/mnm \rightarrow P nnm$

We identify all the subgroups of $P 4_2/mnm$ of index 2, and hence determine the corresponding dichromatic groups shown in Figure 12.6:

$$\begin{array}{ll}
 \mathbb{N} & \mathbb{M}^{\text{III}} \\
 P 4_2 2_1 2 \Rightarrow \left\{ (E|\mathbf{0}), (C_4|\boldsymbol{\tau}), (C_4^{-1}|\boldsymbol{\tau}), (C_2|\mathbf{0}), \right. & \left. (C_{2xy}|\mathbf{0}), (C_{2x\bar{y}}|\mathbf{0}), (C_{2x}|\boldsymbol{\tau}), (C_{2y}|\boldsymbol{\tau}), \right\} \Rightarrow P 4_2/\underline{mnm} \\
 P \frac{4_2}{m} \Rightarrow \left\{ (E|\mathbf{0}), (C_4|\boldsymbol{\tau}), (C_4^{-1}|\boldsymbol{\tau}), (C_2|\mathbf{0}), \right. & \left. (I|\mathbf{0}), (\sigma_h|\mathbf{0}), (S_4|\boldsymbol{\tau}), (S_4^{-1}|\boldsymbol{\tau}), \right\} \Rightarrow P 4_2/\underline{mnm} \\
 P 4_2 mn \Rightarrow \left\{ (E|\mathbf{0}), (C_4|\boldsymbol{\tau}), (C_4^{-1}|\boldsymbol{\tau}), (C_2|\mathbf{0}), \right. & \left. (\sigma_x|\boldsymbol{\tau}), (\sigma_y|\boldsymbol{\tau}), (\sigma_{xy}|\mathbf{0}), (\sigma_{x\bar{y}}|\mathbf{0}), \right\} \Rightarrow P 4_2/\underline{mnm} \\
 P nnm \Rightarrow \left\{ (E|\mathbf{0}), (C_2|\mathbf{0}), (C_{2x}|\boldsymbol{\tau}), (C_{2y}|\boldsymbol{\tau}), \right. & \left. (I|\mathbf{0}), (\sigma_h|\mathbf{0}), (\sigma_x|\boldsymbol{\tau}), (\sigma_y|\boldsymbol{\tau}), \right\} \Rightarrow P \underline{4}_2/\underline{mnm} \\
 P mmm \Rightarrow \left\{ (E|\mathbf{0}), (C_2|\mathbf{0}), (C_{2xy}|\mathbf{0}), (C_{2x\bar{y}}|\mathbf{0}), \right. & \left. (I|\mathbf{0}), (\sigma_h|\mathbf{0}), (\sigma_{xy}|\mathbf{0}), (\sigma_{x\bar{y}}|\mathbf{0}), \right\} \Rightarrow P \underline{4}_2/\underline{mnm} \\
 P \bar{4}_2 2d \Rightarrow \left\{ (E|\mathbf{0}), (C_2|\mathbf{0}), (C_{2xy}|\mathbf{0}), (C_{2x\bar{y}}|\mathbf{0}), \right. & \left. (S_4|\boldsymbol{\tau}), (S_4^{-1}|\boldsymbol{\tau}), (\sigma_x|\boldsymbol{\tau}), (\sigma_y|\boldsymbol{\tau}), \right\} \Rightarrow P \underline{4}_2/\underline{mnm} \\
 P \bar{4}_2 m 2_1 \Rightarrow \left\{ (E|\mathbf{0}), (C_2|\mathbf{0}), (C_{2x}|\boldsymbol{\tau}), (C_{2y}|\boldsymbol{\tau}), \right. & \left. (S_4|\boldsymbol{\tau}), (S_4^{-1}|\boldsymbol{\tau}), (\sigma_{xy}|\boldsymbol{\tau}), (\sigma_{x\bar{y}}|\boldsymbol{\tau}), \right\} \Rightarrow P \underline{4}_2/\underline{mnm}
 \end{array}$$

(ii) **Dichromatic space-groups of type IV** We can construct three different types of colored primitive tetragonal lattices, shown in Figure 12.5:

- For $\boldsymbol{\tau}_0 = \frac{1}{2}\mathbf{a}_3$, we obtain a P_c lattice, which is associated with the dichromatic space-group $P_c 4_2/mnm$.
- For $\boldsymbol{\tau}_0 = \frac{1}{2}(\mathbf{a}_1 + \mathbf{a}_2)$, we obtain a P_C lattice, which is associated with the dichromatic space-group $P_C 4_2/mnm$.
- For $\boldsymbol{\tau}_0 = \frac{1}{2}(\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3)$, we obtain a P_I lattice, which is associated with the dichromatic space-group $P_I 4_2/mnm$.

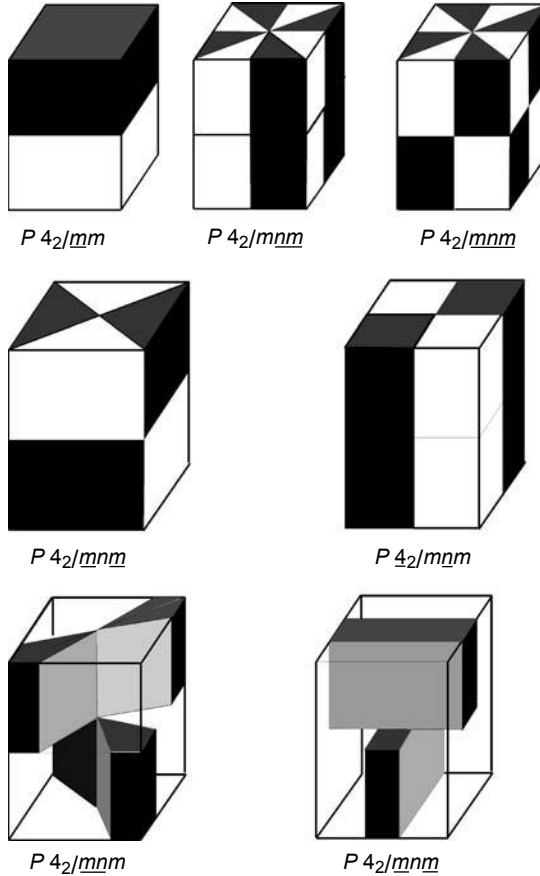


Fig. 12.6. Realizations of the $P4_2/mnm$ type III color space-groups.

12.4.2 Polychromatic groups

We now extend the concept of dichromatic, or black and white, groups to polychromatic ones. The motivation behind this is that such groups find applications in systems with helical, canted, and other complex spin structures, as well as in quasi-crystals. They may also be applied to systems with more complex internal dynamical degrees of freedom than simple spin-1/2.

In general, the construction of such polychromatic groups can be accomplished by attaching a group $\mathfrak{C}$, associated with color transformations, to a geometrical group $\mathcal{G}$, such that a composite element, denoted by (C, R) , $C \in \mathfrak{C}$ and $R \in \mathcal{G}$, satisfies some group composition law. The variety of polychromatic groups can thus be classified according to either the particular group $\mathfrak{C}$, or the specific composition law used.

Polychromatic groups are classified, according to their binary composition law, into four categories: P-type (direct product of $\mathfrak{C}$ and $\mathcal{G}$), Q-type (semidirect product of $\mathfrak{C}$ and $\mathcal{G}$),

W_P -type (wreath product of $\mathfrak{C}$ and $\mathcal{G}$), and W_Q -type (generalized wreath product of $\mathfrak{C}$ and $\mathcal{G}$). The definition of the wreath symmetry groups and their construction will be deferred to Chapter 18, where it is relevant to the symmetry of quasi-periodic systems.

Here, we focus on generalizing the property of type III dichromatic groups, with $\mathcal{M} \sim \mathcal{G}$, to polychromatic ones. In the same spirit, we extend the idea of normal subgroup decomposition beyond those of index 2. We find that, in the case of a normal subgroup $\mathcal{N}$ of index $g/n > 2$ in $\mathcal{G}$, we can identify a color permutation group $\mathfrak{P}$, with elements $\mathfrak{p}_i$, which is isomorphic to the factor group $\mathcal{Q}$, namely,

$$\mathfrak{P} \simeq \mathcal{Q} = \frac{\mathcal{G}}{\mathcal{N}}. \quad (12.105)$$

By expanding $\mathcal{G}$ in terms of left cosets of $\mathcal{N}$,

$$\mathcal{G} = \sum_i \underline{R}_i \mathcal{N},$$

we establish the one-to-one correspondence of the isomorphism as

$$\mathfrak{p}_i \iff \underline{R}_i, \quad i = 1, \dots, g/n, \quad (12.106)$$

where $\underline{R}_i$ are coset representatives. The P-type color group $\mathcal{M}^P$ can then be expressed as

$$\mathcal{M}^P = \sum_i (\mathfrak{p}_i; \underline{R}_i) \mathcal{N}, \quad (12.107)$$

where an element of $\mathcal{M}^P$ is given by

$$(\mathfrak{p}_i; \underline{R}_i N), \quad N \in \mathcal{N}. \quad (12.108)$$

We may recast the examples given above for $\mathcal{M}^{\text{III}}$, namely those derived from $\mathcal{C}_{3v}$ and $\mathcal{C}_{4v}$, in terms of P-type color groups by simply considering the operation of black–white exchange as a permutation! This allows us to consider a class of P-type color groups where the groups $\mathfrak{P}$ are permutation groups, i.e. $\mathfrak{P} \subseteq \mathcal{S}_n$, the symmetric group of degree n .

Example 12.6

We consider, say, $\mathcal{C}_{3v}$, and choose $\mathcal{N} = \mathcal{C}_1(1)$, and $\mathfrak{P} = \mathcal{S}_3$, the symmetric group of degree 3: $(1)(2)(3)$, (123) , (132) , $(1)(23)$, $(13)(2)$, $(12)(3)$, so that $\mathcal{G} \simeq \mathfrak{P}$. We obtain the

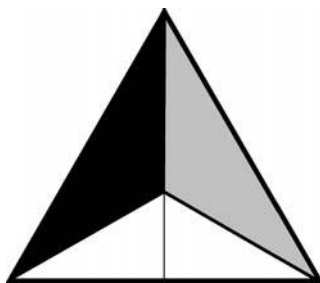


Fig. 12.7. Tri-chromatic P-type permutation point-group derived from $\mathcal{C}_{3v}$.

three-color group

$$\begin{array}{lll} ((1)(2)(3); E) & ((123); C_3) & ((132); C_3^{-1}) \\ ((1)(23); \sigma_1) & ((13)(2); \sigma_2) & ((12)(3); \sigma_3) \end{array}$$

12.5 The time-reversed representation: theory of corepresentations

Thus far we have explored the action of Θ on state kets, quantum mechanical operators, as well as symmetry operators. We constructed type II dichromatic groups (gray groups) in which Θ is included as a “stand-alone” symmetry operation, and type III dichromatic groups, in which Θ is not a symmetry element by itself, but rather appears in combination with geometric operations. We next study its effect on a representation basis set.

We start by considering how the combined operation of Θ together with other unitary or antiunitary operators would affect the transformation of a basis set. We consider, in particular, the case when Θ , and to this effect any antilinear operator, is applied to a Rep basis function following the action of some linear (or antilinear) operator $\mathcal{O}$. This yields,

$$\begin{aligned} \Theta \mathcal{O} \psi_\mu &= \Theta \sum_\nu \psi_\nu \Gamma_{\nu\mu}(\mathcal{O}) = \sum_\nu (\Theta \psi_\nu) \Gamma_{\nu\mu}^*(\mathcal{O}) \\ &= \sum_{\nu\lambda} \psi_\lambda \Sigma_{\lambda\nu}(\Theta) \Gamma_{\nu\mu}^*(\mathcal{O}), \end{aligned} \quad (12.109)$$

since Θ complex-conjugates (c-conjugates) all quantities to its right. This demonstrates that the product of the two operators does not lead to just a product of the corresponding matrix representatives, but leads, in addition, to a c-conjugation of the matrix representative of $\mathcal{O}$. Thus, when Θ is included in a symmetry group, we must seek not ordinary matrix representations, but what Wigner coined as *corepresentations*, that is, representations consistent with (12.109) [2, 60, 61, 62, 71].

12.5.1 Construction of corepresentations (CoRep)

In order to develop the formalism of corepresentations we consider a magnetic group $\mathcal{M}$, which we write as

$$\mathcal{M} = \mathcal{N} + \mathcal{A}\mathcal{N},$$

where $\mathcal{N}$ is a unitary subgroup of index 2 in $\mathcal{M}$, i.e. a normal subgroup, and $\mathcal{A} \notin \mathcal{N}$ is an antiunitary element of $\mathcal{M}$. We denote the elements of $\mathcal{N}$ by R, S, T , etc., and those of $\mathcal{A}\mathcal{N}$ by $\mathcal{A}, \mathcal{B}$, etc., but we should remember that $\mathcal{A}^2, \mathcal{A}\mathcal{B} \in \mathcal{N}$.

We start with applying Θ to a basis set $\{\psi_\mu\} \equiv \Psi$ which engenders an Irrep Δ of $\mathcal{N}$, namely,

$$\begin{aligned} R \psi_\mu &= \sum_\nu \psi_\nu \Delta_{\nu\mu}(R), \\ R \Psi &= \Psi \Delta(R), \end{aligned} \quad R \in \mathcal{N}. \quad (12.110)$$

Next, we define the time-reversed set $\Phi \equiv \{\phi_\mu\} = \{\Theta \psi_\mu\}$ such that

$$R \Phi = \Phi \check{\Delta}(R), \quad (12.111)$$

but, since $\Theta R = R \Theta$, we have

$$\begin{aligned} R \Theta \Psi &= \Theta (R \Psi) = \Theta (\Psi \Delta(R)) \\ &= (\Theta \Psi) \Delta^*(R) = \Phi \Delta^*(R). \end{aligned} \quad (12.112)$$

$$\check{\Delta}(R) = \Delta^*(R). \quad (12.113)$$

The time-reversed representation $\check{\Delta}$ is **identical** to the complex conjugate representation Δ^* .

If we set $\mathcal{A} = S \Theta$, where $S \in \mathcal{N}$, then the basis vectors $\mathcal{A} \Psi$ generate a *generalized time-reversed representation*, namely,

$$\begin{aligned} R (\mathcal{A} \Psi) &= (\mathcal{A} \Psi) {}^A \Delta(R) \\ &= R S \Theta \Psi = S (S^{-1} R S) \Theta \Psi \\ &= (S \Theta \Psi) \Delta^*(S^{-1} R S) = (\mathcal{A} \Psi) \Delta^*(S^{-1} R S). \end{aligned} \quad (12.114)$$

$${}^A \Delta(R) = \Delta^*(S^{-1} R S), \quad (12.115)$$

where $\Delta(S^{-1} R S)$ is an Irrep conjugate to $\Delta(R)$, since $\mathcal{N}$ is a normal subgroup.

Here we list two points to keep in mind:

- (i) $\Delta^*(S^{-1} R S)$ is an Irrep conjugate to $\Delta^*(R)$. Moreover, if $\Delta(R)$ is real, for all $R \in \mathcal{N}$, then

$$\begin{aligned} \Delta^*(S^{-1} R S) &= \Delta(S^{-1} R S) \sim \Delta(R), \\ {}^A \Delta^*(S^{-1} R S) &= \Delta(S^{-2} R S^2) = \Delta(S^{-2}) \Delta(R) \Delta(S^2) \\ &= (\Delta(S^2))^{-1} \Delta(R) \Delta(S^2). \end{aligned} \quad (12.116)$$

- (ii) The usefulness of (12.115) is encountered in the case of type III color groups, where Θ itself does not commute with the Hamiltonian, but $S \Theta$ does, and where S is a spatial symmetry operation that reverses axial vectors, such as magnetic fields and spin angular momenta. Yet, in such cases, we find that $\mathcal{A}^2 = \pm S^2$ and $\mathcal{A}^{-1} R \mathcal{A} = S^{-1} R S$ do commute with the Hamiltonian.

We now construct the Rep Γ engendered by the combined basis $F = [\Psi, \mathcal{A} \Psi]$, namely,

$$\begin{aligned} R F &= F \Gamma(R) \\ &= \begin{bmatrix} \Psi & \mathcal{A} \Psi \end{bmatrix} \begin{pmatrix} \Delta(R) & \mathbf{0} \\ \mathbf{0} & \Delta^*(S^{-1} R S) \end{pmatrix}, \quad \forall R \in \mathcal{N}. \end{aligned} \quad (12.117)$$

Next we apply an operation $\mathcal{B} = \mathcal{A}T$, $T \in \mathcal{N}$, and obtain

$$\begin{aligned}
 \mathcal{B}\Psi &= \mathcal{A}T\Psi \\
 &= \mathcal{A}\Psi\Delta(T) = (\mathcal{A}\Psi)\Delta^*(T) \\
 &= (\mathcal{A}\Psi)\Delta^*(\mathcal{A}^{-1}\mathcal{B}), \\
 \mathcal{B}(\mathcal{A}\Psi) &= \mathcal{B}\mathcal{A}\Psi = \Psi\Delta(\mathcal{B}\mathcal{A}), \quad \mathcal{B}\mathcal{A} \in \mathcal{N}.
 \end{aligned} \tag{12.118}$$

We then find

$$\begin{aligned}
 \mathcal{B}F &= F\Gamma(\mathcal{B}) \\
 &= \begin{bmatrix} \Psi & \mathcal{A}\Psi \end{bmatrix} \begin{pmatrix} \mathbf{0} & \Delta(\mathcal{B}\mathcal{A}) \\ \Delta^*(\mathcal{A}^{-1}\mathcal{B}) & \mathbf{0} \end{pmatrix}, \quad \forall \mathcal{B} \in \mathcal{AN}.
 \end{aligned}$$

(12.119)

A simple inspection shows that the matrix representatives Γ do not obey the ordinary multiplication relations associated with unitary groups, but rather obey

$$\begin{aligned}
 \Gamma(R)\Gamma(S) &= \Gamma(RS), & \Gamma(R)\Gamma(\mathcal{B}) &= \Gamma(R\mathcal{B}), \\
 \Gamma(\mathcal{B})\Gamma^*(R) &= \Gamma(\mathcal{B}R), & \Gamma(\mathcal{B})\Gamma^*(\mathcal{C}) &= \Gamma(\mathcal{B}\mathcal{C}),
 \end{aligned} \tag{12.120}$$

where $R, S \in \mathcal{N}$ and $\mathcal{B}, \mathcal{C} \in \mathcal{AN}$.

The set of unitary matrices defined by (12.117) and (12.119) form a *corepresentation* (CoRep) of $\mathcal{M}$, derived from the unitary Irrep Δ of its normal subgroup $\mathcal{N}$ and satisfying the multiplication rules (12.120).

We note that all the CoReps engendered above comprise Irreps Δ , their c-conjugates Δ^* , and conjugate Irreps derived from Δ and Δ^* . This raises the quintessential questions regarding the equivalence of Δ and Δ^* .

12.5.2 Reality of Irreps

Before we discuss the irreducibility of Γ , it is useful at this point to explore the classification of the Irreps Δ of $\mathcal{N}$ according to the concept of *reality*. We consider an Irrep $\Delta^{\Re}$ to be *real* if

$$\Delta^{\Re}(R) = (\Delta^{\Re}(R))^*, \quad \forall R \in \mathcal{N}. \tag{12.121}$$

Consequently, an Irrep Δ is called *potentially real* if it is equivalent to a $\Delta^{\Re}$, even when Δ is complex. Moreover, a potentially real Δ is equivalent to its complex conjugate Δ^* , since

$$\begin{aligned}
 \Delta^{\Re}(R) &= U^{-1}\Delta(R)U = (U^*)^{-1}\Delta^*(R)U^*, \\
 \Delta^*(R) &= (U(U^*)^{-1})^{-1}\Delta(R)(U(U^*)^{-1}).
 \end{aligned} \tag{12.122}$$

However, we find that the converse is not necessarily true:

Δ may be equivalent to Δ^* but may not be equivalent to any real Irrep.

To explore the consequences of $\Delta \sim \Delta^*$, we write

$$\begin{aligned}\Delta^*(R) &= V^{-1} \Delta(R) V, \\ \Delta(R) &= (V^{-1})^* \Delta^*(R) V^*,\end{aligned}\tag{12.123}$$

which yields

$$\Delta^*(R) = (V^* V)^{-1} \Delta^*(R) V^* V.\tag{12.124}$$

Since Δ and Δ^* are unitary, we choose V to be unitary, and, therefore,

$$V^{-1} = \tilde{V}^*, \quad \text{or} \quad \tilde{V}^* V = \tilde{V} V^* = \mathbb{I},\tag{12.125}$$

and applying Schur's lemma to (12.124) and then using (12.125), we get

$$\begin{aligned}V^* V &= \alpha \mathbb{I}, \quad \text{Schur's lemma,} \\ V &= \alpha \tilde{V} \quad \Rightarrow \quad \tilde{V} = \alpha V, \\ V &= \alpha^2 \mathbb{I} V, \quad \Rightarrow \quad \alpha = \pm 1,\end{aligned}\tag{12.126}$$

where the last line was obtained by multiplying the first line by $\tilde{V}$ and using the relations of the second line.

We identify the two possibilities for the equivalence of Δ and its c-conjugate Irrep, (12.112), according to $\alpha = \pm 1$, as

$$\Delta^*(R) = V^{-1} \Delta(R) V \Rightarrow \begin{cases} \tilde{V} = V & \Delta \text{ real} \\ \tilde{V} = -V & \Delta \text{ pseudo-real.} \end{cases}\tag{12.127}$$

Two conclusions can be surmised from (12.127): first, that

$$\Delta^*(R) \sim \Delta(R) \quad \text{implies} \quad \chi^*(R) = \chi(R), \quad \forall R \in \mathcal{N},\tag{12.128}$$

and hence

An Irrep is potentially real or pseudo-real, if its characters are all real.

Second, that

A pseudo-real Irrep must have an even dimension

because

$$\det(V^* V) = \alpha^d = (-1)^d > 0.\tag{12.129}$$

We can classify the reality of Irreps of $\mathcal{N}$, and for that purpose any $\mathcal{G}$, into three types:

- (i) **Type 1:** The Irrep Δ is real, $\Delta^*(R) \sim \Delta(R) \sim \Delta^{\Re}(R)$, $\alpha = 1$.
- (ii) **Type 2:** The Irrep Δ is pseudo-real, $\Delta^*(R) \sim \Delta(R) \not\sim \Delta^{\Re}(R)$, $\alpha = -1$.
- (iii) **Type 3:** The Irrep Δ is complex $\Delta^*(R) \not\sim \Delta(R)$.

Table 12.10. *Classification of Irreps by reality properties.*

Type	Name	Equivalence	Symmetry	$\Delta \sim \Delta^{\Re?}$	$\chi(R)$	$\frac{1}{n} \sum \chi(R^2)$
1	Real	$\Delta^* = \mathbb{V}^{-1} \Delta \mathbb{V}$	$\tilde{\mathbb{V}} = \mathbb{V}$	Yes	Real	+1
2	Pseudo-real	$\Delta^* = \mathbb{V}^{-1} \Delta \mathbb{V}$	$\tilde{\mathbb{V}} = -\mathbb{V}$	No	Real	-1
3	Complex	$\Delta^* \not\sim \Delta$	—	No	Complex	0

Frobenius and Schur devised a construction that allows the identification of the reality type of an Irrep. This construction is based on character sum rules, and can be derived with the aid of the great orthogonality theorem

$$\sum_{R \in \mathcal{N}} {}^{(\mu)} \Delta_{ij}^*(R) {}^{(\nu)} \Delta_{kl}(R) = \frac{n}{d_\mu} \delta_{\mu\nu} \delta_{ik} \delta_{jl}.$$

(i) For a complex Irrep, ${}^{(\nu)} \Delta(R) = {}^{(\mu)} \Delta^*(R) \not\sim {}^{(\mu)} \Delta(R)$, we have

$$\sum_{R \in \mathcal{N}} {}^{(\mu)} \Delta_{ij}^*(R) {}^{(\nu)} \Delta_{kl}(R) = \sum_{R \in \mathcal{N}} {}^{(\mu)} \Delta_{ij}^*(R) {}^{(\mu)} \Delta_{kl}^*(R) = 0; \quad (12.130)$$

setting $i = l$ and $j = k$, and summing over i, j , we obtain

$$\sum_{R \in \mathcal{N}} {}^{(\mu)} \chi(R^2) = 0. \quad (12.131)$$

(ii) When ${}^{(\mu)} \Delta^* \sim {}^{(\mu)} \Delta$, or ${}^{(\mu)} \Delta(R) = V {}^{(\mu)} \Delta^*(R) V^{-1}$, then we can write

$$\begin{aligned} \sum_{R \in \mathcal{N}} {}^{(\mu)} \chi(R^2) &= \sum_{R \in \mathcal{N}} \sum_{ij} {}^{(\mu)} \Delta_{ij}(R) {}^{(\mu)} \Delta_{ji}(R) \\ &= \sum_{ij;kl} \sum_{R \in \mathcal{N}} {}^{(\mu)} \Delta_{ij}(R) V_{jk} {}^{(\mu)} \Delta_{kl}^*(R) V_{li}^{-1} \\ &= \frac{n}{d_\mu} \sum_{ij} \delta_{ik} \delta_{jl} V_{ji} V_{ji}^{-1} = \frac{n}{d_\mu} \text{Tr}(\tilde{V} V^{-1}) \\ &= \frac{n}{d_\mu} \alpha \text{Tr}(V V^{-1}) = \alpha n. \end{aligned} \quad (12.132)$$

We summarize the Frobenius/Schur character sum rules as

$$\sum_{R \in \mathcal{N}} {}^{(\mu)} \chi(R^2) = \begin{cases} n & {}^{(\mu)} \Delta \text{ is a real Irrep,} \\ 0 & {}^{(\mu)} \Delta \text{ is a complex Irrep,} \\ -n & {}^{(\mu)} \Delta \text{ is a pseudo-real Irrep.} \end{cases} \quad (12.133)$$

This classification is summarized in Table 12.10.

12.5.3 Equivalence of CoIrreps

As we have seen in Chapter 4, establishing the equivalence of Reps or Irreps is essential in studying reducibility of representations. In order to establish an equivalence relationship among CoIrreps of the group $\mathcal{M}$, we explore how a unitary transformation U of the basis F ,

$$F' = F U, \quad (12.134)$$

changes the representative matrices Γ . We are by now familiar with the transformation of $\Gamma(R)$, of a unitary R , namely

$$\Gamma'(R) = U^{-1} \Gamma(R) U. \quad (12.135)$$

In order to obtain the transformation of $\Gamma(\mathcal{B})$ under U , we consider the action of $\mathcal{B}$ on F' ,

$$\begin{aligned} \mathcal{B} F' &= F' \Gamma'(\mathcal{B}) = F U \Gamma'(\mathcal{B}) \\ \mathcal{B} F' &= \mathcal{B} F U = F \Gamma(\mathcal{B}) U^* = (F U) U^{-1} \Gamma(\mathcal{B}) U^*, \end{aligned} \quad (12.136)$$

which yields

$$\Gamma'(\mathcal{B}) = U^{-1} \Gamma(\mathcal{B}) U^*. \quad (12.137)$$

Equations (12.135) and (12.137) define the equivalence between Γ' and Γ .

12.5.4 Reducibility of Γ

The question of reducibility of Γ entails whether there exists a unitary transformation that will render an equivalent block-diagonal Rep Γ^{block} or not. Because of the structure of the Rep Γ given in (12.117) and (12.120), we should examine the relationship between the Irreps $\Delta(R)$ and ${}^A\Delta = \Delta^*(S^{-1}RS)$ in terms of their reality type, and we follow the argument given by Bradley and Davies [60]:

- (i) $\Delta(R) \not\sim {}^A\Delta = \Delta^*(S^{-1}RS)$. We examine the reducibility of Γ by exploring the possibility of constructing a unitary matrix U that reduces Γ . U must then preserve the block-diagonal form of $\Gamma(R)$, while transforming $\Gamma(\mathcal{B})$ into block-diagonal form. To this end we have

$$\begin{aligned} \Gamma(R) \quad U &= U \quad \Gamma'(R) \\ \begin{bmatrix} \Delta(R) & \mathbf{0} \\ \mathbf{0} & {}^A\Delta(R) \end{bmatrix} \begin{pmatrix} \mathbf{a} & \mathbf{b} \\ \mathbf{c} & \mathbf{d} \end{pmatrix} &= \begin{pmatrix} \mathbf{a} & \mathbf{b} \\ \mathbf{c} & \mathbf{d} \end{pmatrix} \begin{bmatrix} \Delta'(R) & \mathbf{0} \\ \mathbf{0} & \Delta''(R) \end{bmatrix} \\ \begin{bmatrix} \Delta(R) \mathbf{a} & \Delta(R) \mathbf{b} \\ {}^A\Delta(R) \mathbf{c} & {}^A\Delta(R) \mathbf{d} \end{bmatrix} &= \begin{bmatrix} \mathbf{a} \Delta'(R) & \mathbf{b} \Delta''(R) \\ \mathbf{c} \Delta'(R) & \mathbf{d} \Delta''(R) \end{bmatrix}, \end{aligned} \quad (12.138)$$

which requires

$$\begin{aligned}\Delta(R) \mathbf{a} &= \mathbf{a} \Delta'(R) \Rightarrow \Delta'(R) \sim \Delta(R) \\ {}^A\Delta(R) \mathbf{d} &= \mathbf{d} \Delta''(R) \Rightarrow \Delta''(R) \sim {}^A\Delta(R) \\ \Delta(R) \mathbf{b} &= \mathbf{b} \Delta''(R) \Rightarrow \Delta''(R) \sim \Delta(R) \\ {}^A\Delta(R) \mathbf{c} &= \mathbf{c} \Delta'(R) \Rightarrow \Delta'(R) \sim {}^A\Delta(R)\end{aligned}$$

Since $\Delta \not\sim \Delta''$ and ${}^A\Delta \not\sim \Delta'$, $\mathbf{b}$ and $\mathbf{c}$ must be zero, according to Schur's lemma. And a diagonal matrix such as $\begin{pmatrix} \mathbf{a} & \mathbf{0} \\ \mathbf{0} & \mathbf{d} \end{pmatrix}$ cannot block-diagonalize $\Gamma(\mathcal{B})$. Hence the corresponding Γ is irreducible.

- (ii) If $\Delta(R) \sim {}^A\Delta = \Delta^*(S^{-1}RS)$, where $\mathcal{A} = \Theta S$, i.e. the generalized time-reversed Irrep is equivalent to the original Irrep, then there exists a unitary transformation $\mathbb{V}$ such that

$$\Delta^{\mathcal{A}}(R) = \Delta^*(\mathcal{A}^{-1}R\mathcal{A}) = \mathbb{V}^{-1} \Delta(R) \mathbb{V}, \quad \forall R \in \mathcal{N}, \quad (12.139)$$

and c-conjugating both sides of (12.139), we obtain

$$\begin{aligned}\Delta(\mathcal{A}^{-1}R\mathcal{A}) &= (\mathbb{V}^{-1})^* \Delta^*(R) \mathbb{V}^* \\ &= (\mathbb{V}^{-1})^* \mathbb{V}^{-1} \Delta(\mathcal{A}R\mathcal{A}^{-1}) \mathbb{V} \mathbb{V}^*.\end{aligned} \quad (12.140)$$

Next, we replace R by SRS^{-1} in (12.140),

$$\begin{aligned}\Delta(R) &= (\mathbb{V}^{-1})^* \mathbb{V}^{-1} \Delta(S^2RS^{-2}) \mathbb{V} \mathbb{V}^* \\ &= (\Delta(S^{-2}) \mathbb{V} \mathbb{V}^*)^{-1} \Delta(R) (\Delta(S^{-2}) \mathbb{V} \mathbb{V}^*).\end{aligned} \quad (12.141)$$

This is just (12.124) but with V^*V replaced by $\Delta(S^{-2}) \mathbb{V} \mathbb{V}^*$, and we obtain

$$\mathbb{V} \mathbb{V}^* = \pm \Delta(S^2) = \pm \Delta(\mathcal{A}^2). \quad (12.142)$$

Next, we show that the sign which applies in (12.142) determines the reducibility of Γ . We first apply the unitary transformation

$$\mathbb{U} = \begin{pmatrix} \mathbb{I} & \mathbf{0} \\ \mathbf{0} & \mathbb{V}^{-1} \end{pmatrix} \quad (12.143)$$

such that

$$\Gamma'(R) = \mathbb{U}^{-1} \begin{bmatrix} \Delta(R) & \mathbf{0} \\ \mathbf{0} & {}^A\Delta(R) \end{bmatrix} \mathbb{U} = \begin{bmatrix} \Delta(R) & \mathbf{0} \\ \mathbf{0} & \Delta(R) \end{bmatrix}, \quad (12.144)$$

$$\Gamma'(\mathcal{B}) = \mathbb{U}^{-1} \begin{bmatrix} \mathbf{0} & \Delta(\mathcal{B}\mathcal{A}) \\ \Delta^*(\mathcal{A}^{-1}\mathcal{B}) & \mathbf{0} \end{bmatrix} \mathbb{U}^* = \begin{bmatrix} \mathbf{0} & \Delta(\mathcal{B}\mathcal{A}) (\mathbb{V}^*)^{-1} \\ \mathbb{V} \Delta^*(\mathcal{A}^{-1}\mathcal{B}) & \mathbf{0} \end{bmatrix}. \quad (12.145)$$

Next, we seek a unitary transformation $\mathbb{W}$ that does not change $\Gamma'(R)$, but block-diagonalizes $\Gamma'(\mathcal{B})$. Transformation $\mathbb{W}$ must satisfy:

$$\begin{aligned} \text{Schur's lemma} &\Rightarrow \Gamma'(R) \mathbb{W} = \mathbb{W} \Gamma'(R) \Rightarrow \mathbb{W} = \begin{pmatrix} a\mathbb{I} & b\mathbb{I} \\ c\mathbb{I} & d\mathbb{I} \end{pmatrix} \\ \text{Unitarity} &\Rightarrow \begin{cases} aa^* + bb^* = 1 \\ ac^* + bd^* = 0 \\ cc^* + dd^* = 1 \end{cases} \end{aligned} \quad (12.146)$$

$$\text{Nonsingularity} \Rightarrow ad \neq bc$$

$$\text{Block-diagonal} \Rightarrow \mathbb{W} \Gamma'(\mathcal{B}) \mathbb{W}^* = \begin{bmatrix} \mathbb{X} & \mathbf{0} \\ \mathbf{0} & \mathbb{Y} \end{bmatrix} = \Gamma''(\mathcal{B})$$

Setting $\mathcal{B} = \mathcal{A}$, the block-diagonalization conditions require

$$\begin{aligned} ad\mathbb{V} + bc\Delta(\mathcal{A}^2)(\mathbb{V}^*)^{-1} = \mathbf{0} &\Rightarrow ad\mathbb{V}\mathbb{V}^* + bc\Delta(\mathcal{A}^2) = \mathbf{0} \\ bc\mathbb{V} + ad\Delta(\mathcal{A}^2)(\mathbb{V}^*)^{-1} = \mathbf{0} &\Rightarrow bc\mathbb{V}\mathbb{V}^* + ad\Delta(\mathcal{A}^2) = \mathbf{0} \end{aligned} \quad (12.147)$$

which, with the aid of (12.142), yield the relation

$$(ad \pm bc)\Delta(\mathcal{A}^2) = \mathbf{0}.$$

Since the nonsingularity of $\mathbb{W}$ requires $ad \neq bc$, then we cannot obtain a reduction for the case $\mathbb{V}\mathbb{V}^* = -\Delta(\mathcal{A}^2)$. The only nontrivial solution is $ad = -bc$, and hence $\mathbb{V}\mathbb{V}^* = +\Delta(\mathcal{A}^2)$. In this case, using the unitarity conditions we may choose

$$\mathbb{W} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix},$$

and obtain

$$\begin{aligned} \Gamma''(\mathcal{A}) &= \frac{1}{2} \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix} \begin{bmatrix} \mathbf{0} & \Delta(\mathcal{A}^2)(\mathbb{V}^*)^{-1} \\ \mathbb{V} & \mathbf{0} \end{bmatrix} \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix} \\ &= \frac{1}{2} \begin{bmatrix} \Delta(\mathcal{A}^2)(\mathbb{V}^*)^{-1} + \mathbb{V} & \mathbf{0} \\ \mathbf{0} & -(\Delta(\mathcal{A}^2)(\mathbb{V}^*)^{-1} + \mathbb{V}) \end{bmatrix} \\ &= \begin{bmatrix} \mathbb{V} & \mathbf{0} \\ \mathbf{0} & -\mathbb{V} \end{bmatrix} \leftrightarrow \Delta(\mathcal{A}^2)(\mathbb{V}^*)^{-1} = \mathbb{V}. \end{aligned} \quad (12.148)$$

We can obtain the reduced matrix for the general antiunitary group element $\mathcal{B} = R\mathcal{A}$ as

$$\begin{aligned} \Gamma''(\mathcal{B}) &= \Gamma''(R\mathcal{A}) = \Gamma'(R) \Gamma''(\mathcal{A}) \\ &= \Gamma'(\mathcal{B}\mathcal{A}^{-1}) \Gamma''(\mathcal{A}) \end{aligned}$$

$$\begin{aligned}
&= \begin{bmatrix} \Delta(\mathcal{BA}^{-1}) & \mathbf{0} \\ \mathbf{0} & \Delta(\mathcal{BA}^{-1}) \end{bmatrix} \begin{bmatrix} \mathbb{V} & \mathbf{0} \\ \mathbf{0} & -\mathbb{V} \end{bmatrix} \\
&= \begin{bmatrix} \Delta(\mathcal{BA}^{-1}) \mathbb{V} & \mathbf{0} \\ \mathbf{0} & -\Delta(\mathcal{BA}^{-1}) \mathbb{V} \end{bmatrix}. \tag{12.149}
\end{aligned}$$

Notice that $\Delta(\mathcal{BA}^{-1}) \mathbb{V} \sim -\Delta(\mathcal{BA}^{-1}) \mathbb{V}$. We should also mention that when $\mathbb{V}\mathbb{V}^* = -\Delta(\mathcal{A}^2)$,

$$\Delta(\mathcal{BA})(\mathbb{V}^*)^{-1} = \Delta(\mathcal{BA}^{-1})\Delta(\mathcal{A}^2)(\mathbb{V}^*)^{-1} = -\Delta(\mathcal{BA}^{-1})\mathbb{V}. \tag{12.150}$$

We also find, with the aid of (12.139), that

$$\mathbb{V} \Delta^*(\mathcal{A}^{-1}\mathcal{B}) = \Delta(\mathcal{BA}^{-1})\mathbb{V}, \tag{12.151}$$

in which case we rewrite (12.144) as

$$\Gamma'(\mathcal{B}) = \begin{bmatrix} \mathbf{0} & -\Delta(\mathcal{BA}^{-1})\mathbb{V} \\ \Delta(\mathcal{BA}^{-1})\mathbb{V} & \mathbf{0} \end{bmatrix}. \tag{12.152}$$

Summarizing, we have three possible types of CoIrreps

- (a) $\mathcal{A}\Psi = \Phi$ reproduces the set Ψ . The CoRep $^{(\mu)}\Gamma$ of $\mathcal{M}$ corresponds to a single Irrep $^{(\mu)}\Delta$ of $\mathcal{N}$, and has the same dimension. In this case no new degeneracy is introduced by the coset $\mathcal{AN}$.
- (b) $\mathcal{A}\Psi$ produces the set Φ which is independent of the set Ψ , but which also forms a basis for $^{(\mu)}\Delta$ of $\mathcal{N}$. The CoRep $^{(\mu)}\Gamma$ of $\mathcal{M}$ corresponds again to a single Irrep $^{(\mu)}\Delta$ of $\mathcal{N}$, but with twice the dimension. In this case the dimension of $^{(\mu)}\Delta$ is doubled.
- (c) The set $\Phi = \mathcal{A}\Psi$ is independent of Ψ , and forms a basis for the Irrep $^{(\nu)}\Delta$ of $\mathcal{N}$ which is inequivalent to $^{(\mu)}\Delta$. In this case the CoRep $^{(\mu)}\Gamma$ corresponds to two inequivalent Irreps of $\mathcal{N}$. The antiunitary operators cause $^{(\mu)}\Delta$ and $^{(\nu)}\Delta$ to become degenerate.

This classification is summarized in Table 12.11.

Table 12.11. *Classification of Irreps according to behavior under generalized time-reversal $S\Theta$.*

Type	α	$\chi^{\mathcal{A}}(R)$	Equivalence	Symmetry	$\Delta^{\mathcal{A}}(R) = \Delta(R)?$
(a)	1	$= \chi(R)$	$\Delta^{\mathcal{A}}(R) = \mathbb{V}^{-1}\Delta(R)\mathbb{V}$	$\mathbb{V}^*\mathbb{V} = +\Delta(S^2)$	If $\Delta(S^2) = \Delta(E)$
(b)	-1	$= \chi(R)$	$\Delta^{\mathcal{A}}(R) = \mathbb{V}^{-1}\Delta(R)\mathbb{V}$	$\mathbb{V}^*\mathbb{V} = -\Delta(S^2)$	If $\Delta(S^2) = -\Delta(E)$
(c)	0	$\neq \chi(R)$	$\Delta^{\mathcal{A}}(R) \not\sim \Delta(R)$	—	No

$$\alpha = \frac{1}{n} \sum \chi((RS)^2); \quad \chi^{\mathcal{A}}(R) = \chi^*(S^{-1}RS); \quad \Delta^{\mathcal{A}}(R) \equiv \Delta^*(S^{-1}RS).$$

Dimmock and Wheeler's (DW) character sum rule

To identify the type of CoIrrep associated with a given Irrep Δ of $\mathcal{N}$, Dimmock and Wheeler [71] devised a test in terms of a character sum rule similar to that of Frobenius and Schur for identifying the reality type of an Irrep. To obtain that sum rule we begin with the sum

$$\begin{aligned} \sum_{\mathcal{B} \in \mathcal{AN}} \sum_i {}^{(\mu)}\Delta_{ii}(\mathcal{B}^2) &= \sum_{R \in \mathcal{N}} \sum_i {}^{(\mu)}\Delta_{ii}(\mathcal{A}R\mathcal{A}R) \\ &= \sum_{R \in \mathcal{N}} \sum_{ijk} {}^{(\mu)}\Delta_{ij}(\mathcal{A}^2) {}^{(\mu)}\Delta_{jk}(\mathcal{A}^{-1}R\mathcal{A}) {}^{(\mu)}\Delta_{ki}(R) \\ &= \sum_{ijk} {}^{(\mu)}\Delta_{ij}(\mathcal{A}^2) \sum_{R \in \mathcal{N}} {}^{(\mu)}\Delta_{jk}(\mathcal{A}^{-1}R\mathcal{A}) {}^{(\mu)}\Delta_{ki}(R), \end{aligned} \quad (12.153)$$

and determine its value for each type of Irrep of $\mathcal{N}$:

(i) ${}^{(\nu)}\Delta(R) = {}^{(\mu)}\Delta^*(S^{-1}RS) \not\sim {}^{(\mu)}\Delta(R)$, we obtain

$$\sum_{ijk} \Delta_{ij}(\mathcal{A}^2) \sum_{R \in \mathcal{N}} {}^{(\nu)}\Delta_{jk}^*(R) {}^{(\mu)}\Delta_{ki}(R) = 0. \quad (12.154)$$

(ii) ${}^{(\nu)}\Delta(R) = {}^{(\mu)}\Delta^*(S^{-1}RS) = \mathbb{V}^{-1} {}^{(\mu)}\Delta(R) \mathbb{V}$, we obtain

$$\begin{aligned} \sum_{ijk} {}^{(\mu)}\Delta_{ij}(\mathcal{A}^2) \sum_{R \in \mathcal{N}} \sum_{mn} (\mathbb{V}^*)_{jm}^{-1} {}^{(\mu)}\Delta^*(R)_{mn} \mathbb{V}_{nk} {}^{(\mu)}\Delta_{ki}(R) \\ = \frac{n}{d_\mu} \sum_{ijk} {}^{(\mu)}\Delta_{ij}(\mathcal{A}^2) \delta_{mk} \delta_{ni} \mathbb{V}_{mj} \mathbb{V}_{nk}^* \\ = \frac{n}{d_\mu} \sum_{ijk} {}^{(\mu)}\Delta_{ij}(\mathcal{A}^2) \mathbb{V}_{kj} \mathbb{V}_{ik}^* = \pm \frac{n}{d_\mu} \sum_{ij} {}^{(\mu)}\Delta_{ij}(\mathcal{A}^2) {}^{(\mu)}\Delta_{ji}^*(\mathcal{A}^2) \\ = \pm \frac{n}{d_\mu} \sum_{ij} {}^{(\mu)}\Delta_{ij}(\mathcal{A}^2) {}^{(\mu)}\Delta_{ji}^*([\mathcal{A}^{-1}]^2) \\ = \pm \frac{n}{d_\mu} \sum_i {}^{(\mu)}\Delta_{ii}^{-1}(E) = \pm n. \end{aligned} \quad (12.155)$$

We obtain expressions similar to those of Frobenius and Schur, namely

$$\boxed{\sum_{\mathcal{B} \in \mathcal{AN}} {}^{(\mu)}\chi(\mathcal{B}^2) = \begin{cases} n & \text{type (a),} \\ -n & \text{type (b),} \\ 0 & \text{type (c).} \end{cases}} \quad (12.156)$$

12.5.5 Double-valued corepresentations and Kramers' theorem

As we discussed earlier, single-valued Irreps are used when a physical system has zero or integer spin, while double-valued Irreps are needed when we have half-integer spin quantum numbers, for example, when we have an odd number of electrons. In such cases (12.50) implies that

$$\Delta(\Theta^2) = -\mathbb{I},$$

where $\mathbb{I}$ is the $d_\Delta \times d_\Delta$ unit matrix. Thus, when $\mathcal{A} = \Theta$, as in type II Shubnikov groups, we should modify (12.156) to read

$$\sum_{\mathcal{B} \in \mathcal{AN}} {}^{(\mu)}\chi(\mathcal{B}^2) = \begin{cases} +\lambda n & \text{type (a),} \\ -\lambda n & \text{type (b),} \\ 0 & \text{type (c).} \end{cases} \quad (12.157)$$

We consider here the particular case of a system with half-integer spin and spatial symmetry $1(\mathcal{C}_1)$, and hence its effective symmetry is $\mathfrak{D}1$, whose double-valued Irrep is

$$\begin{array}{cc} E & \bar{E} \\ 1 & -1 \end{array}$$

The DW rule gives $\chi(E^2) + \chi(\bar{E}^2) = 2\chi(E) = 2 = -\lambda n$, since $\lambda = -1$ in this case. This system thus belongs to case (b), where each level is 2-fold degenerate. This degeneracy, which arises solely due to time-reversal symmetry, is referred to as *Kramers' theorem*.

In the case of type III Shubnikov groups, we identify two possible scenarios, depending on the nature of the operator $\mathcal{A} = \Theta S$:

- (i) $S = I$: Since the spinor may be chosen to have even parity, section 12.3 and [57], the corresponding action of I is just that of the identity operator E , and thus the action of ΘI is just that of Θ , and Kramers' rule still applies:

$$\Delta((\Theta I)^2) = \Delta((\Theta I \bar{E})^2) = \Delta(\Theta^2) = -\mathbb{I}.$$

Moreover, since I commutes with all symmetry operations, we find

$$\Delta^{\mathcal{A}}(R) = \Delta^*(\mathcal{A}^{-1}R\mathcal{A}) = \Delta^*(R).$$

Consequently, we still have $\lambda = -1$ for double-valued Irreps.

- (ii) $S \neq I$: Here, the operation of time-reversal is not present on its own, but appears in combination with other point-group operations, and we do not expect Kramers' rule to hold.

12.5.6 Examples

Example 12.7

CoIrreps of $\mathcal{O}(3)_1$

We consider an Irrep $\mathcal{D}^{(j)}(R)$ of $\mathcal{O}(3)$, of dimension $2j+1$ and characters given by (12.84):

$${}^{(j)}\chi(R(\phi)) = \frac{\sin((j+1/2)\phi)}{\sin(\phi/2)}.$$

In order to use the DW rule we have to replace the summation by an integral of the form

$$\frac{1}{g} \sum_R \chi(R^2) \rightarrow \frac{1}{4\pi} \int_0^{4\pi} d\phi \sin^2(\phi/2) \frac{\sin(2j+1)\phi}{\sin \phi} = \begin{cases} +1 & j \text{ integer,} \\ -1 & j \text{ half-integer.} \end{cases}$$

Since the half-integer case corresponds to $\lambda = -1$, we find that both cases belong to type (a) CoIrreps:

$$\mathcal{D}^{(j)}(R) \leftrightarrow \theta \mathcal{D}^{(j)}(R).$$

Example 12.8

CoIrreps of $\underline{m}3(\mathfrak{D}\underline{m}3)$ dichromatic group

$m3(\mathfrak{D}m3)$ has $\mathcal{N} = 23(\mathfrak{D}23)$ as a subgroup of index 2,

$$\underline{m}3 = 23 + \Theta I 23 = \mathcal{T} + \Theta I \mathcal{T},$$

$$\mathfrak{D}\underline{m}3 = \mathfrak{D}23 + \Theta I \mathfrak{D}23 = \mathfrak{D}\mathcal{T} + \Theta I \mathfrak{D}\mathcal{T}.$$

Irreps of $23(\mathfrak{D}23)$ are given in Table 12.12.

The DW sum-rule gives

$$\sum_{\mathcal{B} \in \mathcal{AN}} {}^{(\mu)}\chi(\mathcal{B}^2) = 2(1) {}^{(\mu)}\chi(E) + 6(3) {}^{(\mu)}\chi(\bar{E}) + 8(4) {}^{(\mu)}\chi(\bar{C}_3^-) + 8(4) {}^{(\mu)}\chi(\bar{C}_3^+).$$

We first consider single-valued Irreps. We find that for Irreps A_1 and T the DW sum-rule yields n , and they are thus of type (a). By contrast, Irreps B_1 and B_2 yield 0, and are of type (c). The corresponding matrices are obtained with the aid of (12.117) and (12.119)

$$E^M(R) = \begin{pmatrix} \Delta(R) & \mathbf{0} \\ \mathbf{0} & \Delta^*(R) \end{pmatrix}, \quad E^M(R\mathcal{A}) = \begin{pmatrix} \mathbf{0} & \Delta(R\mathcal{A}^2) \\ \Delta^*(R) & \mathbf{0} \end{pmatrix},$$

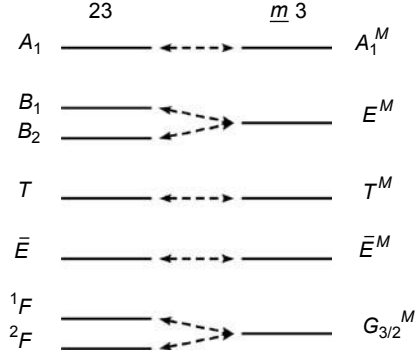
yielding

$$\begin{aligned} E^M(E) &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, E^M(c_{2i}) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \\ E^M(C_{3j}^+) &= \begin{pmatrix} \omega & 0 \\ 0 & \omega^* \end{pmatrix}, \\ E^M(C_{3j}^-) &= \begin{pmatrix} \omega^* & 0 \\ 0 & \omega \end{pmatrix}, \end{aligned}$$

Table 12.12. *Character table of 23 and $\mathfrak{D}23$.*

	E	$\bar{E}$	$3C_2$	$4C_3^+$	$4\bar{C}_3^+$	$4C_3^-$	$4\bar{C}_3^-$	Type
			$3\bar{C}_2$					
A_1	1	1	1	1	1	1	1	(a)
B_1	1	1	1	ω	ω	ω^*	ω^*	} (c)
B_2	1	1	1	ω^*	ω^*	ω	ω	
$\bar{E}$	2	-2	0	1	-1	1	-1	(a)
${}^1\bar{F}$	2	-2	0	ω^*	$-\omega^*$	ω	$-\omega$	} (c)
${}^2\bar{F}$	2	-2	0	ω	$-\omega$	ω^*	$-\omega^*$	
T	3	3	-1	0	0	0	0	(a)

$\omega = \exp[i2\pi/3]$

Fig. 12.8. Compatibility of Irreps of 23 and $\mathfrak{D}23$ and CoIrreps of $\underline{m}3$.

$$\begin{aligned}
 E^M(\Theta I) &= \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad E^M(\Theta I\sigma_i) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \\
 E^M(\Theta I_{6j}^-) &= \begin{pmatrix} 0 & \omega \\ \omega^* & 0 \end{pmatrix}, \\
 E^M(\Theta IS_{6j}^+) &= \begin{pmatrix} 0 & \omega^* \\ \omega & 0 \end{pmatrix}.
 \end{aligned}$$

For the double-valued Irreps the DW sum has to be multiplied by $\lambda = -1$. For $\bar{E}$, we find that the DW sum gives

$$-(2 \times 2 + 6 \times (-2) + 8 \times (-1) + 8 \times (-1)) = 24 = n,$$

and thus is of type (a). Irreps ${}^1\bar{F}$ and ${}^2\bar{F}$ give

$$\begin{aligned}
 -(2 \times 2 + 6 \times (-2) + 8 \times (-\omega^*) + 8 \times (-\omega)) &= 0, \\
 -(2 \times 2 + 6 \times (-2) + 8 \times (-\omega) + 8 \times (-\omega^*)) &= 0,
 \end{aligned}$$

and

$${}^1\bar{F}^A = {}^2\bar{F}, \quad {}^2\bar{F}^A = {}^1\bar{F},$$

and they form a type (c) pair.

Example 12.9

CoIrreps of dichromatic groups derived from 422 ($\mathcal{D}_4$)

The unitary group $\mathcal{D}_4$ has three subgroups of index 2: $\mathcal{C}_4 = E, C_4, C_2, C_4^{-1}$, $\mathcal{D}_2 = E, C_2, U^1, U^2$, and $\mathcal{D}'_2 = E, C_2, U_d^1, U_d^2$. The Irreps of $\mathcal{D}_4$, $\mathcal{C}_4$, and $\mathcal{D}_2$ are given in Table 12.13.

Table 12.13. Irreps of the unitary groups $\mathcal{D}_4$, $\mathcal{C}_4$, and $\mathcal{D}_2$.

	Irreps of $\mathcal{D}_4$					Irreps of $\mathcal{C}_4$				Irreps of $\mathcal{D}_2$					
	E	$2C_4$	C_2	$2U$	$2U_d$	E	C_4	C_4^{-1}	C_2	E	C_2	U^1	U^2		
												U_d^1	U_d^2		
$(1)\Gamma$	1	1	1	1	1	$(1)\Delta$	1	1	1	1	$(1)\Delta$	1	1	1	1
$(2)\Gamma$	1	1	1	-1	-1	$(2)\Delta$	1	-1	-1	1	$(2)\Delta$	1	1	-1	-1
$(3)\Gamma$	1	-1	1	1	-1	$(3)\Delta$	1	i	$-i$	-1	$(3)\Delta$	1	-1	1	-1
$(4)\Gamma$	1	-1	1	-1	1	$(4)\Delta$	1	$-i$	i	-1	$(4)\Delta$	1	-1	-1	1
$(5)\Gamma$	2	0	-2	0	0										

(i) $\underline{422}, \underline{422} : \mathcal{D}_4(\mathcal{D}_2)$

Here, we choose the subgroup $\mathcal{N} = \mathcal{D}_2$ and $\mathcal{A} = \Theta C_4$ to obtain the dichromatic point-group $\underline{422}$. The DW sum-rule test yields

$$\begin{aligned}
 \sum_{\mathcal{B} \in \mathcal{AN}} {}^{(\mu)}\chi(\mathcal{B}^2) &= {}^{(\mu)}\chi\left((\Theta C_4)^2\right) + {}^{(\mu)}\chi\left((\Theta C_4^{-1})^2\right) \\
 &\quad + {}^{(\mu)}\chi\left((\Theta U^{d1})^2\right) + {}^{(\mu)}\chi\left((\Theta U^{d2})^2\right) \\
 &= 2 {}^{(\mu)}\chi(C_2) + 2 {}^{(\mu)}\chi(E),
 \end{aligned}$$

and applying this test to the Irreps of $\mathcal{D}_2$, we obtain

$$\sum_{\mathcal{B} \in \mathcal{AN}} {}^{(\mu)}\chi(\mathcal{B}^2) = \begin{cases} 4 \Rightarrow (1)\Delta, (2)\Delta, \\ 0 \Rightarrow (3)\Delta, (4)\Delta. \end{cases}$$

Irreps $(1)\Delta$ and $(2)\Delta$ are of type (a), so that $\Delta(\mathcal{B}) = \Delta(\mathcal{BA}^{-1}) = \Delta(R)$, where $\mathcal{B} = R\mathcal{A}$. The CoIrreps of the nonunitary group $\underline{422}$ obtained from $(1)\Delta$ and $(2)\Delta$ of $\mathcal{D}_2$ are given in Table 12.14.

The double-valued Irrep of $\mathfrak{D}222$ is

	E	$\bar{E}$	C_2	U_1	U_2
			$\bar{C}_2$	$\bar{U}_1$	$\bar{U}_2$
$(5)\Delta(\bar{E})$	2	-2	0	0	0

The DW sum in this case is

$$\begin{aligned}
 \sum_{\mathcal{B} \in \mathcal{AN}} {}^{(5)}\chi(\mathcal{B}^2) &= - [2 {}^{(5)}\chi(E) + 6 {}^{(5)}\chi(\bar{E})] \\
 &= - [2 \times 2 + 6 \times (-2)] = 8,
 \end{aligned}$$

so $\bar{E}$ is of type (a).

Table 12.14. *CoIrreps of $\underline{422}$ and $\underline{422}$.*

$\underline{422}$	E	C_2	U^1	U^2	ΘC_4	ΘC_4^{-1}	ΘU_d^1	ΘU_d^2
$\underline{422}$	E	C_2	U_d^1	U_d^2	ΘC_4	ΘC_4^{-1}	ΘU^1	ΘU^2
$\Gamma(^{(1)}\Delta)$	1	1	1	1	1	1	1	1
$\Gamma(^{(2)}\Delta)$	1	1	-1	-1	1	1	-1	-1
$\Gamma(^{(3,4)}\Delta)$	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$	$\begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & -1 \\ -1 & 0 \end{bmatrix}$

As for the type (c) $^{(3)}\Delta$ and $^{(4)}\Delta$, we start with $^{(4)}\Delta$ and obtain

R	$\mathcal{A}^{-1}RA$	$^{(4)}\Delta(R)$
E	E	$^{(4)}\Delta(E) = 1$
C_2	C_2	$^{(4)}\Delta(C_2) = -1$
U^1	U^2	$^{(4)}\Delta(U^2) = 1$
U^2	U^1	$^{(4)}\Delta(U^1) = -1$

so that $^{(4)}\Delta(S^{-1}RS) = ^{(3)}\Delta$; and we construct the two-dimensional CoRep of $\underline{422}$ from $^{(3)}\Delta$ and $^{(4)}\Delta$, $\Gamma(^{(3,4)}\Delta)$ given in Table 12.14, using (12.117) and (12.119),

$$\Gamma(R) = \begin{pmatrix} \Delta(R) & \mathbf{0} \\ \mathbf{0} & \Delta^*(S^{-1}RS) \end{pmatrix}, \quad \Gamma(\mathcal{B}) = \begin{pmatrix} \mathbf{0} & \Delta(\mathcal{B}A) \\ \Delta^*(\mathcal{A}^{-1}\mathcal{B}) & \mathbf{0} \end{pmatrix}.$$

Table 12.15. *CoIrreps of $\underline{422}$.*

	E	C_4	C_4^{-1}	C_2	ΘU^1	ΘU^2	ΘU_d^1	ΘU_d^2
$\Gamma(^{(1)}\Delta)$	1	1	1	1	1	1	1	1
$\Gamma(^{(2)}\Delta)$	1	-1	-1	1	1	1	-1	-1
$\Gamma(^{(3)}\Delta)$	1	i	$-i$	-1	1	-1	i	$-i$
$\Gamma(^{(4)}\Delta)$	1	$-i$	i	-1	1	-1	$-i$	i

(ii) $\underline{422} \mathcal{D}_4(\mathcal{C}_4)$

We consider here $\mathcal{N} = \mathcal{C}_4$, $\mathcal{A} = \Theta U_d^1$, which induces the dichromatic point-group $\underline{422}$. Since $(\Theta U^1)^2 = (\Theta U^2)^2 = (\Theta U_d^1)^2 = (\Theta U_d^2)^2 = E$, the DW sum yields +4, for all the Irreps of $\mathcal{C}_4$. Hence, all the CoIrreps of $\underline{422}$ are of type (a).

Example 12.10

CoIrreps of $4/\underline{mmm}$ dichromatic group

This nonunitary dichromatic group is induced from the unitary group $\mathcal{D}_4 \subset 4/mmm$, index 2

$$4/\underline{mmm} = \mathcal{D}_4 + \Theta I \mathcal{D}_4.$$

Since $S = I$, the DW sum-rule for $\mathcal{D}_4$ gives

$$\begin{aligned} \sum_{\mathcal{B} \in \mathcal{AN}} {}^{(\mu)}\chi(\mathcal{B}^2) &= \sum_{\mathcal{N}} {}^{(\mu)}\chi(R^2) \\ &= 6 {}^{(\mu)}\chi(E) + 2 {}^{(\mu)}\chi(C_2), \end{aligned}$$

Table 12.16. *CoIrreps of $4/\underline{mmm}$.*

$\mathcal{D}_4$ ($\mathfrak{D}\mathcal{D}_4$)	E	$\bar{E}$	$2C_4$	$2\bar{C}_4$	C_2 $\bar{C}_2$	$2U$ $2\bar{U}_2$	$2U_d$ $2\bar{U}_2^d$	Type
$(1)\Gamma$	1	1	1	1	1	1	1	(a)
$(2)\Gamma$	1	1	1	1	1	-1	-1	(a)
$(3)\Gamma$	1	1	-1	-1	1	1	-1	(a)
$(4)\Gamma$	1	1	-1	-1	1	-1	1	(a)
$(5)\Gamma$	2	2	0	0	-2	0	0	(a)
$(6)\Gamma$	2	-2	$\sqrt{2}$	$-\sqrt{2}$	0	0	0	(a)
$(7)\Gamma$	2	-2	$-\sqrt{2}$	$\sqrt{2}$	0	0	0	(a)

which yields +8 for all the single-valued Irreps of $\mathcal{D}_4$. Thus we obtain the first five CoIrreps listed in Table 12.16.

As for the two double-valued Irreps of $\mathfrak{D}\mathcal{D}_4$, the DW sum reads

$$\begin{aligned} \sum_{\mathcal{B} \in \mathcal{AN}} {}^{(\mu)}\chi(\mathcal{B}^2) &= -\left(2 {}^{(\mu)}\chi(E) + 10 {}^{(\mu)}\chi(\bar{E}) + 2 {}^{(\mu)}\chi(C_2) + 2 {}^{(\mu)}\chi(\bar{C}_2)\right) \\ &= -(2 \times 2 + 10 \times (-2) + 2 \times 0 + 2 \times 0) = 16, \end{aligned}$$

and we have two more type (a) CoIrreps.

Example 12.11

CoIrreps of $4/\underline{m}$ dichromatic group

In this case the subgroup of index 2 is $\mathcal{N} = C_4$,

$$4/\underline{m} = C_4 + \Theta I C_4,$$

Table 12.17. *Double-valued Irreps of $\mathfrak{DC}_4$ ($\tau = \exp[i\pi/4]$).*

		E	C_4^+	C_4^-	C_2	$\bar{E}$	$\bar{C}_4^+$	$\bar{C}_4^-$	$\bar{C}_2$	Type
$^1E_1$	$(^5)\Delta$	1	τ	$-\tau^*$	$-i$	-1	$-\tau$	τ^*	i	} (c)
$^1E_2$	$(^6)\Delta$	1	τ^*	$-\tau$	i	-1	$-\tau^*$	τ	$-i$	
$^2E_1$	$(^7)\Delta$	1	$-\tau$	τ^*	$-i$	-1	τ	$-\tau^*$	i	} (c)
$^2E_2$	$(^8)\Delta$	1	$-\tau^*$	τ	i	-1	τ^*	$-\tau$	$-i$	

and we take $\mathcal{A} = \Theta \mathbf{I}$. The Irreps of $\mathcal{C}_4$ were given in Table 12.15, and the extra Irreps of $\mathfrak{DC}_4$ are given in Table 12.17.

Since $S = I$, the DW sum is

$$\begin{aligned} \sum_{\mathcal{B} \in \mathcal{AN}} {}^{(\mu)}\chi(\mathcal{B}^2) &= - \left(2 {}^{(\mu)}\chi(E) + 2 {}^{(\mu)}\chi(\bar{E}) + 2 {}^{(\mu)}\chi(C_2) + 2 {}^{(\mu)}\chi(\bar{C}_2) \right) \\ &= - \left(2 \times 2 + 2 \times (-2) + 2 \times (\pm i) + 2 \times (\mp i) \right) = 0, \end{aligned}$$

for all four double-Irreps, so they are of type (c). We also find that they form two conjugate pairs $\{^1E_1, ^1E_2\}$ and $\{^2E_1, ^2E_2\}$.

12.6 Theory of crystal fields

12.6.1 Conventional theory of crystal fields

Because of the spherical symmetry of atomic potentials, electronic spectra of atomic electrons are usually classified in terms of Irreps of $\mathcal{O}(3)$ or $\mathcal{SU}(2)$, depending on the effective spin of the atom. However, when these electrons are placed in a crystalline environment, they are reclassified in terms of the site-symmetry group $\mathcal{G} \subset \mathcal{O}(3)$ or $\mathcal{DG} \subset \mathcal{SU}(2)$, as determined by their location in the crystal. The new potential experienced by such electrons is referred to as the *crystal field*. The ensuing reduction in symmetry leads to the splitting of atomic energy levels, which is just the manifestation of the subduction

$$\begin{aligned} \mathcal{D}^{(j)}(\mathcal{O}(3)) &\downarrow {}^{(\mu)}\Gamma(\mathcal{G}), \\ \mathcal{D}^{(j)}(\mathcal{SU}(2)) &\downarrow {}^{(\mu)}\Gamma(\mathcal{DG}), \end{aligned} \tag{12.158}$$

where $\mathcal{D}^{(j)}$ are Irreps of $\mathcal{O}(3)$ or $\mathcal{SU}(2)$. Given the characters, (12.84),

$$\chi^j(R(2\pi/n)) = \frac{\sin[(2j+1)\pi/n]}{\sin(\pi/n)},$$

for both proper and improper rotations, we express the frequency $\langle \mathcal{D}^{(j)} | {}^{(\mu)}\Gamma \rangle$

$$\langle \mathcal{D}^{(j)} | {}^{(\mu)}\Gamma \rangle = \frac{1}{g} \sum_{R \in \mathcal{G}} \chi^j(R) \chi^\mu(R). \tag{12.159}$$

However, (12.158) suggests that there are at least two reduction schemes which may ensue, and which depend on the relative strength of the crystal-field splitting V_{cf} and the atomic LS -coupling:

(i) LS negligible: we carry out the subduction $\mathcal{D}^{(j)}(\mathcal{O}(3)) \downarrow {}^{(\mu)}\Gamma(\mathcal{G})$,

(ii) $V_{\text{cf}} \gg LS$: we start with (i) and then

$${}^{(\mu)}\Gamma(\mathcal{G}) \otimes \mathcal{D}^{(1/2)} \downarrow {}^{(\mu)}\Gamma(\mathfrak{D}\mathcal{G}),$$

(iii) $LS \gg V_{\text{cf}}$ we use the subduction

$$\mathcal{D}^{(j)}(SU(2)) \downarrow {}^{(\mu)}\Gamma(\mathfrak{D}\mathcal{G}).$$

Example 12.12

A single electron in a p -manifold at a 422 site-symmetry

(i) Case (i): we start with the subduction $\mathcal{D}^{(1)} \downarrow {}^{(\mu)}\Gamma(422)$. The Irreps of 422 are given in Table 12.13, and the corresponding characters in $\mathcal{D}^{(1)}$ are

R	E	$2C_4$	C_2	$2U_2$	$2U_2^d$
$\chi^1(R)$	3	1	-1	-1	-1

yielding the subduction

$$\mathcal{D}^{(1)} \downarrow \left({}^{(2)}\Gamma(A_2) \oplus {}^{(5)}\Gamma(E) \right);$$

which for the p -orbitals read

$$p_z \rightarrow {}^{(2)}\Gamma, \quad (p_x, p_y) \rightarrow {}^{(5)}\Gamma.$$

(ii) Case (ii): we decompose the direct products

$${}^{(2)}\Gamma(A_2) \otimes \mathcal{D}^{(1/2)} = {}^{(7)}\Gamma(\overline{E}_2),$$

$${}^{(5)}\Gamma(E) \otimes \mathcal{D}^{(1/2)} = {}^{(6)}\Gamma \oplus {}^{(7)}\Gamma.$$

(iii) Case (iii): we have a single electron occupying one of the three-fold degenerate p -manifolds, namely, $\ell = 1$, $s = 1/2$. Addition of angular momenta leads to a four-fold manifold $j = 3/2$, and a two-fold manifold $j = 1/2$, and we have to consider the subordinations $\mathcal{D}^{(1/2)} \downarrow \mathfrak{D}422$ and $\mathcal{D}^{(3/2)} \downarrow \mathfrak{D}422$. The Irreps of $\mathfrak{D}422$ are given in Table 12.1, and the corresponding characters of $\mathcal{D}^{(1/2)}$ and $\mathcal{D}^{(3/2)}$ are

R	E	$\overline{E}$	$2C_4$	$2\overline{C}_4$	C_2	$2U_2$	$2U_2^d$
					$\overline{C}_2$	$2\overline{U}_2$	$\overline{U}_2^d$
$\chi^{1/2}(R)$	2	-2	$\sqrt{2}$	$-\sqrt{2}$	0	0	0
$\chi^{3/2}(R)$	4	-4	0	0	0	0	0

It is clear that $\mathcal{D}^{(1/2)} \rightarrow \overline{E}_1$, and we obtain the subduction

$$\mathcal{D}^{(3/2)} \downarrow \left({}^{(6)}\Gamma(\overline{E}_1) \oplus {}^{(7)}\Gamma(\overline{E}_2) \right).$$

Example 12.13

A singly occupied 3d manifold in a cubic environment 432

(i) Case (i): we need the subduction

$$\mathcal{D}^{(2)} \downarrow {}^{(\mu)}\Gamma(432) = {}^{(3)}\Gamma \oplus {}^{(5)}\Gamma.$$

(ii) Case (ii):

$${}^{(3)}\Gamma(E) \otimes \mathcal{D}^{(1/2)} = {}^{(8)}\Gamma(\overline{G}),$$

$${}^{(5)}\Gamma(T) \otimes \mathcal{D}^{(1/2)} = {}^{(7)}\Gamma \oplus {}^{(8)}\Gamma.$$

(iii) Case (iii): the atomic configuration is $\ell = 2, s = 1/2$, with $j = 5/2, 3/2$. Using Table 12.5 we obtain the subduced characters $\mathcal{O}(3) \downarrow \mathfrak{D}432$ as

R	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
$\chi^{3/2}(R)$	4	-4	0	-1	1	0	0	0
$\chi^{5/2}(R)$	6	-6	0	0	0	$-\sqrt{2}$	$\sqrt{2}$	0

Next, we use Table 12.6 to obtain the decompositions

$$\mathcal{D}^{(3/2)} = {}^{(8)}\Gamma,$$

$$\mathcal{D}^{(5/2)} = {}^{(7)}\Gamma \oplus {}^{(8)}\Gamma.$$

A list of Irrep decompositions from $\mathcal{O}(3)$ to 432 is given in Table 12.18.

Table 12.18. *Compatibilities of 432 with $\mathcal{O}(3)$.*

$\mathcal{O}(3) \leftrightarrow 432$		$\mathfrak{D}\mathcal{O}(3) \leftrightarrow \mathfrak{D}432$	
$\mathcal{D}^0$	Γ_1	$\mathcal{D}^{1/2}$	Γ_6
$\mathcal{D}^1$	Γ_4	$\mathcal{D}^{3/2}$	Γ_8
$\mathcal{D}^2$	$\Gamma_3 \oplus \Gamma_5$	$\mathcal{D}^{5/2}$	$\Gamma_7 \oplus \Gamma_8$
$\mathcal{D}^3$	$\Gamma_2 \oplus \Gamma_4 \oplus \Gamma_5$	$\mathcal{D}^{7/2}$	$\Gamma_6 \oplus \Gamma_7 \oplus \Gamma_8$
$\mathcal{D}^4$	$\Gamma_1 \oplus \Gamma_3 \oplus \Gamma_4 \oplus \Gamma_5$	$\mathcal{D}^{9/2}$	$\Gamma_6 \oplus 2\Gamma_8$
$\mathcal{D}^5$	$\Gamma_3 \oplus 2\Gamma_4 \oplus \Gamma_5$	$\mathcal{D}^{11/2}$	$\Gamma_6 \oplus \Gamma_7 \oplus 2\Gamma_8$
$\mathcal{D}^6$	$\Gamma_1 \oplus \Gamma_2 \oplus \Gamma_3 \oplus \Gamma_4 \oplus 2\Gamma_5$	$\mathcal{D}^{13/2}$	$\Gamma_6 \oplus 2\Gamma_7 \oplus 2\Gamma_8$
$\mathcal{D}^7$	$\Gamma_2 \oplus \Gamma_3 \oplus 2\Gamma_4 \oplus 2\Gamma_5$	$\mathcal{D}^{15/2}$	$\Gamma_6 \oplus \Gamma_7 \oplus 3\Gamma_8$
$\mathcal{D}^8$	$\Gamma_1 \oplus 2\Gamma_3 \oplus 2\Gamma_4 \oplus 2\Gamma_5$	$\mathcal{D}^{17/2}$	$2\Gamma_6 \oplus \Gamma_7 \oplus 3\Gamma_8$
$\mathcal{D}^9$	$\Gamma_1 \oplus \Gamma_2 \oplus \Gamma_3 \oplus 3\Gamma_4 \oplus 2\Gamma_5$	$\mathcal{D}^{19/2}$	$2\Gamma_6 \oplus 2\Gamma_7 \oplus 3\Gamma_8$
$\mathcal{D}^{10}$	$\Gamma_1 \oplus \Gamma_2 \oplus 2\Gamma_3 \oplus 2\Gamma_4 \oplus 3\Gamma_5$	$\mathcal{D}^{21/2}$	$\Gamma_6 \oplus 2\Gamma_7 \oplus 4\Gamma_8$
$\mathcal{D}^{11}$	$\Gamma_2 \oplus 2\Gamma_3 \oplus 3\Gamma_4 \oplus 3\Gamma_5$	$\mathcal{D}^{23/2}$	$2\Gamma_6 \oplus 2\Gamma_7 \oplus 4\Gamma_8$

12.6.2 Extension of crystal-field theory to Shubnikov point-groups

In order to consider paramagnetic systems (gray point-groups) that undergo phase transitions, at low temperatures, to magnetically ordered structures with dichromatic symmetry, it is desirable to extend the crystal-field theory to compatibilities between gray groups and dichromatic ones [72, 73]. We then consider atomic symmetries under the action of the gray $\mathcal{O}(3)$ group, $\Theta\mathcal{O}(3) = \{E + \Theta\} \otimes \mathcal{O}(3)$, where the subduction now has to be modified to

$$\Theta\mathcal{D}^j(\mathcal{O}(3)) \downarrow^{(\mu)} \theta\Gamma(\mathcal{M}), \quad (12.160)$$

where $\theta\Gamma$ are CoIrreps of $\mathcal{M}$, and

$$\mathcal{M} = \mathcal{G} + A\mathcal{G},$$

with

$$\mathcal{A} = \begin{cases} \Theta & \text{gray point groups,} \\ \Theta R, R \in (\mathcal{H} - \mathcal{G}) & \text{dichromatic point groups,} \end{cases}$$

where $\mathcal{H}$ is a unitary group isomorphous to $\mathcal{M}$.

We stress, however, that the subduction process in such cases is not straightforward. The reason is that in CoIrreps the characters of antiunitary operations are not necessarily invariant under unitary transformations! Consequently, the character orthogonality relation cannot be employed here, since it is based on the equivalence of Irreps, or CoIrreps, which requires character invariance under unitary transformations.

Alternatively, we can still employ the character orthogonality if we proceed through the group relations:

$$\Theta\mathcal{O}(3) \leftarrow \mathcal{O}(3) \downarrow \mathcal{G} \rightarrow \mathcal{M}. \quad (12.161)$$

We recall here the result of Example 12.7, that all CoIrreps of $\Theta\mathcal{O}(3)$ are of type (a), namely that

$$\mathcal{D}^{(j)}(R) \leftrightarrow \theta\mathcal{D}^{(j)}(R).$$

Hence, for atomic terms $^{(2S+1)}L$, we still can apply the familiar decomposition

$$\theta\mathcal{D}^{(L)}(R) \otimes \theta\mathcal{D}^{(S)}(R) = \sum_{j=|L-S|}^{|L+S|} \theta\mathcal{D}^{(j)}(R). \quad (12.162)$$

We then modify the three crystal-field scenarios listed above to read:

(i) $LS \sim 0$:

$$\begin{aligned} \mathcal{D}^{(L)}(\mathcal{O}(3)) &= \sum_{\mu}^{(\mu)} \Gamma(\mathcal{G}), \\ \Gamma(\mathcal{G}) &\leftrightarrow \theta\Gamma(\mathcal{M}), \\ \theta\mathcal{D}^{(L)}(\Theta\mathcal{O}(3)) &= \sum_{\nu}^{(\nu)} \theta\Gamma(\mathcal{M}). \end{aligned} \quad (12.163)$$

- (ii) $LS \ll V_{\text{cf}}$: For integer spin we use a procedure similar to (12.163) to obtain the CG expansion of $\mathcal{D}^{(L)}(R) \otimes \mathcal{D}^{(S)}(R)$. For half-integer spin we use

$$\begin{aligned}
 \mathcal{D}^{(L)}(\mathcal{O}(3)) &= \sum_{\mu}^{(\mu)} \Gamma(\mathcal{G}), \\
 \mathcal{D}^{(S)}(SU(2)) &= \sum_{\nu}^{(\nu)} \bar{\Gamma}(\mathfrak{D}\mathcal{G}), \\
 \bar{\Gamma}(\mathfrak{D}\mathcal{G}) &\leftrightarrow \bar{\theta}\bar{\Gamma}(\mathfrak{D}\mathcal{M}), \\
 \mathcal{D}^{(L)}(\mathcal{O}(3)) \otimes \mathcal{D}^{(S)}(SU(2)) &= \sum_{\mu\nu}^{(\mu)} \Gamma(\mathcal{G}) \otimes^{(\nu)} \bar{\Gamma}(\mathfrak{D}\mathcal{G}) \\
 &\rightarrow \sum_{\sigma}^{(\sigma)} \bar{\theta}\bar{\Gamma}(\mathfrak{D}\mathcal{M}). \tag{12.164}
 \end{aligned}$$

where the barred representations are double-valued.

- (iii) $LS \gg V_{\text{cf}}$

$$\begin{aligned}
 \mathcal{D}^{(j)}(SU(2)) &= \sum_{\mu}^{(\mu)} \bar{\Gamma}(\mathfrak{D}\mathcal{G}), \\
 \bar{\Gamma}(\mathfrak{D}\mathcal{G}) &\leftrightarrow \bar{\theta}\bar{\Gamma}(\mathfrak{D}\mathcal{M}), \\
 \theta\mathcal{D}^{(j)}(\Theta SU(2)) &= \sum_{\nu}^{(\nu)} \bar{\theta}\bar{\Gamma}(\mathfrak{D}\mathcal{M}). \tag{12.165}
 \end{aligned}$$

Example 12.14

${}^2P$ in $\underline{422}$

- (i) Case (i): Using

222	E	C_2	U_1	U_2
	3	-1	-1	-1

and Table 12.13 we obtain

$$\mathcal{D}^{(1)} = {}^{(2)}\Delta(B_1) \oplus {}^{(3)}\Delta(B_2) \oplus {}^{(4)}\Delta(B_3).$$

With the aid of Table 12.14 we obtain

$$\theta\mathcal{D}^{(1)} = \theta B_1 \oplus \theta B$$

where $\theta B = {}^{(3,4)}\Delta$.

- (ii) Case (ii): Example 12.9 shows that the double-valued CoIrrep $\bar{\theta}\bar{E}$ of $\underline{422}$ is of type (a), and we also find that

$$\mathcal{D}^{(1/2)} \downarrow \bar{E},$$

thus, the outer-product

$$\mathcal{D}^{(1)} \otimes \mathcal{D}^{(1/2)} = \begin{cases} B_1 \otimes \bar{E} = \bar{E} \\ \oplus \\ B_2 \otimes \bar{E} = \bar{E} \\ \oplus \\ B_3 \otimes \bar{E} = \bar{E}, \end{cases}$$

and we obtain

$$\begin{aligned} \theta \bar{E} \otimes \theta B_1 &= \theta \bar{E}, \\ \theta \bar{E} \otimes \theta B &= 2\theta \bar{E}. \end{aligned}$$

Comparison with case (i) shows that LS splits the θB level into two doubly degenerate levels.

(iii) Case (iii):

$$\begin{aligned} \mathcal{D}^{(1)} \otimes \mathcal{D}^{(1/2)} &= \mathcal{D}^{(1/2)} \oplus \mathcal{D}^{(3/2)}, \\ \mathcal{D}^{(1/2)} &= \bar{E}, \\ \mathcal{D}^{(3/2)} &= 2\bar{E}. \end{aligned}$$

Thus,

$$\begin{aligned} \theta \mathcal{D}^{(1/2)} &= \theta \bar{E}, \\ \theta \mathcal{D}^{(3/2)} &= 2\theta \bar{E}. \end{aligned}$$

A weak CF does not split $\theta \mathcal{D}^{(1/2)}$, but splits $\theta \mathcal{D}^{(3/2)}$ into two 2-fold degenerate levels.

Example 12.15

${}^2D$ in $\underline{32}$ and $\bar{6}$ in case (iii)

(i) $\underline{32}$

$$\begin{aligned} \mathcal{D}^{(3/2)} &\downarrow 2\bar{A} \oplus \bar{B}_1 \oplus \bar{B}_2 \\ \mathcal{D}^{(5/2)} &\downarrow 2\bar{A} \oplus 2\bar{B}_1 \oplus 2\bar{B}_2 \end{aligned}$$

$$\underline{32} = 3 + \Theta_{\sigma_1} 3$$

ColIrrep	$\bar{A}$	$\bar{B}_1$	$\bar{B}_2$
Type	(a)	(a)	(a)

$$\begin{aligned} \theta \mathcal{D}^{(3/2)} &\downarrow 2\theta \bar{A} \oplus \theta \bar{B}_1 \oplus \theta \bar{B}_2 \\ \theta \mathcal{D}^{(5/2)} &\downarrow 2\theta \bar{A} \oplus 2\theta \bar{B}_1 \oplus 2\theta \bar{B}_2 \end{aligned}$$

Table 12.19. Double-valued Irreps of 3.

	E	$\bar{E}$	C_3^+	C_3^-	$\bar{C}_3^+$	$\bar{C}_3^-$	CoIrrep type
$\bar{A}$	1	-1	-1	-1	1	1	(a)
$\bar{B}_1$	1	-1	$-\omega$	$-\omega^*$	ω	ω^*	} (c)
$\bar{B}_2$	1	-1	$-\omega^*$	$-\omega$	ω^*	ω	

$$^2D = \mathcal{D}^{(3/2)} \oplus \mathcal{D}^{(5/2)}.$$

(ii) $\bar{6}$

	$\bar{6} = 3 + \Theta_{\sigma_h} 3$		
CoIrrep	$\bar{A}$	$\underbrace{\bar{B}_1 \bar{B}_2}_{(c)}$	
Type	(a)	(c)	
	$\theta \mathcal{D}^{(3/2)} \downarrow 2\theta \bar{A} \oplus \theta \bar{B}$		
	$\theta \mathcal{D}^{(5/2)} \downarrow 2\theta \bar{A} \oplus 2\theta \bar{B}$		

12.7 Onsager reciprocity theorem (Onsager relations) and transport properties

12.7.1 Irreversible thermodynamics and time-reversal symmetry

The extension of equilibrium thermodynamics to the realm of rates of physical processes close to equilibrium is known as the theory of *irreversible thermodynamics*. It is based on the postulates of equilibrium thermostatics together with the *time-reversal symmetry of physical laws* [74, 75], which is the subject of this chapter, and which we have already expounded on. The linkage between equilibrium and irreversible thermodynamics is established through the equilibrium theory of fluctuations. In order to demonstrate the manifestations of time-reversal symmetry inherent in transport processes, we follow the analysis of Callen *et al.* [76, 77, 78, 79]. We begin this section with an introduction to fluctuation theory, followed by the construction of the general linear transport relations and definition of the relevant physical quantities. Finally, we demonstrate the time-reversal symmetry manifest in the coefficients appearing in the transport relations, and known as *kinetic coefficients*.

Theory of fluctuations

The thermodynamic properties of a closed system are described in terms of its fundamental relation. This relation may be expressed as an internal energy U or entropy S function, namely,

$$U = TS + \sum_{i=1} P_i X_i = TS - PV + \cdots, \quad (\text{Energy representation}) \quad (12.166)$$

$$P_i = \frac{\partial U}{\partial X_i},$$

$$S = \sum_{i=0} F_i X_i = \frac{1}{T}U + \frac{P}{T}V - \cdots, \quad (\text{Entropy representation}) \quad (12.167)$$

$$F_i = \frac{\partial S}{\partial X_i}, \quad F_0 = \frac{1}{T}, \quad F_i = \frac{-P_i}{T}, \quad i \geq 1,$$

where X_i is an extensive variable, $X_0 = U$, and P_i, F_i are the conjugate intensive variables in the energy and entropy representations, respectively. These relations describe a system that is in a state of thermodynamic equilibrium, and thus constitute the foundation of thermostatic theory. They are first-degree homogeneous.

In order to obtain the fluctuations of the variables X_i about their mean values, we consider our system as a part of a large closed system, for example, a cubic centimeter of a gas in a large container. We now have the possibility of processes in which the quantities X_i flow from the subsystem to the remainder of the system, called a *reservoir*, and vice versa. These processes are subject only to the condition that there is no change in the value of X_i for the whole closed system. The assumed difference in size between the subsystem and the reservoir implies that these processes may lead to a noticeable change in the state of the subsystem while the quantities X_i and P_i of the reservoir are essentially unchanged.

When a thermodynamic system is in contact with a reservoir, it is allowed to access all its physical microstates with the constraint that the average value of the intensive variable, P_i , associated with the reservoir is fixed by the reservoir. A macroscopic measurement of P_i and its conjugate extensive variable X_i only yields their average values. The access of the different microstates is then described by a probability function P . The deviations of a conjugate pair of thermodynamic variables from their average values P_i and X_i , namely, $\Delta X_i = \tilde{X}_i - X_i$ and $\Delta P_i = \tilde{P}_i - P_i$, are identified as fluctuations about the mean, so that $\langle \Delta \tilde{X}_i \rangle = \langle \Delta \tilde{P}_i \rangle = 0$.

The probability function P is determined through statistical mechanical procedures.

We consider a system in contact with two reservoirs: a thermal reservoir and a reservoir that fixes the average value of another intensive variable P_i . The probability $P(\tilde{E}, \tilde{X}_i)$ is equal to the fraction of the total number of states Ω_{tot} (of system-plus-reservoirs) in which the system is in the state $(\tilde{E}, \tilde{X}_i)$,

$$P(\tilde{E}, \tilde{X}_i) = \frac{\Omega_{\text{res}}(E^{\text{tot}} - \tilde{E}, X_i^{\text{tot}} - \tilde{X}_i)}{\Omega^{\text{tot}}(E^{\text{tot}}, X_i^{\text{tot}})}, \quad (12.168)$$

where Ω_{res} is the number of reservoir accessible states when the system is in state $(\tilde{E}, \tilde{X}_i)$.

Next, we use the Boltzmann relation of Ω to the entropy to write

$$P(\tilde{E}, \tilde{X}_i) = \frac{\exp[k_B^{-1} S_{\text{res}}(E^{\text{tot}} - \tilde{E}, X_i^{\text{tot}} - \tilde{X}_i)]}{\exp[k_B^{-1} S_{\text{tot}}(E^{\text{tot}}, X_i^{\text{tot}})]}. \quad (12.169)$$

With U and X_i the average values of the internal energy and extensive variable X_i of the system, the extensivity of the entropy implies

$$S_{\text{tot}} = S(U, X_i) + S_{\text{res}}(E_{\text{tot}} - U, X_i^{\text{tot}} - X_i), \quad (12.170)$$

where S is the entropy of the system. We expand $S_{\text{res}}(E^{\text{tot}} - \tilde{E}, X_i^{\text{tot}} - \tilde{X}_i)$ around the equilibrium point $(E_{\text{tot}} - U, X_i^{\text{tot}} - X_i)$:

$$\begin{aligned} S_{\text{res}}(E^{\text{tot}} - \tilde{E}, X_i^{\text{tot}} - \tilde{X}_i) &= S_{\text{res}}(E^{\text{tot}} - U + U - \tilde{E}, X_i^{\text{tot}} - X_i + X_i - \tilde{X}_i) \\ &= S_{\text{res}}(E^{\text{tot}} - U, X_i^{\text{tot}} - X_i) + \frac{1}{T} (U - \tilde{E}) - \frac{P_i}{T} (X_i - \tilde{X}_i). \end{aligned}$$

According to the definition of a reservoir, no additional terms in the expansion appear. Inserting the last two equations in the expression for $P(\tilde{E}, \tilde{X}_i)$, we obtain

$$\begin{aligned} P(\tilde{E}, \tilde{X}_i) &= e^{[U - TS(U) + P_i X_i]/k_B T} e^{-(\tilde{E} - P_i \tilde{X}_i)/k_B T} \\ &= e^{\beta[U - TS(U) + P_i X_i]} e^{-\beta(\tilde{E} - P_i \tilde{X}_i)}, \end{aligned} \quad (12.171)$$

where $\beta = \frac{1}{k_B T}$. At this point two possible routes may be taken:

- (i) We work in the energy representation in terms of the appropriate thermodynamic potential $\Psi = U[T, P_i]$, i.e. the Legendre transform in the energy representation with respect to T and X_i , and we write

$$P(\tilde{X}_i) = \exp[\beta(\Psi[T, P_i] - P_i \tilde{X}_i)]. \quad (12.172)$$

As examples, we have

$$\begin{aligned} P(\tilde{E}) &= \exp[\beta(F - \tilde{E})], & \text{thermal reservoir,} \\ P(\tilde{E}, \tilde{V}) &= \exp[\beta(G - \tilde{E} + P\tilde{V})], & \text{thermal and pressure reservoir,} \end{aligned}$$

where F and G are the Helmholtz and Gibbs free energies, respectively.

- (ii) Or, we work in the entropy representation and use the appropriate generalized Massieu function $S[(1/T), (P_i/T)]$, i.e. the Legendre transform of S with respect to X_i :

$$S\left[\frac{1}{T}, \frac{P_i}{T}\right] = S - \frac{1}{T} U - F_i X_i.$$

It is more convenient here to work in the entropy representation, where the probability function may be written in terms of the Massieu function as

$$P(\tilde{E}, \tilde{X}_i) = \exp\left[-\frac{1}{k_B} \left(S\left[\frac{1}{T}, \frac{P_i}{T}\right] + F_i \tilde{X}_i\right)\right].$$

We generalize to the case of a system in contact with reservoirs corresponding to $X_0, X_1, \dots, X_n$, and write the corresponding probability as

$$P(\tilde{\mathbf{X}}) = \exp\left[-\frac{1}{k_B} \left(S[\mathbf{F}] + \mathbf{F} \cdot \tilde{\mathbf{X}}\right)\right]$$

(12.173)

where

$$\tilde{\mathbf{X}} = (\tilde{X}_0, \tilde{X}_1, \dots, \tilde{X}_n)$$

and

$$\mathbf{F} = (F_0, F_1, \dots, F_n).$$

We are now poised to calculate the general second-moment $\langle \Delta \tilde{X}_i \Delta \tilde{X}_j \rangle$. Making use of the relation

$$\frac{\partial \mathcal{P}}{\partial F_j} = \frac{1}{k_B} \left(-\frac{\partial}{\partial F_j} S[\mathbf{F}] - \tilde{X}_j \right) \mathcal{P} = -\frac{1}{k_B} (\tilde{X}_j - X_j) \mathcal{P} = -\frac{1}{k_B} \Delta \tilde{X}_j \mathcal{P},$$

we obtain

$$\begin{aligned} \langle \Delta \tilde{X}_i \Delta \tilde{X}_j \rangle &= \sum_{\text{microstates}} \Delta \tilde{X}_i \Delta \tilde{X}_j \mathcal{P}(\tilde{\mathbf{X}}) \\ &= -k_B \sum_{\text{microstates}} \Delta \tilde{X}_i \frac{\partial \mathcal{P}}{\partial F_j} \\ &= -k_B \left(\frac{\partial}{\partial F_j} \langle \Delta \tilde{X}_i \rangle - \left\langle \frac{\partial}{\partial F_j} \Delta \tilde{X}_i \right\rangle \right) \\ &= -k_B \left(\frac{\partial X_i}{\partial F_j} \right)_{F_0, \dots, F_{j-1}, F_{j+1}, \dots, F_n} \end{aligned} \quad (12.174)$$

Connection between flow and fluctuations of extensive variables

We now return to our 1 cm^3 system and argue that when a large fluctuation involving the flow of an extensive variable X_i , say energy U , from the subsystem to the remainder of the system takes place, a noticeable change in the conjugate intensive variable of the subsystem, here the temperature, immediately arises. This change in the intensive variable could be permanent if the system is instantaneously closed, signaling a loss, or dissipation of X_i . In practice, however, the surrounding reservoir will spontaneously replenish the value of the subsystem's extensive variable, and the fluctuation would decay.

This led Onsager to relate the decay of such macroscopic fluctuations of an extensive variable X_i to its corresponding macroscopic flow processes in a system.

Generalized forces and fluxes

In order to extend the concepts of equilibrium thermodynamics to processes close to equilibrium, we partition the original closed system into closed subsystems, each of which is allowed to reach equilibrium. A process is initiated by the relaxation of an internal constraint, and leads to a redistribution of the corresponding quantity X among the subsystems, and thus constitutes a transition from a constrained to a less constrained equilibrium.

For simplicity, we start by considering a composite closed system consisting of two subsystems characterized by extensive variables X' and X'' , respectively. Because the system is closed

$$X' + X'' = X \text{ (constant)}, \quad \Rightarrow \quad \frac{dX''}{dX'} = -1.$$

When we remove the constraint that fixes the values X' and X'' , their new equilibrium values are obtained by maximizing the total entropy $S = S' + S''$, namely by setting the quantity

$$\mathfrak{F}_i = \left(\frac{\partial S}{\partial X'} \right)_X = \frac{\partial S'}{\partial X'} - \frac{\partial S''}{\partial X''} = F' - F'' = 0. \quad (12.175)$$

Thus, when $\mathfrak{F} = 0$, the system is in equilibrium. When $\mathfrak{F}$ is nonzero it gives rise to an irreversible process that drives the system toward an equilibrium state. Thus, $\mathfrak{F}$ acts as a generalized thermodynamic or entropic force, referred to as *affinity*, which drives the process. When $\mathfrak{F} \neq 0$, (12.175) refers to an internal displacement within a *closed, but no longer homogeneous system*.

As an example, consider the case of $X_0 \equiv U$, such that the two subsystems were initially separated by a thermally insulating wall that constrains their internal energies at U and U' , and that subsequently this wall is replaced by a thermally conducting (diathermal) wall. The nonzero initial affinity

$$\mathfrak{F}_0 = \frac{1}{T} - \frac{1}{T'},$$

i.e. a nonzero difference in the inverse temperatures, drives a flow of heat between the subsystems.

Thus, as a response to a nonzero affinity, a flow associated with the conjugate extensive variable is manifest. In the above example it is a flow of energy in the form of heat.

In general, such flow can be measured by the rate of change of X_i , namely, the *flux* (or *current*) J_i given by

$$J_i = \frac{dX_i}{dt}.$$

The relationship between fluxes and corresponding affinities characterizes the nature of the irreversible processes.

Pedagogically, it is useful to present affinities within the context of the rate of entropy production accompanying an irreversible process. We write the entropy change

$$dS(X_0, X_1, \dots, X_n; t) = \sum_{i=0}^n \frac{\partial S}{\partial X_i} dX_i,$$

and hence,

$$\begin{aligned} \frac{dS}{dt} &= \sum_{i=0}^n \frac{\partial S}{\partial X_i} \frac{dX_i}{dt} \\ &= \sum_i \mathfrak{F}_i J_i, \end{aligned}$$

which shows that the appropriate affinities $\mathfrak{F}_i = \Delta \left(\frac{\partial S}{\partial X_i} \right) = \Delta \left(\frac{P_i}{T} \right)$ are just intensive variables divided by the temperature. Thus, *the rate of production of entropy is the sum of products of each flux with its associated affinity*.

In order to study the correlations between fluxes and affinities in a system, we need to determine the affinities that accompany fluctuations. This is done with the aid of the probability distribution function $W d\tilde{\mathbf{X}}$, where $d\tilde{\mathbf{X}} = d\tilde{X}_0 \dots d\tilde{X}_n$, of finding the system in the range $\tilde{\mathbf{X}}$ and $(\tilde{X}_0 + d\tilde{X}_0, \dots, \tilde{X}_n + d\tilde{X}_n)$. It is given by

$$W d\tilde{\mathbf{X}} = \Omega d\tilde{\mathbf{X}} \mathbf{P}(\tilde{\mathbf{X}}),$$

where $\Omega d\tilde{\mathbf{X}}$ is the number of microstates accessible in the range $d\tilde{X}_0 \dots d\tilde{X}_n$. With Ω_0 being the total number of microstates, we may define the entropy $\tilde{S}$ as

$$\tilde{S} = k_B \ln \left(\frac{\Omega}{\Omega_0} \right), \quad \Rightarrow \Omega = \Omega_0 e^{\tilde{S}/k_B},$$

and we write

$$\begin{aligned} W &= \Omega_0 \exp \left[-\frac{1}{k_B} \left(S[\mathbf{F}] - \tilde{S} + \mathbf{F} \cdot \tilde{\mathbf{X}} \right) \right] \\ &= \Omega_0 \exp \left[-\frac{1}{k_B} \left(S - \tilde{S} + \sum_{i=0}^n F_i (\tilde{X}_i - X_i) \right) \right] \\ &= \Omega_0 \exp \left[\frac{1}{k_B} \left(\Delta \tilde{S} - \sum_{i=0}^n F_i \Delta \tilde{X}_i \right) \right], \end{aligned} \quad (12.176)$$

where $\Delta \tilde{S} = \tilde{S} - S$, and where we used the relation $S[\mathbf{F}] = S - \mathbf{F} \cdot \mathbf{X}$ in obtaining the second line. Next, we define

$$\Delta \mathfrak{F}_j W = (\tilde{F}_j - F_j) W = \left(\frac{\partial \Delta \tilde{S}}{\partial \Delta \tilde{X}_j} - F_j \right) W = k_B \frac{\partial W}{\partial \Delta \tilde{X}_j}.$$

We may now evaluate the moment $\langle \Delta \tilde{X}_i \Delta \mathfrak{F}_j \rangle$, namely

$$\begin{aligned} \langle \Delta \tilde{X}_i \Delta \mathfrak{F}_j \rangle &= \sum_{\text{microstates}} \Delta \tilde{X}_i \Delta \mathfrak{F}_j W \\ &\simeq k_B \int \Delta \tilde{X}_i \frac{\partial W}{\partial \Delta \tilde{X}_j} d\Delta \tilde{\mathbf{X}} \\ &= -k_B \int \left(\frac{\partial \Delta \tilde{X}_i}{\partial \Delta \tilde{X}_j} \right) W d\Delta \tilde{\mathbf{X}} \\ &= -k_B \delta_{ij}. \end{aligned} \quad (12.177)$$

Local equilibrium and continuous systems

Armed with the concepts of affinities and fluxes, we now make the transition to irreversible processes in a continuous system with inhomogeneities in the distribution of its extensive variables, and hence manifest energy and matter flow.

We do so by taking the subsystem divisions to be infinitesimal and assuming that equilibrium conditions hold within an infinitesimal region of the system, so that we can define a local entropy function $S(\mathbf{X}, \mathbf{r})$ at point $\mathbf{r}$, where the extensive variables $\mathbf{X}(\mathbf{r})$ are also local quantities. We also assume that local linear and homogeneous thermodynamic relations, per unit volume, hold, in a manner identical to that for systems under equilibrium conditions, and we define $s = S/V, \dots, x_i = X_i/V \dots$ We write the entropy change per unit volume as

$$ds = \sum_i' F_i dx_i, \quad (12.178)$$

where the primed summation indicates the omission of the volume term.

The flow is now characterized by vector fluxes, or current densities, $\mathbf{J}$, i.e. the flow transported through a unit area per unit time in a given direction, and (12.178) allows us to define the entropy current density $\mathbf{J}_s$ as

$$\mathbf{J}_s = \sum F_i \mathbf{J}_i. \quad (12.179)$$

We now use continuity equations to relate total change rates, ds/dt , to local change rates, $\partial x_i/\partial t$, and current densities:

$$\frac{ds}{dt} = \frac{\partial s}{\partial t} + \nabla \cdot \mathbf{J}_s. \quad (12.180)$$

Assuming that the other extensive variables are conserved, we have,

$$\frac{\partial x_i}{\partial t} + \nabla \cdot \mathbf{J}_i = 0. \quad (12.181)$$

Taking partial derivatives of (12.178) gives

$$\frac{\partial s}{\partial t} = \sum_i' F_i \frac{\partial x_i}{\partial t}, \quad (12.182)$$

while the divergence of (12.179) yields

$$\nabla \cdot \mathbf{J}_s = \nabla \cdot \left(\sum_i F_i \mathbf{J}_i \right) = \sum_i \nabla F_i \cdot \mathbf{J}_i + \sum_i F_i \nabla \cdot \mathbf{J}_i. \quad (12.183)$$

Substituting (12.182) and (12.183) back in (12.180) we obtain

$$\begin{aligned} \frac{ds}{dt} &= \sum_i F_i \frac{\partial x_i}{\partial t} + \sum_i \nabla F_i \cdot \mathbf{J}_i + \sum_i F_i \nabla \cdot \mathbf{J}_i \\ &= \sum_i \nabla F_i \cdot \mathbf{J}_i = \sum_i \mathfrak{F}_i \cdot \mathbf{J}_i. \end{aligned} \quad (12.184)$$

For example, the affinity associated with $\mathbf{J}_0 \equiv \mathbf{Q}$, the heat current density, is $\mathfrak{F}_0 = \nabla(1/T)$.

Linear dissipative systems

In general, the current response, $j(t)$, in a system due to an applied force $\mathfrak{F}$ is given by

$$j = \int_{-\infty}^t dt' \mathcal{L}(t-t') \mathfrak{F}(t').$$

Certain systems are characterized by $\mathcal{L}(t-t') = \delta(t-t')$; in such systems, called Markoffian or dissipative, the fluxes at a given instant depend only on the value of the affinities at that instant, and not on the system's past history. They are also referred to as *purely resistive*. On the other hand, if the fluxes also depended on values of affinities at earlier times, then the system has a *memory*, and is not purely resistive, it acquires a reactive component.

Thus, for purely dissipative systems we assume that a local flux J is a function of the instantaneous values of *all* the intensive variables and affinities, $J(\mathfrak{F}_0, \mathfrak{F}_1, \dots, \mathfrak{F}_j, \dots; F_0,$

$F_1, \dots, F_j, \dots$). Since the flux vanishes when the affinities vanish, we write the expansion

$$J_i = \sum_j L_{ji} \mathfrak{F}_j + \frac{1}{2!} \sum_{jk} L_{jki} \mathfrak{F}_j \mathfrak{F}_k + \dots, \quad (12.185)$$

where

$$\begin{aligned} L_{ji} &= L_{ji}(F_0, F_1, \dots) = \left(\frac{\partial J_i}{\partial \mathfrak{F}_j} \right)_{\mathfrak{F}=0}, \\ L_{jki} &= L_{jki}(F_0, F_1, \dots) = \left(\frac{\partial^2 J_i}{\partial \mathfrak{F}_i \partial \mathfrak{F}_j} \right)_{\mathfrak{F}=0}. \end{aligned} \quad (12.186)$$

L_{jk} are called *kinetic coefficients*, and L_{ijk} are called *second-order kinetic coefficients*, and so on.

The linear response of a purely dissipative system occurs when the affinities are very small, such that only linear terms in the expansion of the fluxes are kept.

12.7.2 The Onsager reciprocity theorem and time-reversal

We are now in a position to establish the effect of time-reversal symmetry of classical physical laws on the properties of transport phenomena.

We exploit the relation between fluctuations and flow, proposed by Onsager, to study the behavior of a system in contact with a pair of reservoirs corresponding to the extensive variables of average values X_j and X_i , and instantaneous values $\tilde{X}_j$ and $\tilde{X}_i$. The fluctuations $\delta\tilde{X} = \tilde{X} - X$, have an average value $\langle \delta\tilde{X} \rangle = 0$. However, the second moment $\langle (\delta\tilde{X}_j)^2 \rangle$, and the correlation moment $\langle \delta\tilde{X}_j \delta\tilde{X}_i \rangle$ need not be zero.

We consider here the more general *delayed correlation moment*

$$\langle \delta\tilde{X}_j(t) \delta\tilde{X}_k(t + \tau) \rangle,$$

which relates fluctuations separated in time by τ . This delayed correlation moment is subject to certain symmetries which follow from the time-reversal symmetry of physical laws. In particular, in the absence of magnetic fields, the delayed correlation moment is symmetric with respect to the change $\tau \rightarrow -\tau$, namely,

$$\langle \delta\tilde{X}_j \delta\tilde{X}_k(\tau) \rangle = \langle \delta\tilde{X}_j \delta\tilde{X}_k(-\tau) \rangle = \langle \delta\tilde{X}_j(\tau) \delta\tilde{X}_k \rangle. \quad (12.187)$$

Subtracting $\langle \delta\tilde{X}_j \delta\tilde{X}_k \rangle$ from both sides of (12.187), we obtain

$$\left\langle \delta\tilde{X}_j \frac{\delta\tilde{X}_k(\tau) - \delta\tilde{X}_k}{\tau} \right\rangle = \left\langle \frac{\delta\tilde{X}_j(\tau) - \delta\tilde{X}_j}{\tau} \delta\tilde{X}_k \right\rangle. \quad (12.188)$$

In the limit $\tau \rightarrow 0$, (12.188) reduces to

$$\langle \delta\tilde{X}_j \delta\ddot{X}_k \rangle = \langle \ddot{X}_j \delta\tilde{X}_k \rangle. \quad (12.189)$$

Now we follow Onsager and assume that the decay of a fluctuation $\delta\tilde{X}_k$ follows the same linear dynamical laws as macroscopic processes, namely

$$\delta\tilde{X}_k = \sum_i L_{ik} \delta\tilde{\mathfrak{F}}_i. \quad (12.190)$$

Inserting these relations back in (12.189) we get

$$\sum_i L_{ik} \langle \delta\tilde{X}_j \delta\tilde{\mathfrak{F}}_i \rangle = \sum_i L_{ij} \langle \delta\tilde{\mathfrak{F}}_i \delta\tilde{X}_k \rangle, \quad (12.191)$$

but, according to (12.177),

$$\langle \delta\tilde{X}_j \delta\tilde{\mathfrak{F}}_i \rangle = \delta_{ij} \langle \delta\tilde{X}_j \delta\tilde{\mathfrak{F}}_j \rangle, \quad (12.192)$$

and we obtain Onsager's relations in the absence of a magnetic field as

$$L_{ik} = L_{ki}. \quad (12.193)$$

When time-reversal is applied in the presence of a magnetic field $\mathbf{H}$, it will reverse the direction of the field, in addition to reversing the directions of velocities and other physical quantities that are odd with respect to this symmetry operation. Time-reversal invariance would then require that this new configuration be equivalent to the original one and we get

$$L_{ik}(\mathbf{H}) = L_{ki}(-\mathbf{H}). \quad (12.194)$$

Exercises

- 12.1 Demonstrate that the time-reversal operator commutes with the inversion operator and all proper rotation operators. (Hint: Write the rotation operator in terms of the angular momentum $\mathbf{J}$.)
- 12.2 Use Table 12.7 to generate the elements of the following double-point-groups, and then determine their Irreps:
 - (i) $\mathfrak{D}3$
 - (ii) $\mathfrak{D}4$
 - (iii) $\mathfrak{D}222$
 - (iv) $\mathfrak{D}32$
 - (v) $\mathfrak{D}42m$.
- 12.3 Consider the crystallographic point-groups $\frac{n}{m} \frac{2}{m} \frac{2}{m}$, $n = 1, 2, 4$, and 6.
 - (i) Enumerate all subgroups of index 2 in each of these point-groups.
 - (ii) Determine the corresponding dichromatic groups.
- 12.4 CoF_2 has the rutile structure in its paramagnetic phase, with gray space-group $P \frac{4_2}{mnm} 1$. In the antiferromagnetic phase, the spins align along the z -axis with the corner spins pointing opposite to the spin at the center of the unit cell.

- (i) Determine the appropriate dichromatic space-group associated with that phase, and identify its unitary subgroup. (Refer to Example 12.5).
 - (ii) Discuss the changes that occur to the Wyckoff site-symmetries of $P \frac{4_2}{mmm}$, listed in Section 10.6.5.
 - (iii) Identify the Brillouin zone of the unitary space-subgroup, and compare its high-symmetry points and lines with those of the primitive tetragonal zone associated with $P \frac{4_2}{mmm}$.
- 12.5 Consider the composite dichromatic/translation operator $\mathcal{C} \hat{\mathbf{a}}_i$, where $\mathbf{a}_i$, $i = 1, 2$, is a translation basis vector.
- (i) Simplify the product

$$\prod_{i=1}^2 (\mathcal{C} \hat{\mathbf{a}}_i)^{m_i},$$

for $(\sum_i m_i)$ even and odd, bearing in mind that $\mathcal{C}^2 = E$, and that the two operators commute.

- (ii) Since the elements R of the lattice holohedry also commute with $\mathcal{C}$, namely $R\mathcal{C} = \mathcal{C}R$, show that

$$R\mathcal{C}\mathbf{t}_1 R^{-1} = \mathcal{C}\mathbf{t}_2, \quad \mathbf{t}_1, \mathbf{t}_2 \in \mathbb{T}.$$

- (iii) Show that the basis sets $(\mathcal{C} \hat{\mathbf{a}}_1, \hat{\mathbf{a}}_2)$ and $(\mathcal{C} \hat{\mathbf{a}}_1, \mathcal{C} \hat{\mathbf{a}}_2)$ produce equivalent lattices.

- 12.6 Determine the translation vectors $\boldsymbol{\tau}_0$ that produce each of the two-dimensional dichromatic lattices of Figure 12.4.
- 12.7 Write down the Seitz operator that would represent a dichromatic screw-axis operation involving an n -fold rotation. Use this for to determine the allowed values of n for dichromatic nonsymmorphic space-groups.
- 12.8 Use the Irreps of $\mathfrak{D}32$, obtained in Exercise 12.2, to derive the CoIrreps of $\mathfrak{D}3m$ and to identify the extra degeneracies associated with each.
- 12.9 Consider a Co^{2+} ion in a CoO crystal. The free ion has a ^4F configuration, that is $L = 3$, $S = 3/2$. In the crystal it has octahedral site-symmetry. Derive the ensuing splitting when:
- (i) we neglect the spin angular momentum,
 - (ii) we include the spin angular momentum.

- 12.10 In their high-temperature paramagnetic phase, CoF_2 and NiF_2 belong to the gray group $P \frac{4_2}{mmm} 1$. Below their respective Néel temperatures, they become antiferromagnetic; CoF_2 has the dichromatic group $P \frac{4_2}{mmm}$, while NiF_2 exhibits additional weak ferromagnetism and has the dichromatic group $P n\overline{m}m$. The free ions Ni^{2+} and Co^{2+} have ground-state configurations $^3F_4$ and $^4F_{9/2}$, respectively. Discuss the ensuing crystal-field splittings for each of these crystals. Derive the CoIrreps of these two dichromatic groups.

13

Tensors and tensor fields

13.1 Tensors and their space-time symmetries

Condensed matter systems have diverse physical properties that are described by tensorial quantities. By this we mean that physical properties of a system are usually defined by, and consist of, relationships between two or more particular measurable quantities associated with the system. These measurable quantities themselves usually assume tensorial forms, so that the ensuing physical properties that characterize a physical system are represented by tensors.

Scalars, i.e. tensors of rank 0, are typified by temperature, pressure, and mass of a homogeneous system, etc., while tensors of rank 1, i.e. vectorial properties, are manifest in electric and magnetic fields and moments, temperature gradients, and currents. Examples of second rank tensors are evident in the characterization of stress and strain in material systems. All these tensors describe either some physical state of a system or some externally applied physical field. For example, the magnitude and direction of the electric polarization is specified in response to an applied external electric field. We call all these tensors, both applied and induced, *physical tensors*.

We also encounter second and higher rank tensors that relate applied and induced physical tensors, for example, the *electric susceptibility* tensor of rank 2 connects the electric polarization with the applied electric fields, and the *elasticity* tensor, of rank 4, relates the strain to the applied stress. In contrast to physical tensors, the latter tensors are system specific: their particular forms, i.e. the number of linearly independent components and their values, are determined by the symmetry and structure of a given system. We refer to these system-specific tensors as *matter*, or *material*, tensors.

Thus, we find that if a system is subjected to an *influence*, represented by a tensor $\mathfrak{F}_{qrs\dots}$ which gives rise to an effect $\mathfrak{R}_{jkl\dots}$, then a linear relationship between influence and effect defines a property (or matter) tensor $\mathfrak{T}_{jkl\dots pqr\dots z}$ according to the equation

$$\mathfrak{R}_{jkl\dots} = \mathfrak{T}_{jkl\dots pqr\dots z} \mathfrak{F}_{qrs\dots} \quad (13.1)$$

13.1.1 Neumann's principle

It is possible to simplify the form of a property tensor by considering a system's *geometrical symmetry*, as well as the *intrinsic symmetry* associated with the physical property that

the tensor is intended to describe and therefore irrespective of the system's geometric symmetry.

As such, *these matter tensors that describe macroscopic properties of physical systems should be invariant under the operations $(R|\mathbf{0})$ of the point-group $\mathbb{P}$ associated with the space-group $\mathbb{S}$ with elements $(R|\boldsymbol{\tau} + \mathbf{t})$.*

The macroscopic nature of these tensorial properties implies that they are invariant to all lattice translations $\mathbf{t}$ associated with $\mathbb{S}$. Moreover, we may justifiably ignore any nonprimitive translations, which are negligibly small on the macroscopic scale.

In $\mathcal{E}(3)$ Euclidean space a matter tensor of rank n has 3^n components, yet they are not all independent. Constraints are imposed on these components, by:

- (i) Intrinsic symmetries derived from the physical property represented by the tensor. Such symmetries lead to some linear relations among the tensor's components. For example, the tensor may be associated with some potential energy function or with the Onsager relations; both require the tensor to be symmetric.
- (ii) The symmetry invariance requirements imposed by the associated point-group.
- (iii) Since tensors describe macroscopic physical properties, they belong to the realm of classical physics and are not subject to quantum mechanical scrutiny. It is therefore important to point out that, under time-reversal, symmetry tensors are not subjected to the antiunitary nature of the quantum mechanical time-reversal operator, instead time-reversal is regarded as the operator which transforms $t \rightarrow -t$, and has the property therefore of changing the sign of certain physical quantities which depend on time, such as velocities, momenta, currents, and magnetic fields, while leaving other quantities unchanged.

In addition to establishing linear dependencies among the tensor components, these constraints may impose a zero value on some of them.

13.1.2 Tensor transformation and invariance under $\mathcal{O}(3)$ operations

Since most physical systems are rooted in $\mathcal{E}(3)$ space, we confine our analysis here to tensors associated with $\mathcal{O}(3)$ operations. Moreover, when such tensors describe physical properties of a system they should remain invariant under operations of $\mathcal{O}(3)$ that leave the system invariant [14, 58, 80, 81, 82].

Note

Since each of the 32 crystallographic point-groups can be generated from a small set of generating matrices, it is sufficient to use the generators of a given point-group to impose all the possible constraints generated by the point-group.

Pseudoscalars

We have seen above that scalars, or tensors of rank zero, are those quantities that remain invariant under all operations of $\mathcal{O}(3)$. By contrast, quantities that are invariant under $\mathcal{SO}(3)$, i.e. proper rotations, but change sign under $I \times \mathcal{SO}(3)$, i.e. improper rotations, are called *pseudoscalars*. Very few pseudoscalar quantities appear in physical applications; later on in this chapter, we will discuss the quantity known as rotary power associated with the phenomenon of optical activity, which transforms like a pseudoscalar. Rotary power is defined as positive when the sense of rotation is the same as the hand of the axes.

Vectors or first-rank tensors

Physical properties represented by vectors fall into two distinct categories: those that are odd under inversion are designated *polar vectors*, such as the electric moment, and those that are even under inversion are called *axial or pseudovectors*, such as the magnetic moment.

True and pseudovectors

A true vector, for example a displacement, is a polar vector, that is, it may be represented by an arrow. The direction in which the arrow points is unambiguous and a polar vector does not change sign upon a transformation which changes the hand of the coordinate axes. An axial vector, however, does change sign (the sign of the coefficients remaining the same). An example of an axial vector is the vector product of two polar vectors. This has the directional properties of an element of area rather than an arrow; the direction of the arrow may be defined as normal to the area but there is no unequivocal rule as to which side of the element of area is the positive direction of the vector.

The area fixes the shank of the arrow but it does not determine which end should bear the point and this must be decided by some purely arbitrary (e.g. right-hand) rule. Axial vectors are sometimes called pseudovectors, and their three components are actually the three components of a second-rank antisymmetrical tensor in three dimensions. (Indeed it is only in three dimensions that it is possible to represent an antisymmetrical tensor by an axial vector.)

In isotropic three-dimensional space, with $O(3)$ symmetry, polar $\mathbf{P}$ and axial $\mathbf{A}$ vectors transform as

$$R\mathbf{P} = \tilde{\mathbf{P}}^{(1)}\Gamma^-(R) = \tilde{\mathbf{P}}^{(v)}\Gamma(R), \quad (13.2)$$

$$R\mathbf{A} = \tilde{\mathbf{A}}^{(1)}\Gamma^+(R) = \tilde{\mathbf{A}}^{(a)}\Gamma(R), \quad (13.3)$$

where $^{(1)}\Gamma^-(R)$ and $^{(1)}\Gamma^+(R)$ are Irreps of $O(3)$ with $l = 1$ and odd and even parity, respectively.

The complete set of orthogonal 3×3 rotation and roto-reflection matrices, R , form a faithful Irrep of $\mathcal{O}(3)$ equivalent to $^{(1)}\Gamma^-$; while an Irrep equivalent to $^{(1)}\Gamma^+$ can be obtained from this set of matrices by multiplying each matrix by its determinant, namely,

$$^{(1)}\Gamma^+(R) = \det(R) R.$$

In general, both types of vectorial properties may be induced in a system when external forces, e.g. electric and magnetic fields, are applied. By contrast, some systems may exhibit permanent moments; in such a case the vectorial moment $\mathbf{M}$ has to remain invariant under the symmetry operations of the point-group $\mathcal{G}$ associated with the system. If we consider such an operation R , then

$$\mathbf{M}' = R\mathbf{M} = \mathbf{M}, \quad \Rightarrow \quad R\mathbf{M} = \mathbf{M} \quad ^{(1)}\Sigma(R), \quad (13.4)$$

i.e. it implies that $\mathbf{M}$ forms a basis for the identity Irrep $^{(1)}\Sigma(R)$ of $\mathcal{G}$. Equations (13.2) and (13.4) require that

$$\begin{aligned} ^{(v)}\Gamma \downarrow \mathcal{G} \ni ^{(1)}\Sigma, & \quad \text{permanent polar moment,} \\ ^{(a)}\Gamma \downarrow \mathcal{G} \ni ^{(1)}\Sigma, & \quad \text{permanent axial moment.} \end{aligned} \quad (13.5)$$

The number of linearly independent components $\mathcal{N}$ of $\mathbf{M}$ is then equal to the number of independent basis vectors of the identity Irrep in the subduction of the vector or axial Irreps, i.e. the corresponding multiplicities, which we obtain using (8.36) as

$$\mathcal{N} = \frac{1}{g} \sum_{R \in \mathcal{G}} ^{(\alpha)} \chi(R), \quad (13.6)$$

where $\alpha \equiv v, a$ and p is the order of $\mathcal{G}$.

Systems with a permanent electric dipole moment are referred to as *ferroelectrics*. The point-groups that satisfy (13.5) are those with only one high-symmetry axis, which coincides with the direction of the electric polarization. They include:

$$\mathcal{C}_1, \mathcal{C}_2, \mathcal{C}_3, \mathcal{C}_4, \mathcal{C}_6, \mathcal{C}_{1v}, \mathcal{C}_{2v}, \mathcal{C}_{3v}, \mathcal{C}_{4v}, \mathcal{C}_{6v}.$$

Similarly, systems with a permanent magnetic dipole moment are referred to as *ferromagnetic*. The point-groups that satisfy (13.5) are those with only one high-symmetry axis, which coincides with the direction of the magnetic moment. They include:

$$\mathcal{C}_1, \mathcal{C}_2, \mathcal{C}_3, \mathcal{C}_4, \mathcal{C}_6, \mathcal{C}_i, \mathcal{C}_{2h}, \mathcal{S}_6, \mathcal{C}_{4h}, \mathcal{C}_{6h}.$$

Most tensors with rank $n > 1$ that we consider generally relate applied forces to vectorial physical quantities they induce, such as electric field and current or polarization. Stress and strain tensors are exceptions. We then find that the transformation properties of these tensors depend on the nature of the individual vector quantities they relate, i.e. whether polar or axial.

Tensors of rank 2

A second-rank tensor $\mathfrak{T}^{(2)}$ may be considered as an outer-product of two first-rank tensors or vectors,

$$\mathfrak{T}^{(2)} = \mathbf{V} : \mathbf{W} = \begin{bmatrix} V_1 \\ V_2 \\ V_3 \end{bmatrix} \begin{bmatrix} W_1 & W_2 & W_3 \end{bmatrix} = \begin{bmatrix} V_1 W_1 & V_1 W_2 & V_1 W_3 \\ V_2 W_1 & V_2 W_2 & V_2 W_3 \\ V_3 W_1 & V_3 W_2 & V_3 W_3 \end{bmatrix}, \quad (13.7)$$

which under a unitary symmetry operation $R \in O(3)$ transforms according to

$$\begin{aligned} \mathfrak{T}^{(2)'} &= R\mathbf{V} : R\mathbf{W} = {}^{(\alpha)}\Gamma(R) \mathbf{V} \widetilde{\mathbf{W}} {}^{(\beta)}\Gamma(R^{-1}) \\ &= \left({}^{(\alpha)}\Gamma(R) \otimes {}^{(\beta)}\Gamma(R) \right) \mathbf{V} \widetilde{\mathbf{W}}, \quad \alpha, \beta \equiv \mathbf{v}, \mathbf{a}, \end{aligned} \quad (13.8)$$

or

$$\boxed{\mathfrak{T}_{ij}^{(2)'} = \sum_{i'j'} {}^{(\alpha)}\Gamma_{ii'}(R) {}^{(\beta)}\Gamma_{jj'}(R) \mathfrak{T}_{i'j'}^{(2)}}, \quad (13.9)$$

so that the elements of the tensor $\mathfrak{T}^{(2)}$, namely $\mathfrak{T}_{ij}^{(2)}$, form a basis for the direct product representation ${}^{(\alpha)}\Gamma(R) \otimes {}^{(\beta)}\Gamma(R)$.

Since for $(v \otimes v)$ and $(a \otimes a)$, $\mathbf{V} : \mathbf{W}$ does not change sign under inversion, the corresponding $\mathfrak{T}^{(2)}$ has even parity.

The Kronecker products ${}^{(\alpha)}\Gamma(R) \otimes {}^{(\beta)}\Gamma(R)$ can be reduced onto the Irreps of $O(3)$ as

$${}^{(v)}\Gamma \otimes {}^{(v)}\Gamma = {}^{(0)}\Gamma^+ \oplus {}^{(1)}\Gamma^+ \oplus {}^{(2)}\Gamma^+, \quad (13.10)$$

$${}^{(a)}\Gamma \otimes {}^{(a)}\Gamma = {}^{(0)}\Gamma^+ \oplus {}^{(1)}\Gamma^+ \oplus {}^{(2)}\Gamma^+, \quad (13.11)$$

$${}^{(v)}\Gamma \otimes {}^{(a)}\Gamma = {}^{(0)}\Gamma^- \oplus {}^{(1)}\Gamma^- \oplus {}^{(2)}\Gamma^-. \quad (13.12)$$

Irreducible spherical tensor components Upon examining (13.10) and (13.11), we find that:

- the trace $\text{Tr}(\mathbf{V} : \mathbf{W}) = \mathbf{V} \cdot \mathbf{W}$ is a scalar invariant under all operations in $\mathcal{O}(3)$, and hence transforms according to ${}^{(0)}\Gamma^+$;
- the vector cross-product for two polar vectors is invariant under inversion, i.e. it has even parity,

$$(I\mathbf{V}) \times (I\mathbf{W}) = (-\mathbf{V}) \times (-\mathbf{W}) = \mathbf{V} \times \mathbf{W}.$$

We then discern that the vector cross-products of two axial or polar vectors transform like $^{(1)}\Gamma^+$; in which case we rewrite (13.7) as

$$\mathfrak{T}_{ij}^{(2)} = \frac{\mathbf{V} \cdot \mathbf{W}}{3} \delta_{ij} + \frac{V_i W_j - V_j W_i}{2} + \left(\frac{V_i W_j + V_j W_i}{2} - \frac{\mathbf{V} \cdot \mathbf{W}}{3} \delta_{ij} \right). \quad (13.13)$$

We can, therefore, decompose a general second-rank tensor, relating two polar or two axial vectors, into the irreducible spherical tensors:

- a scalar,
- a 3×3 tensor that transforms like an axial vector, and
- a symmetric, traceless second-rank tensor.

Such a tensor is referred to as a *polar second-rank tensor*.

By contrast, a second-rank tensor relating a polar vector and an axial vector, has odd parity, and can be decomposed into:

- a pseudoscalar (a scalar that is odd under inversion),
- a 3×3 tensor that transforms like a polar vector (one that corresponds to a cross-product of a polar and an axial vector), and
- a symmetric traceless second-rank tensor with odd parity.

Such a tensor is referred to as an *axial second-rank tensor*.

Note pseudo- or axial vectors transform like a cross-product of two polar vectors, which in turn transform according to the antisymmetrized outer-product of a vector space, namely

$$\mathcal{V}_a = \{\mathcal{V}_p^2\}. \quad (13.14)$$

We may, therefore, replace a pseudovector index i by two polar indices jl with a cyclic sequence $1 \rightarrow 23, 2 \rightarrow 31, 3 \rightarrow 12$.

If there exists a symmetry axis C_n , with $n \geq 2$ along, say, the z -axis, then the nonvanishing components of the antisymmetric tensor should lie along z , and we obtain

$$\mathfrak{T}_A^{(2)} = \begin{bmatrix} 0 & h & 0 \\ -h & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}. \quad (13.15)$$

We thus classify second-rank tensors as either axial or polar, according to their transformation, namely,

$$\boxed{\mathfrak{T}_{ij}^{(2)'} = \begin{cases} \sum_{kl} R_{ik} R_{jl} \mathfrak{T}_{kl}^{(2)} & \text{polar} \\ \det(R) \sum_{kl} R_{ik} R_{jl} \mathfrak{T}_{kl}^{(2)} & \text{axial} \end{cases}} \quad (13.16)$$

Geometric representation of a rank-2 symmetric tensor: the tensor ellipsoid

The symmetric tensor, comprising $\left({}^{(0)}\Gamma \oplus {}^{(2)}\Gamma^+ \right)$,

$$\mathfrak{T}_S^{(2)} = \begin{bmatrix} a & d & e \\ d & b & f \\ e & f & c \end{bmatrix}, \quad (13.17)$$

may be associated with a bilinear form, a potential function, of the form

$$\mathbf{x}^T : \mathfrak{T}_S^{(2)} : \mathbf{x},$$

where $\mathbf{x}^T$ is a row-vector. We may associate the following conical surface (ellipsoid or hyperboloid) with this bilinear form, namely,

$$a x_1^2 + b x_2^2 + c x_3^2 + 2d x_1 x_2 + 2e x_2 x_3 + 2f x_3 x_1 = 1. \quad (13.18)$$

The diagonalization of (13.17) corresponds to a unitary transformation of the coordinate axes to a set that coincides with the *principal axes* (PAs) of the conical surface, so that (13.18) becomes

$$A x_1^2 + B x_2^2 + C x_3^2 = 1. \quad (13.19)$$

A, B, C are called the *principal values* of the tensor $\mathfrak{T}_S^{(2)}$, or of the physical property associated with the tensor. When the principal values are all positive, as is the case with most matter tensors, (13.19) defines an ellipsoidal surface known as the *tensor ellipsoid*, and shown in Figure 13.1.

Expressions for polar symmetric second-rank tensors defined with respect to the crystallographic axes are given in Table 13.1. The following comments are useful:

- In the case of *triclinic* symmetry, the PAs do not necessarily coincide with the crystallographic axes. Thus, when the dielectric tensor is written with respect to the latter, all six independent tensor components are needed in order to specify the magnitudes of

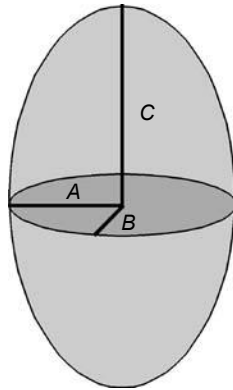


Fig. 13.1. The tensor ellipsoid and its principal axes.

Table 13.1. *Symmetry-adapted polar symmetric second-rank tensors.*

Crystal system	Point-group	Symmetry-adapted tensor
Triclinic	$C_1(1), C_i(\bar{1})$	$\begin{bmatrix} a & d & e \\ d & b & f \\ e & f & c \end{bmatrix}$
Monoclinic	$C_2(2), C_s(m), C_{2h}(2/m)$	$\begin{bmatrix} a & d & 0 \\ d & b & 0 \\ 0 & 0 & c \end{bmatrix}$
Orthorhombic	$222, mm2, mmm$	$\begin{bmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{bmatrix}$
Trigonal Tetragonal Hexagonal	$\left. \begin{array}{l} 3, \bar{3}, 32, 3m, \bar{3}m \\ 4, \bar{4}, 4/m, 422, 4mm, \bar{4}2m, 4/mmm \\ 6, \bar{6}, 6/m, 622, 6mm, \bar{6}2m, 6mmm \end{array} \right\}$	$\begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{bmatrix}$
Cubic	$23, m\bar{3}, 432, \bar{4}3m, m\bar{3}m$	$\begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{bmatrix}$

the principal values and the orientation of the PAs with respect to the crystallographic axes.

- For the *monoclinic* system, one PA coincides with the c -axis, while the orientation of the other two requires the specification of one angle with respect to the a - and b -axes. Thus, four independent components are required to define the tensor with respect to the crystallographic axes.
- Since the *orthorhombic* system has three mutually perpendicular axes, the PAs coincide with them and we only need three independent components.
- For *tetragonal*, *trigonal*, and *hexagonal* crystal systems, there exists a high-symmetry axis C_n with $n > 2$, along z ; then the minor axes along x_1, x_2 must be equal and we obtain a symmetric matrix of the form

$$\begin{bmatrix} A & 0 & 0 \\ 0 & A & 0 \\ 0 & 0 & C \end{bmatrix}. \quad (13.20)$$

Tensors of rank 3 and higher

We now extend our classification of tensors to ranks higher than 2 by extending the definition (13.16) to a rank k tensor, as

$$\mathfrak{T}_{ab\dots k}^{(k)'} = \begin{cases} \sum_{pq\dots z} R_{ap} R_{bq} \dots R_{kz} \mathfrak{T}_{pq\dots z}^{(k)} & \text{polar} \\ = \det(R) \sum_{pq\dots z} R_{ap} R_{bq} \dots R_{kz} \mathfrak{T}_{pq\dots z}^{(2)} & \text{axial} \end{cases} \quad (13.21)$$

For centrosymmetric systems, i.e. systems with space-inversion symmetry, we find that $R_{ij} = -\delta_{ij}$, $i, j = 1, 2, 3$. Inspection of (13.21) immediately shows that the condition of tensor invariance under such symmetry requires that:

All polar tensors of odd rank and all axial tensors of even rank must vanish identically, i.e. they are null tensors.

13.1.3 Tensors and time-reversal symmetry

For the 32 classical type I magnetic point-groups, $\mathcal{G}$, Equations (13.21) still apply, and since Θ is not a symmetry operator, the forms of both time-symmetric and time-antisymmetric tensors may be obtained accordingly.

We consider systems with symmetries belonging to one of the Shubnikov groups $\mathcal{M}$ where exactly half the elements involve the time-reversal operator Θ . We find that two situations arise [58, 82, 83]:

- (i) For a nonmagnetic crystal class, that is for a diamagnetic or paramagnetic crystal, $\mathcal{M}$ is one of the type II gray groups, and hence $\Theta \in \mathcal{M}$, i.e.

$$\mathcal{M} = \mathcal{G} + \Theta \mathcal{G},$$

where $\mathcal{G}$ is a unitary point-group. In this case the corresponding material tensor must be invariant under Θ . Thus, for nonmagnetic crystals, all time-antisymmetric tensors vanish identically, whilst the forms of time-symmetric tensors may be obtained according to (13.21).

- (ii) $\mathcal{M}$ is one of the dichromatic groups, and Θ is only a symmetry element when combined with certain elements of a covering unitary group, i.e.

$$\begin{aligned} \mathcal{M} &= \mathcal{N} + \mathcal{A}\mathcal{N}, \quad \mathcal{N} \subset \mathcal{G}, \quad g/n = 2, \\ \mathcal{A} &= \Theta S, \quad S \notin \mathcal{N}, \quad S \in \mathcal{G}, \end{aligned}$$

where $\mathcal{N}$ is a unitary, normal subgroup of the unitary covering group $\mathcal{G}$ of index 2. Thus, for the 58 additional magnetic point-groups, $\mathcal{M}$, it is necessary to distinguish not only between polar and axial tensors but also between time-symmetric and time-antisymmetric tensors, that is between tensors which are invariant (i -tensors) under time-inversion and those whose components all change sign (c -tensors) under time-inversion.

In this case we find that Θ^2 is still a symmetry operation under which the tensor should remain invariant.

Table 13.2. Generalized classification of tensors.

	Even rank			Odd rank		
	Θ	I	ΘI	Θ	I	ΘI
Polar i -tensors	+1	+1	+1	+1	-1	-1
Polar c -tensors	-1	+1	-1	-1	-1	+1
Axial i -tensors	+1	-1	-1	+1	+1	+1
Axial c -tensors	-1	-1	+1	-1	+1	-1

Table 13.3. Magnetic point-groups containing I or ΘI .

Type I	Type II	Type III	
$I \in \mathcal{G}$	$I \in \mathcal{G} + \Theta \mathcal{G}$	I	ΘI
$\bar{1}, 2/m, mmm$	$\bar{1}, 2/\mathbf{m}, \mathbf{mmm}$	$\underline{2}/\underline{m}$ $\underline{mmm}$	$\bar{1}, 2/\underline{m}\underline{2}/\underline{m}$ $\underline{mmm}, \underline{mmm}, 4/\underline{m}$
$4/m, 4/mmm, \bar{3}$	$4/\mathbf{m}, 4/\mathbf{mmm}, \bar{3}$	$\underline{4}/\underline{m}, \underline{4}/\underline{mmm}$ $4/\underline{mmm}, \bar{3}\underline{m}$	$\underline{4}/\underline{m}, 4/\underline{mmm}, \underline{4}/\underline{mmm}$ $4/\underline{mmm}, \bar{3}, \bar{3}\underline{m}, \bar{3}\underline{m}$
$\bar{3}m, 6/m, 6/mmm$	$\bar{3}\mathbf{m}, 6/\mathbf{m}, 6/\mathbf{mmm}$	$\underline{6}/\underline{m}$ $\underline{6}/\underline{mmm}, 6/\underline{mmm}$	$6/\underline{m}, \underline{6}/\underline{m}, 6/\underline{mmm}$ $\underline{6}/\underline{mmm}, 6/\underline{mmm}$
$m3, m3m$	$\mathbf{m3}, \mathbf{m3m}$	$\underline{m3m}$	$\underline{m3}, \underline{m3m}, \underline{m3m}$

Thus, under Θ a tensor transformation involves multiplication by either +1 (i -tensor) or -1 (c -tensor).

Tensors that describe systems with symmetries belonging to one of the 58 dichromatic groups can then be classified into the four categories described in Table 13.2. Table 13.3 lists the point-groups that contain either I or ΘI .

Inspection of Tables 13.2 and 13.3 enables us to write the following rules:

- (a) Since type II Shubnikov (gray) groups contain Θ as a symmetry operation, it follows that:

For type II Shubnikov group symmetries: All c -tensors are null ones, irrespective of rank.

- (b) **For type I or II centrosymmetric Shubnikov groups**, i.e. groups that include space-inversion $I(\bar{1})$ as a group operation:

Axial i -tensors of even rank and polar i -tensors of odd rank are null tensors.

There are 11 such groups among the 32 type I (and hence of type II) listed in Table 13.3.

(c) **For type III centrosymmetric Shubnikov groups:**

1. Axial c -tensors and polar i -tensors of odd rank are null tensors.
2. Axial i -tensors and polar c -tensors of even rank are null tensors.

13.1.4 Intrinsic symmetry

As we mentioned at the beginning of this section, tensors may have extra symmetries that arise from the physical phenomena they represent or relate. For example, if the tensor components appear as coefficients of a thermodynamic, or thermostatic, potential energy function, an extra symmetry involving transposition of some indices emerges. Such symmetry is called the intrinsic symmetry of a tensor $\mathfrak{T}$.

In considering intrinsic symmetry here, we confine our attention to linear response, and omit any symmetry arising from nonlinear constraints. Within linear response, a further distinction can be made between two types of intrinsic symmetries.

Intrinsic symmetry arising from thermostatic considerations

The electric susceptibility tensor, which relates the induced polarization to the external electric field as

$$P_i = \sum_j \chi_{ij} E_j, \quad (13.22)$$

is an example of matter tensors characterizing static properties. According to the second law of thermodynamics, because these properties are static, they may be described in terms of a succession of equilibrium states; changes between these states are effected through quasi-static processes, which are reversible. The terms comprising the corresponding potential energy, or free energy, must be perfect differentials. The intrinsic symmetry of these tensors that emerges is a direct consequence of the reversibility of the order in which the free energy may be successively differentiated with respect to the components of the external force field. Thus, (13.22) is derived from the potential energy function

$$U = \frac{1}{2} \sum_{ij} \chi_{ij} E_i E_j,$$

where the quadratic form of the potential leads to relations of the form $\chi_{ij} = \chi_{ji}$.

Intrinsic symmetry arising from steady-state considerations

Electrical conductivity is a typical example of transport processes which are physically characterized by a steady state, i.e. dynamic rather than static equilibrium, for which reversibility laws do not apply. In an electrical conduction process, an applied *force* – a potential gradient – gives rise to a *flux* – an electrical current. Similarly, in other transport processes, a *force* X is applied, such as a temperature or concentration gradient, which gives rise to a *flux* J , such as heat flow, or a flow of matter of a component in a mixture.

In an isotropic medium, the components of the vector representing the force, X_i , and those representing the corresponding flux, J_i , are related by

$$J_i = \sigma X_i,$$

while in anisotropic media, the proportionality must be generalized to

$$J_i = \sum_j L_{ij} X_j,$$

indicating that any force component may give rise to any flux component.

Familiar examples of such proportionality for irreversible processes are provided by Ohm's law (relating electrical current to potential gradient), Fourier's law (relating heat flow to temperature gradient), and Fick's law (relating flow of matter of a component in a mixture to its concentration gradient).

As we discussed in Section 12.6, intrinsic symmetry for irreversible processes is a consequence of the concept of microscopic reversibility, which is the basis of Onsager's theorem of irreversible thermodynamics, rather than macroscopic reversibility implicit in the second law of thermostatics. The Onsager relations are given by

$$L_{ik} = L_{ki}, \quad (13.23)$$

in the absence of magnetic fields, and by

$$L_{ik}(\mathbf{B}) = L_{ki}(-\mathbf{B}), \quad (13.24)$$

when a magnetic field $\mathbf{B}$ is present, where L_{ij} is a transport tensor element.

Permutation groups associated with intrinsic symmetry

The set of all possible index permutations associated with the intrinsic symmetry of a tensor $\mathfrak{T}$ forms a group $\mathcal{P}$ whose operations leave the tensor invariant. $\mathcal{P}$ may be one of the symmetric groups $\mathcal{S}_n$ or a subgroup of $\mathcal{S}_n$. We introduce linear permutation operators P on the tensor space such that

$$\begin{aligned} P \mathfrak{T}_{ab\dots k} x_{ab\dots k} &= \mathfrak{T}_{ab\dots k} x_{P(ab\dots k)} = \mathfrak{T}_{P(ab\dots k)} x_{ab\dots k}, \\ x_{ab\dots k} &\equiv x_a x_b \dots x_k, \\ P(ab\dots k) &= \text{permutation of indices } ab\dots k. \end{aligned} \quad (13.25)$$

With the aid of these permutation operators on the space of $\mathfrak{T}$ we engender a Rep Γ_T of $\mathcal{P}$.

In all important physical applications, intrinsic symmetry permutations do not produce linear combinations of tensor elements, but rather have three possible consequences:

- (i) Tensor components are left invariant under index permutation, in which case the tensor is *symmetric*. It transforms like the invariant Irrep of $\mathcal{P}$, $(^1)\Delta$. If $(^1)\Delta$ is contained s times in $\Gamma_T \downarrow (^1)\Delta$, the invariant vectors of the symmetric tensor $\mathfrak{T}$ will all be contained in the s -dimensional subspace L^s , which transforms like $\left(^{(1)}\Delta\right)^s \equiv (^1)\Delta$.

Thus, the invariant tensor under $\mathcal{P}$ is obtained with the aid of the projection

$$\frac{1}{p} \sum_{P \in \mathcal{P}} P. \quad (13.26)$$

- (ii) Tensor components change sign under odd permutations, and remain invariant under even permutations; such a tensor is labeled *antisymmetric*. It transforms like the alternating Irrep of $\mathcal{P}$. The antisymmetrized components are obtained with the aid of the projection operator

$$\frac{1}{p} \sum_{P_l \in \mathcal{P}} (-1)^l P_l, \quad (13.27)$$

where l is the number of transpositions involved in the permutation.

- (iii) Permutations are irrelevant to the tensor symmetry, and the tensor is called *general*.

Maximum number of independent components allowed by intrinsic symmetry

Since a general tensor of rank k is considered as the outer-product of k vectors, its transformation under a three-dimensional symmetry operation R is just $(\otimes^{(v)} \Gamma(R))^k$ with character

$$\chi_T(R) = \begin{cases} \left({}^{(v)}\chi(R) \right)^k = (2 \cos \phi \pm 1)^k & \text{polar tensor,} \\ (\pm 2 \cos \phi + 1)^k & \text{axial tensor,} \end{cases} \quad (13.28)$$

$$(13.29)$$

where R involves a rotation through ϕ , and the $(-)$ sign corresponds to a roto-reflection. Now, if the corresponding physical system is invariant under a point-group $\mathcal{G}$, then the tensor should transform according to the invariant Irrep $^{(1)}\Gamma$, and the number of its independent components is then given by

$$\mathcal{N} = \langle (\otimes^{(v)} \Gamma(R))^k | {}^{(1)}\Gamma \rangle = \frac{1}{g} \sum_{R \in \mathcal{G}} \chi_T(R). \quad (13.30)$$

When the tensor possesses an intrinsic symmetry group $\mathcal{P}$, then (13.28) and (13.29) become

$$\chi_T(R) = \frac{1}{p} \sum \pm {}^{(v)}\chi(R^l) {}^{(v)}\chi(R^m) \dots {}^{(v)}\chi(R^p), \quad (13.31)$$

where $l, m, \dots, p$ are the permutation cycle-lengths, and the $\pm$ apply for even and odd permutations.

Example 13.1

- (i) **Rank-2 symmetric polar tensor** $\mathcal{P} = (1)(2), (12)$

$$\begin{aligned} \chi_T(R) &= \frac{1}{2} \left({}^{(v)}\chi(R) {}^{(v)}\chi(R) + {}^{(v)}\chi(R^2) \right) \\ &= \frac{1}{2} \left((2 \cos \phi \pm 1)^2 + (2 \cos(2\phi) + 1) \right) \\ &= 4 \cos^2 \phi \pm 2 \cos \phi. \end{aligned}$$

Table 13.4. *Physical tensors.*

Related tensor types	Character $\chi(R)$ ($c = \cos \phi$)	Maximum # of constants
Scalar $\Leftrightarrow$ vector	$2c \pm 1$	3
Scalar $\Leftrightarrow [ij]^a$ Vector $\Leftrightarrow$ vector $\left. \vphantom{\begin{matrix} \text{Scalar} \\ \text{Vector} \end{matrix}} \right\}$	$(2c \pm 1)^2$	9
Scalar $\Leftrightarrow [ij = ji]^b$ Vector $\Leftrightarrow$ vector (S) $\left. \vphantom{\begin{matrix} \text{Scalar} \\ \text{Vector} \end{matrix}} \right\}$,	$4c^2 \pm 2c$	6
Vector $\Leftrightarrow [ij]$	$(2c \pm 1)(2c \pm 1)^2$	27
Vector $\Leftrightarrow [ij = ji]$	$(2c \pm 1)(4c^2 \pm 2c)$	18
$[ij = ji] \Leftrightarrow [kl = lk]$	$(4c^2 \pm 2c)^2$	36
$[ij = ji] \Leftrightarrow [kl = lk]$	$16c^4 \pm 8c^3 - 4c^2 + 1$	21
$[ik = ki], [il = li], [jk = kj], [jl = lj]$		
$[ij = ji] \Leftrightarrow [kl]$	$(4c^2 \pm 2c)(2c \pm 1)^2$	54
$[ij] \Leftrightarrow [kl]$	$(2c \pm 1)^2(2c \pm 1)^2$	81

^a $[ij]$ general tensor of rank 2. ^b $[ij = ji]$ symmetric tensor of rank 2.

(ii) **Rank-2 antisymmetric polar tensor** $\mathcal{P} = (1)(2), (12),$

$$\begin{aligned}
 \chi_T(R) &= \frac{1}{2} \left({}^{(v)}\chi(R){}^{(v)}\chi(R) - {}^{(v)}\chi(R^2) \right) \\
 &= \frac{1}{2} \left((2 \cos \phi \pm 1)^2 - (2 \cos(2\phi) + 1) \right) \\
 &= \pm 2 \cos \phi - 1.
 \end{aligned}$$

Sometimes a general tensor is symmetric with respect to one set of its indices and antisymmetric with respect to another set. In such a case, consider the tensor as a direct product of two tensors, one symmetric and the other antisymmetric in their indices.

13.2 Construction of symmetry-adapted tensors

The problem of constructing symmetrized tensors has been extensively handled in the past, first by Birss [83], Bhagavantam [85], and, Erdős [84]. Subsequently, Bradley and Davies [60], building on this body of work, proposed a method, using the full power of group theory, to classify and determine any tensor that satisfies the symmetries of any of the 58 magnetic point-groups. This general method will, of course, cover the remaining 32 geometric point-groups. However, we begin this section with a computational method that we propose, and that uses the full power of symbolic and permutation manipulations available in *Mathematica*.

13.2.1 Method using Mathematica

We propose a method that can be tailored for the generation of symmetry-adapted tensors of any rank. However, our presentation here is limited to tensors up to rank 6. It is based on the generation of two tensors as outer vectorial products. The first, comprising tensor indices, can be easily amenable to symmetrization with respect to the intrinsic permutations, namely (13.26) and (13.27). The second tensor, comprising outer-products of symbolic vectors, is symmetry-adapted with respect to the corresponding roto-reflection group $\mathcal{G}$. This is accomplished by first simultaneously operating on the constituent vectors by a roto-reflection operation $R \in \mathcal{G}$, and then taking the outer vector products, namely

$$\mathfrak{T}(R) = R\mathbf{A} : R\mathbf{B} : R\mathbf{C} : \dots, \quad (13.32)$$

and the roto-reflection symmetrization is effected according to the projection

$$\mathfrak{T} = \sum_{R \in \mathcal{G}} \mathfrak{T}(R). \quad (13.33)$$

Finally the two tensors are merged to produce the complete symmetry-adapted form.

Computer program

Below we provide a complete version of a program based on the proposed method. It is specifically applied to the construction of the elastic constants tensor, which is of rank 4. We carry out the computation for a material system with $\mathcal{O}$ symmetry.

PROGRAM TENSOR

```
<<DiscreteMath'Combinatorica'
<<NumberTheory'NumberTheoryFunctions'
<<C:Path:/0.txt
RANK=4

⇒
PERM is the permutation group associated with intrinsic symmetry.
←

PERM={Range[4],{2,1,3,4},{1,2,4,3},{2,1,4,3},{3,4,1,2},
      {4,3,2,1},{3,4,2,1},{4,3,1,2}};
X={1,2,3};
f[a_,b_,c_,d_-]:={a,b,c,d};

⇒
```

TENS is a rank 4 tensor whose entries are 4 integers corresponding to the indices of the entry location. It is operated on by the permutation group so that it incorporates the intrinsic symmetry.

←

```
TENS=Outer[f,X,X,X,X];
```

```
Store={};
```

```
Do[
```

```
  Do[
```

```
    i1=TENS[i,j,k,l,PERM[[m,1]]];i2=TENS[i,j,k,l,PERM[[m,2]]];
```

```
    i3=TENS[i,j,k,l,PERM[[m,3]]];i4=TENS[i,j,k,l,PERM[[m,4]]];
```

```
    Switch[MemberQ[Store,TENS[[i1,i2,i3,i4]]],False,
```

```
      TENS[[i1,i2,i3,i4]]=TENS[[i,j,k,l]]
```

```
    ],{m,1,Length[PERM]}
```

```
  ];AppendTo[Store,TENS[[i,j,k,l]]],
```

```
  {i,1,3},{j,1,3},{k,1,3},{l,1,3}
```

```
];
```

⇒

Generate the Roto-reflection symmetry group.

←

```
Group[P, NG, NP, G, 0]; ⇒
```

VECT contains 6 vectors that can be used to construct a tensor, up to rank 6, as an outer vector product.

←

```
VECT={{a1,a2,a3,a4},{b1,b2,b3,b4},{c1,c2,c3,c4},
```

```
  {d1,d2,d3,d4},{e1,e2,e3,e4},{f1,f2,f3,f4}}
```

⇒

The roto-reflection symmetry-adapted "TENSOR" is generated as a linear combination of outer products of roto-reflected vectors.

←

```
j1=1;VT=VECT[[1]];
```



```

While[j1<RANK,j1++;VETS=VECT[[j1]];VT=Outer[Times,VT,VETS];
      ];TENSOR=VT;
Print["Tensor dimension = ",Dimensions[TENSOR]];
Do[
      j1=1;VT=Rot[i].VECT[[1]];
While[j1<RANK,j1++;VETS=Rot[i].VECT[[j1]];
      VT=Outer[Times,VT,VETS];
      ];TENSOR=TENSOR+VT,{i,2,g}
];

```

⇒

Intrinsic symmetry is incorporated into "TENSOR" with the aid of TENS.

```

⇐ Do[
      i1=TENS[i,j,k,1,1];i2=TENS[i,j,k,1,2]];
      i3=TENS[i,j,k,1,3];i4=TENS[i,j,k,1,4]];
      TENSOR[[i,j,k,1]]=TENSOR[[i1,j1,k1,1]],
      {i,1,3},{j,1,3},{k,1,3},{1,1,3}
];

```

⇒

Finally, a simplified version of the symmetry-adapted tensor is generated by replacing the nonzero entries with letters of the alphabet.

⇐

```

abc={a,b,c,d,e,f,g,h,o,p,q};FX={};ij=1;
Do[
      Switch[FreeQ[TENSOR[[i,j,k,1]],0],True,
      Switch[FreeQ[abc,TENSOR[[i,j,k,1]]],True,
      Switch[FreeQ[FX,TENSOR[[i,j,k,1]]],True,
      xx=TENSOR[[i,j,k,1]];
      TENSOR[[i,j,k,1]]=abc[[ij]];
      Do[
      Switch[TENSOR[[i1,j1,k1,1]]==xx,
      True,

```

```

        TENSOR[[i1,j1,k1,l1]]=abc[[ij]]
    ],
    {i1,1,3},{j1,1,3},{k1,1,3},{l1,1,3}
];
Print[abc[[ij]], " = [", i, j, k, l, ""]; ij++;
AppendTo[FX, xx]
]
]
], {i,1,3},{j,1,3},{k,1,3},{l,1,3}
]
Print[MatrixForm[TENSOR]]

```

Output

The elastic stiffness tensor is used here as an example.

It is a 4th rank tensor with intrinsic symmetry group:

```
{Range[4], 2, 1, 3, 4, {1, 2, 4, 3}, {2, 1, 4, 3}, {3, 4, 1, 2},
  {4, 3, 2, 1}, {3, 4, 2, 1}, {4, 3, 1, 2}},
```

and it is determined for a system with $\mathcal{O}$ symmetry.

Independent parameters correspond to the following indices:

```
a=[1111], b=[1122], c=[1212].
```

The symmetry-adapted tensor is

$$\left(\begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & b \end{pmatrix} \begin{pmatrix} 0 & c & 0 \\ c & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 & c \\ 0 & 0 & 0 \\ c & 0 & 0 \end{pmatrix} \right)$$

$$\left(\begin{pmatrix} 0 & c & 0 \\ c & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} b & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & c \\ 0 & c & 0 \end{pmatrix} \right)$$

$$\left(\begin{pmatrix} 0 & 0 & c \\ 0 & 0 & 0 \\ c & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & c \\ 0 & c & 0 \end{pmatrix} \begin{pmatrix} b & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & a \end{pmatrix} \right)$$

13.2.2 The method of Erdős

We consider a tensor $\mathfrak{T}^{(k)}$ of rank k , which is invariant under the operations of $\mathcal{G}$. We consider the tensor components as a vector in a 3^k -dimensional vector space $\mathcal{V}^k$, that is left invariant under the action of the $3k \times 3k$ matrices corresponding to the $\left(\otimes^{(v)}\Gamma\right)^k$ Rep of $\mathcal{G}$. If $\mathbf{v}$ is any vector of $\mathcal{V}^k$, then

$$\mathbf{u} = \sum_{R \in \mathcal{G}} \left(\otimes^{(v)}\Gamma(R)\right)^k \mathbf{v} \quad (13.34)$$

is an invariant vector of the group of matrices $\left(\otimes^{(v)}\Gamma(R)\right)^k$. Since every invariant vector $\mathbf{u}$ represents an invariant tensor of rank k , the problem is then reduced to the construction of all linearly independent vectors $\mathbf{u}$. Erdős proposed the following procedure for the construction of all invariant $\mathbf{u}$ s [84]: We start by writing

$$\left(\otimes^{(v)}\Gamma(R)\right)^k = \left(\otimes^{(v)}\Gamma(R)\right)^{k-1} \otimes^{(v)}\Gamma(R), \quad (13.35)$$

and we subduce $\left(\otimes^{(v)}\Gamma(R)\right)^{k-1}$ into Irreps of $\mathcal{G}$ as

$$\left(\otimes^{(v)}\Gamma(R)\right)^{k-1} = \sum_{\mu=1}^p \oplus^{(\mu)} \Gamma, \quad (13.36)$$

with corresponding basis vectors f_l^μ , $l = 1, \dots, d_\mu$, such that

$$\left(\otimes^{(v)}\Gamma(R)\right)^{k-1} f_l^\mu = \sum_j f_j^\mu {}^{(\mu)}\Gamma_{jl}(R). \quad (13.37)$$

Next, we consider the two possible cases for ${}^{(v)}\Gamma(R)$:

- (i) The vector Rep ${}^{(v)}\Gamma$ is an Irrep of $\mathcal{G}$ with basis vectors e_m , $m = 1, 2, 3$. This is the case for $\mathcal{T}$, $\mathcal{O}$, $\mathcal{T}_d$, $\mathcal{T}_h$, $\mathcal{O}_h$. An arbitrary vector $\mathbf{v}$ of $\mathcal{V}^k$ can be expressed as

$$\mathbf{v} = \sum_{\mu, lm} a_{lm}^\mu (f_l^\mu \otimes e_m), \quad \text{with } a_{lm}^\mu \text{ arbitrary.} \quad (13.38)$$

Substituting (13.38) in (13.34) we obtain

$$\begin{aligned} \mathbf{u} &= \sum_{\mu, lm} a_{lm}^\mu (f_l^\mu \otimes e_m) \sum_{R \in \mathcal{G}} \left(\otimes^{(v)}\Gamma(R)\right)^{k-1} \otimes^{(v)}\Gamma(R) \\ &= \sum_{\mu; \substack{m \\ l \ i}} a_{lm}^\mu (f_j^\mu \otimes e_i) \sum_{R \in \mathcal{G}} {}^{(\mu)}\Gamma_{jl}(R) {}^{(v)}\Gamma_{im}(R) \\ &= \frac{g}{3} \sum_{\mu; \substack{m \\ l \ i}} a_{lm}^\mu (f_l^\mu \otimes e_m) \delta_{\mu\nu} \delta_{lm} \delta_{ij} \\ &= \sum_{\nu; i} a_{ii}^\nu (f_i^\nu \otimes e_i), \quad \forall \nu \simeq v, \end{aligned} \quad (13.39)$$

where we used the great orthogonality theorem and the fact that $d_v = 3$ in obtaining the last line. Notice that the last summation is only over Irreps ν equivalent to the vector Irrep v .

(ii) The vector $\text{Rep } {}^{(v)}\Gamma$ is reducible in $\mathcal{G}$, such that

$${}^{(v)}\Gamma = \sum_{\sigma=1}^s \oplus {}^{(\sigma)}\Gamma, \quad \text{with } d_{\sigma} = 1, \text{ or } 2; \text{ and } s = 2 \text{ or } 3,$$

which is the case for all point-groups other than the ones listed above. The basis functions associated with the decomposition are written as

$$e_j^{\sigma} \Rightarrow {}^{(v)}\Gamma(R) e_j^{\sigma} = \sum_{i=1}^r e_i^{\sigma} {}^{(\sigma)}\Gamma_{ij}(R), \quad r = 1 \text{ or } 2.$$

We then obtain

$$\begin{aligned} \mathbf{u} &= \sum_{\mu, \sigma; \substack{m \\ l \ i}} a_{lm}^{\mu} (f_j^{\mu} \otimes e_i^{\sigma}) \sum_{R \in \mathcal{G}} {}^{(\mu)}\Gamma_{jl}(R) {}^{(\sigma)}\Gamma_{im}(R) \\ &= \sum_{\nu, \sigma; i} a_{ii}^{\nu \sigma} (f_i^{\nu} \otimes e_i^{\sigma}). \end{aligned} \quad (13.40)$$

The summation over ν here is over the components of $\left(\otimes {}^{(v)}\Gamma(R) \right)^{k-1}$, which are equivalent to the Irrep ${}^{(\sigma)}\Gamma$.

Example 13.2

Let us consider a fourth-rank tensor $\mathfrak{T}_{abcd}$ associated with a system having $\mathcal{O}$ symmetry. The vector $\text{Rep } {}^{(v)}\Gamma \equiv \Gamma_{15}$, i.e. it is an Irrep of $\mathcal{O}$, with

$${}^{(v)}\Gamma \otimes {}^{(v)}\Gamma = \Gamma_1 + \Gamma_{12} + \Gamma_{15'} + \Gamma_{25'}.$$

If we choose a basis e_1, e_2, e_3 for ${}^{(v)}\Gamma$, the bases of the Irreps are written as

$$\begin{aligned} \Gamma_1 &: e_i \cdot e_i \\ \Gamma_{12} &: \begin{cases} e_1 \cdot e_1 + \omega e_2 \cdot e_2 + \omega^2 e_3 e_3 \\ e_1 \cdot e_1 + \omega^2 e_2 \cdot e_2 + \omega e_3 \cdot e_3 \end{cases} \quad \omega = \exp[i2\pi/3] \\ \Gamma_{15'} &: \begin{cases} e_2 \cdot e_3 + e_3 \cdot e_2 \\ e_3 \cdot e_1 + e_1 \cdot e_3 \\ e_1 \cdot e_2 + e_2 \cdot e_1 \end{cases} \quad \Gamma_{25'} : \begin{cases} e_3 \cdot e_2 - e_2 \cdot e_3 \\ e_3 \cdot e_1 - e_1 \cdot e_3 \\ e_1 \cdot e_2 - e_2 \cdot e_1 \end{cases} \end{aligned}$$

Next, we consider the following permutation symmetries:

- (i) Symmetry with respect to (a, b) with elements $\mathcal{S}_2 = \{E, (ab)\}$, so that the projection operator is

$$\mathcal{P} = \frac{1}{2} (E + (ab)),$$

gives

$$\mathcal{P} ({}^{(v)}\Gamma \otimes {}^{(v)}\Gamma) = \Gamma_1 + \Gamma_{12} + \Gamma_{15'} = [{}^{(v)}\Gamma^2].$$

- (ii) Symmetry with respect to (a, b) and (c, d) constituting the permutation group $\{E, (ab), (cd), (ab)(cd)\} \equiv \mathcal{S}_2 \otimes \mathcal{S}_2$, with

$$\mathcal{P} = \frac{1}{4} (E + (ab) + (cd) + (ab)(cd)) .$$

13.2.3 The method of Bradley and Davies for magnetic crystals

The starting point of this method [60] is to identify the covering group $\mathcal{G}$ isomorphic with $\mathcal{M}$, and the normal subgroups $\mathcal{N} \in \mathcal{G}$ with index 2. The method then proceeds as follows:

- (i) We identify among the Irreps of $\mathcal{G}$ the following one-dimensional Irreps:
- (a) the invariant (or totally symmetric) Irrep $^{(s)}\Gamma \equiv {}^{(1)}\Gamma$,
 - (b) the Irrep in which $\mathcal{N}$ is a kernel, i.e. where all the elements of $\mathcal{N}$ are represented by +1 and those of $\mathcal{AN}$ by -1, $^{(m)}\Gamma$,
 - (c) the pseudoscalar Irrep, $^{(ps)}\Gamma$, where all proper rotations are represented by +1, and improper rotations by -1,
 - (d) the outer-product Irrep $^{(m \otimes ps)}\Gamma = {}^{(m)}\Gamma \otimes {}^{(ps)}\Gamma$.

In some cases $^{(ps)}\Gamma$ may coincide with $^{(m)}\Gamma$ or $^{(1)}\Gamma$, but this does not matter.

In what follows, we will continue to use our notation defined in Chapter 12, namely $\mathcal{B} \in \mathcal{AN}$, and $R, S \in \mathcal{N}$, and, in addition, we will denote $\mathcal{R} \in \mathcal{M}$ and the corresponding element in $\mathcal{G}$ by R .

- (ii) We define the vector representation $^{(v)}\Gamma$ engendered by $R \in \mathcal{O}(3)$ as

$$x'_i = \sum_{j=1}^3 {}^{(v)}\Gamma_{ij}(R) x_j, \quad (13.41)$$

where $^{(v)}\Gamma_{ij}(R)$ is the orthogonal matrix representing R .

- (iii) We define an α -tensor, $\alpha = s, m, ps$, or $m \otimes ps$, of rank k in $\mathcal{M}$ to be one that transforms under $\mathcal{R}$ like the direct product of k vector representations $^{(v)}\Gamma(R)$, namely $(\otimes {}^{(v)}\Gamma(R))^k$, multiplied by a phase factor $^{(\alpha)}\chi(R)$, where $^{(\alpha)}\chi(R)$ is the character of R in the α -Irrep.

$$\begin{aligned} \mathfrak{T}_{abc\dots k}^{(k, \alpha)'} &= \mathcal{R} \mathfrak{T}_{pq\dots z}^{(k, \alpha)} \\ &= {}^{(\alpha)}\chi(R) \sum_{pq\dots z} R_{ap} R_{bq} \dots R_{kz} \mathfrak{T}_{pq\dots z}^{(k, \alpha)}, \quad R \in \mathcal{G}. \end{aligned} \quad (13.42)$$

Conversely, $\mathfrak{T}^{(k)}$ is an α -tensor of rank k if its transformation by $\mathcal{B} = \mathcal{AR}$ satisfies (13.42).

A comparison of the definition (13.42) with the classification of Table 13.2 reveals that

$$\begin{aligned}
 s\text{-tensor} &\Leftrightarrow \text{polar } i\text{-tensor}, \\
 m\text{-tensor} &\Leftrightarrow \text{polar } c\text{-tensor}, \\
 ps\text{-tensor} &\Leftrightarrow \text{axial } i\text{-tensor}, \\
 m \otimes ps\text{-tensor} &\Leftrightarrow \text{axial } c\text{-tensor}.
 \end{aligned} \tag{13.43}$$

According to (13.42) we notice that the components of $\mathfrak{T}^{(k)}$ transform according to the direct product $\text{Rep } {}^{(\alpha)}\Gamma \otimes {}^{(v)}\Gamma^k$. However, the fact that $\mathfrak{T}^{(k)}$ must also be invariant under all operations of $\mathcal{M}$ introduces constraints and, thus, new relations among the components of the tensor. The symmetry-adapted tensor is thus obtained when these relations have been satisfied. If the relations cannot be satisfied nontrivially for systems invariant under $\mathcal{M}$, then the physical effect described by the tensor is forbidden in these systems.

(iv) With the aid of *group theoretical methodology* we obtain:

- (a) The number of independent components $\mathcal{N}$ will equal the frequency of ${}^{(1)}\Gamma$ in the direct product ${}^{(\alpha)}\Gamma \otimes V^k$,

$$\mathcal{N} = \frac{1}{m} \sum_{R \in \mathcal{G}} {}^{(\alpha)}\chi(R) {}^{(v)}\chi^k(R). \tag{13.44}$$

Since ${}^{(\alpha)}\chi$ is real, this is also the frequency $\langle \otimes {}^{(v)}\Gamma^k | {}^{(\alpha)}\Gamma \rangle$.

- (b) The symmetry-adapted form of an α -tensor of rank k that is invariant under $\mathcal{M}$ is obtained with the aid of applying the projection operator

$$\mathcal{P}_s = \frac{1}{m} \sum_{\mathcal{R} \in \mathcal{M}} {}^{(s)}\chi(\mathcal{R}) \mathcal{R}, \tag{13.45}$$

to $\mathfrak{T}^{(k, \alpha)}$ that satisfy a transformation similar to (13.42) under $\mathcal{R}$. If we eye (13.45) from the perspective of (13.42), we may infer that it is exactly the same as applying the projection operator

$$\mathcal{P}_\alpha = \frac{1}{m} \sum_{R \in \mathcal{G}} {}^{(\alpha)}\chi(R) R, \tag{13.46}$$

to a polar i -tensor of rank k . Hence an α -tensor that is invariant under $\mathcal{M}$ is subject to exactly the same restrictions as a polar i -tensor that transforms not under ${}^{(s)}\Gamma$ but under ${}^{(\alpha)}\Gamma$.

Example 13.3

The magnetoelectric effect

The tensor invariant under the magnetic point-group $\mathcal{C}_{4v}(\mathcal{C}_{2v})$

The representative matrices for the $\mathcal{C}_{4v}$ elements in the $(^{(v)}\Gamma)$ Rep are

$$\begin{aligned}
 E &= \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} & C_2 &= \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} & C_4^+ &= \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \\
 C_4^- &= \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} & \sigma_x &= \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} & \sigma_y &= \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \\
 \sigma_{d1} &= \begin{bmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} & \sigma_{d2} &= \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}
 \end{aligned}$$

Since $\mathbf{E}$ is a polar i -tensor of rank 1 and $\mathbf{H}$ is an axial c -tensor of rank 1, the magnetoelectric tensor is an axial c -tensor of rank 2. From Table 13.5, we find that the appropriate Irrep of $\mathcal{C}_{4v}$ is therefore $(^{(m\otimes p)}\Gamma) = B_2$, when $\sigma_x, \sigma_y \in \mathcal{C}_{2v}$, and $(^{(m\otimes p)}\Gamma) = B_1$, when $\sigma_{d1}, \sigma_{d2} \in \mathcal{C}_{2v}$.

The number of independent components is

$$N = \frac{1}{8} (9 + 1 - 1 - 1 - 1 - 1 - 1 + 1 + 1) = 1.$$

Next, we consider the case $\sigma_x, \sigma_y \in \mathcal{C}_{2v}$, and apply the projection operator,

$$\mathcal{P}_{m\otimes p} = \frac{1}{8} (E + C_2 - C_4^+ - C_4^- - \sigma_x - \sigma_y + \sigma_{d1} + \sigma_{d2}),$$

Table 13.5. Character tables of $\mathcal{C}_{4v}$ and $\mathcal{C}_{2v}$.

$\mathcal{C}_{4v}$	E	C_2	$C_4^\pm$	σ_x, σ_y	σ_{d1}, σ_{d2}	$\mathcal{C}_{2v}$	E	C_2	σ_x	σ_y
									σ_{d1}	σ_{d2}
$A_1 = (^{(s)}\Gamma)$	1	1	1	1	1	A_1	1	1	1	1
$A_2 = (^{(ps)}\Gamma)$	1	1	1	-1	-1	A_2	1	1	-1	-1
$B_1 = (^{(m)}\Gamma)$	1	1	-1	1	-1	B_1	1	-1	1	-1
$B_2 = (^{(m\otimes ps)}\Gamma)$	1	1	-1	-1	1	B_2	1	-1	-1	1
E	2	-2	0	0	0					
$(^{(v)}\Gamma)$	3	-1	1	1	1					

to bilinear products $x_a x_b (a, b = 1, 2, 3)$. We may write the bilinear product, say, $x_1 x_2$, as

$$\begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} : \begin{bmatrix} 0 & 1 & 0 \end{bmatrix},$$

and when we operate on this bilinear form with a symmetry element R we obtain

$$R \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} : \begin{bmatrix} 0 & 1 & 0 \end{bmatrix} \tilde{R}.$$

Thus, if we choose $R = C_2$, we obtain

$$\begin{aligned} \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} : \begin{bmatrix} 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} &= \begin{bmatrix} -1 \\ 0 \\ 0 \end{bmatrix} : \begin{bmatrix} 0 & -1 & 0 \end{bmatrix} \\ &= \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} = x_1 x_2. \end{aligned}$$

On the other hand, if we choose $R = C_4^+$, we obtain

$$\begin{aligned} \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} : \begin{bmatrix} 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} &= \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} : \begin{bmatrix} -1 & 0 & 0 \end{bmatrix} \\ &= \begin{bmatrix} 0 & 0 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} = -x_2 x_1. \end{aligned}$$

When we carry out this procedure for all operators of $\mathcal{C}_{4v}$ we obtain the projection

$$\frac{1}{2} (x_1 x_2 + x_2 x_1).$$

Upon repeating this procedure for the remaining bilinear forms, we find that they all vanish. Hence, we obtain $\mathfrak{T}_{12} = \mathfrak{T}_{21} = \lambda$, and we write the magnetoelectric tensor as

$$\begin{pmatrix} 0 & \lambda & 0 \\ \lambda & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

When $\sigma_{d1}, \sigma_{d2} \in \mathcal{C}_{2v}$, the projection operator becomes

$$\mathcal{P}_{m \otimes p} = \frac{1}{8} (E + C_2 - C_4^+ - C_4^- + \sigma_x + \sigma_y - \sigma_{d1} - \sigma_{d2}).$$

In contrast to the previous case, we find that $\mathcal{P}_{m \otimes p} x_1 x_2 = 0$. The nonzero components are found to be

$$\begin{aligned}\mathcal{P}_{m \otimes p} x_1 x_1 &= \frac{1}{2} (x_1 x_1 - x_2 x_2), \\ \mathcal{P}_{m \otimes p} x_2 x_2 &= \frac{1}{2} (x_2 x_2 - x_1 x_1),\end{aligned}$$

and we obtain

$$\begin{pmatrix} \lambda & 0 & 0 \\ 0 & -\lambda & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

13.2.4 Method of invariants

If the tensor $\mathfrak{T}_{ab\dots k}^{(k)}$ transforms as a vector with respect to the indices $abc\dots$, and as a pseudovector with respect to the indices $fg\dots k$, then the homogeneous polynomial function of degree k ,

$$F(\mathbf{x}, \mathbf{x}', \mathbf{m}, \dots) = \sum \mathfrak{T}_{ab\dots k}^{(k)} x_a x'_b \dots m_f \dots, \quad (13.47)$$

is an invariant under the group $\mathcal{G}$, if $\mathfrak{T}^{(k)}$ is an invariant tensor under $\mathcal{G}$.

Our procedure is therefore to write down an invariant polynomial whose degree is equal to the rank of the tensor. The tensor can then be read off as the coefficients in the polynomial.

For example, under the full rotation group $\mathcal{O}(3)$, the only invariant that can be formed out of $\mathbf{x}$, $\mathbf{x}'$, and $\mathbf{m}$ is

$$\mathbf{x} \times \mathbf{x}' \cdot \mathbf{m} = \epsilon_{ijk} x_i x'_j m_k,$$

which is constructed with the aid of the properties:

- (i) For $\mathcal{SO}(n)$ an arbitrary invariant polynomial Σ in n vectors $\mathbf{x}_1, \dots, \mathbf{x}_n$ can be written in the form

$$\Sigma_1 + J \Sigma_2,$$

where Σ_1 and Σ_2 are polynomials in the scalar products $\mathbf{x}_i \cdot \mathbf{x}_j$ and $J = \det(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n)$.

- (ii) Any arbitrary function Σ of $\mathbf{x}_1, \dots, \mathbf{x}_n$ invariant under $\mathcal{SO}(n)$ can be expressed as some arbitrary function $\Sigma(\mathbf{x}_i \cdot \mathbf{x}_j)$ of the basic invariants $\mathbf{x}_i \cdot \mathbf{x}_j$.

13.3 Description and classification of matter tensors

A partial list of matter tensors is given in Table 13.6, describing the physical quantities they relate and the defining relations. The physical quantities tabulated are:

Mass	Δm	Volume	ΔV
Temperature	T	Entropy	ΔS
Temperature gradient	∇T	Heat flux	$\mathbf{q}$
Electric field	$\mathbf{E}$	Electric polarization	$\mathbf{P}$
		Current density	$\mathbf{J}$
Magnetic field	$\mathbf{H}$	Magnetization	$\mathbf{M}$
Strain	ε	Stress	$\boldsymbol{\sigma}$

Since matter tensors of rank 1 were discussed in Section 13.1.1, we start our discussion here with second-rank matter tensors.

Table 13.6. *Matter tensors.*

Physical property	Tensor		$N_{\max}$	Defining relation	Related quantities	
	Rank	Symbol				
Density	0	ρ	1	$\Delta m = \rho \Delta V$	Δm	ΔV
Specific heat	0	c	1	$\Delta S = c \frac{\Delta T}{T}$	ΔS	T
Pyroelectricity	1	$[p_i]$	3	$\Delta P_i = p_i \Delta T$	$\mathbf{P}$	T
Electrocaloric effect				$\Delta S = p_i \Delta E_i$	ΔS	$\mathbf{E}$
Electric susceptibility	2	$\boldsymbol{\alpha}$	6	$P_i = \alpha_{ij} E_j$	$\mathbf{P}$	$\mathbf{E}$
Magnetic susceptibility	2	$\boldsymbol{\mu}$	6	$M_i = \mu_{ij} H_j$	$\mathbf{M}$	$\mathbf{H}$
Electric conductivity	2	$\boldsymbol{\sigma}$	6	$J_i = \sigma_{ij} E_j$	$\mathbf{J}$	$\mathbf{E}$
Electric resistivity	2	$\boldsymbol{\rho}$	6	$E_i = \rho_{ij} J_j$	$\mathbf{E}$	$\mathbf{J}$
Thermal conductivity	2	$\boldsymbol{\kappa}$	6	$q_i = \kappa_{ij} \frac{\partial T}{\partial x_j}$	$\mathbf{q}$	∇T
Thermal expansion	2	$\boldsymbol{\alpha}$	6	$\epsilon_{ij} = \alpha_{ij} \Delta T$	ε	T
Seebeck effect	2	$\boldsymbol{\beta}$	9	$E_i = \beta_{ij} \frac{\partial T}{\partial x_j}$	$\mathbf{E}$	∇T
Peltier effect	2	$\boldsymbol{\pi}$	9	$q_i = \pi_{ij} J_j$	$\mathbf{q}$	$\mathbf{J}$
Hall effect	3	$[\rho_{ijk}]$	9	$E_i = \rho_{ijk} J_j H_k$	$\mathbf{E}$	$\mathbf{J}, \mathbf{H}$
Piezoelectric effect	3	$[d_{ijk}]$	18	$P_i = d_{ijk} \sigma_{ijk}$	$\mathbf{P}$	$\boldsymbol{\sigma}$
Inverse piezoelectric effect	3	$[d_{ijk}]$	18	$\varepsilon_{jk} = d_{ijk} E_i$	ε	$\mathbf{E}$
Piezomagnetic effect	3	$[Q_{ijk}]$	18	$M_i = Q_{ijk} \sigma_{jk}$	$\mathbf{M}$	$\boldsymbol{\sigma}$

Table 13.6. (*cont.*)

Physical property	Tensor		$N_{\max}$	Defining relation	Related quantities	
	Rank	Symbol				
Electro-optical effect	3	$[r_{ijk}]$	18	$\Delta\beta_{ij} = r_{ijk} E_k$	$[\beta_{ij}]$	$\mathbf{E}$
Second-harmonic generation	3	$[d_{ijk}]$	18	$P_i(2\omega) = d_{ijk} E_j E_k$	$\mathbf{P}(2\omega)$	$\mathbf{E}$
Elastic stiffness	4	$[c_{ijkl}]$	21	$\sigma_{ij} = c_{ijkl} \varepsilon_{kl}$	$\boldsymbol{\sigma}$	$\boldsymbol{\varepsilon}$
Elastic compliance	4	$[s_{ijkl}]$	21	$\varepsilon_{ij} = s_{ijkl} \sigma_{kl}$	$\boldsymbol{\varepsilon}$	$\boldsymbol{\sigma}$
Piezo-optic effect	4	$[\pi_{ijkl}]$	36	$\Delta\beta_{ij} = \pi_{ijkl} \sigma_{kl}$	$[\beta_{ij}]$	$\boldsymbol{\sigma}$
Kerr effect	4	$[R_{ijkl}]$	36	$\Delta\beta_{ij} = R_{ijkl} E_k E_l$	$[\beta_{ij}]$	$\mathbf{E}$
Electrostriction	4	$[\gamma_{ijkl}]$	36	$\varepsilon_{kl} = \gamma_{ijkl} E_i E_j$	$\boldsymbol{\varepsilon}$	$\mathbf{E}$
Third-order elastic stiffness	6	$[c_{ijklmn}]$	56	$\sigma_{ij} = c_{ijklmn} \varepsilon_{kl} \varepsilon_{mn}$	$\boldsymbol{\sigma}$	$\boldsymbol{\varepsilon}$

13.3.1 Symmetric second-rank matter tensors

Many second-rank matter tensors are symmetric tensors. For tensors describing phenomena under thermodynamic equilibrium, it is a consequence of an associated potential energy function, while for transport and other nonequilibrium thermodynamic processes it is a result of the Onsager relations.

- (i) **Symmetric tensors derived from potential functions** As an example, we consider the electric polarizability tensor,

$$\mathbf{P} = \boldsymbol{\alpha} \mathbf{E}, \quad (13.48)$$

where both $\mathbf{P}$ and $\mathbf{E}$ are polar vectors. This relation is derivable from the potential energy,

$$\mathcal{W} = \frac{1}{2} \tilde{\mathbf{E}} \boldsymbol{\alpha} \mathbf{E},$$

and hence satisfies the relation

$$\frac{\partial P_i}{\partial E_j} = \frac{\partial P_j}{\partial E_i} \Rightarrow \alpha_{ij} = \alpha_{ji}.$$

Under a symmetry operation $R \in O(3)$, (13.10) transforms to

$$\begin{aligned} \mathbf{P}' &= R \mathbf{P} = \boldsymbol{\alpha}' \mathbf{E}' \\ &= R \boldsymbol{\alpha} R^{-1} (R \mathbf{E}) \\ &= \left[{}^{(v)}\Gamma(R) \otimes {}^{(v)}\Gamma(R) \right] \boldsymbol{\alpha} \mathbf{E}', \end{aligned} \quad (13.49)$$

that is, the elements of α form a basis for the symmetrized Kronecker product representation $\left[{}^{(v)}\Gamma(R) \otimes {}^{(v)}\Gamma(R) \right]$, since α is a symmetric tensor. Because α is a matter tensor, we require that for a system invariant under the point-group $\mathcal{G}$,

$$\alpha = \left[{}^{(v)}\Gamma(R) \otimes {}^{(v)}\Gamma(R) \right] \alpha, \quad \forall R \in \mathcal{G}, \quad (13.50)$$

i.e. α belongs to the identity Irrep of $\mathcal{G}$. The number of nonvanishing independent components of α is obtained from

$$\mathcal{N} = \frac{1}{2g} \sum_{R \in \mathcal{G}} \left({}^{(v)}\chi^2(R) + {}^{(v)}\chi(R^2) \right). \quad (13.51)$$

As demonstrated in (13.11) and (13.12), both combinations (v, v) and (a, a) have the same decomposition. Hence the number of independent components of the magnetic susceptibility, which relates the magnetic moment M and the magnetic field $\mathbf{H}$, can also be obtained using (13.51).

All second-rank symmetric tensors relating two polar or axial vectors transform like ${}^{(0)}\Gamma \oplus {}^{(2)}\Gamma^+$.

We make use of (13.17 and 13.18) to compile in Table 13.7 the symmetry-adapted forms of second-rank, symmetric matter tensors for the different crystal classes.

- (ii) **Symmetric tensors associated with the Onsager relations** As we discussed in Chapter 12, transport coefficients, which are components of corresponding

Table 13.7. *Second-rank matter tensors.*

Tensor	Relation	Related vectors	Vector type
Electric conductivity	$\mathbf{J} = \sigma \mathbf{E}$	Electric current $\mathbf{J}$ and electric field $\mathbf{E}$	Polar Polar
Thermal conductivity	$\mathbf{Q} = \kappa \nabla T$	Heat flux $\mathbf{Q}$ and temperature gradient ∇T	Polar Polar
Thermal expansion			Polar
Electric susceptibility	$\mathbf{P} = \chi \mathbf{E}$	Electric polarization $\mathbf{P}$ and electric field $\mathbf{E}$	Polar Polar
Magnetic ^a susceptibility	$\mathbf{M}_x = \chi_x \mathbf{H}$	Magnetic polarization $\mathbf{M}_x$ and magnetic field $\mathbf{H}$	Axial Axial
Optical activity	$G = \ell^T \mathbf{g} \ell$	Rotation G and directional cosines ℓ	Pseudoscalar Rank 2
Magneto electric effect	$\mathbf{M} = [\mathbf{Q}] \mathbf{E}$	Magnetic polarization $\mathbf{M}$ and magnetic field $\mathbf{H}$	Axial Axial

^a The subscript x stands for D, P, F, dia-, para-, and ferromagnetic.

material transport tensors, satisfy the Onsager relations, namely,

$$L_{ij}(\mathbf{B}) = L_{ji}(-\mathbf{B}),$$

where $\mathbf{B}$ is an applied magnetic field. In the absence of a field $\mathbf{B}$, the relations reduce to $L_{ij} = L_{ji}$. We demonstrated that these relations were the result of time-reversal invariance of the classical laws of physics.

We may consider here the cases of electric and thermal conductivity tensors, σ and κ ,

$$\mathbf{J} = \sigma \mathbf{E}, \quad \sigma_{ij} = \sigma_{ji}, \quad (13.52)$$

$$\mathbf{Q} = \kappa \nabla T, \quad \kappa_{ij} = \kappa_{ji}, \quad (13.53)$$

where $\mathbf{J}$ and $\mathbf{Q}$ are the electric and thermal currents, respectively, and $\mathbf{E}$ and T , the electric field and temperature.

In the presence of a magnetic field the Onsager relations become

$$\Theta \mathfrak{T}(\mathbf{H}) = \mathfrak{T}^\dagger(-\mathbf{H}), \quad (13.54)$$

so that the tensor $\mathfrak{T}$ is not necessarily symmetric. We consider here a medium that is isotropic in the absence of $\mathbf{H}$ and split the corresponding $\mathfrak{T}$ into its symmetric and antisymmetric parts, namely,

$$\mathfrak{T}^s = \frac{1}{2} [\mathfrak{T} + \mathfrak{T}^\dagger], \quad \mathfrak{T}^a = \frac{1}{2} [\mathfrak{T} - \mathfrak{T}^\dagger],$$

and we obtain

$$\begin{aligned} \mathfrak{T}^s(\mathbf{H}) &= \mathfrak{T}^s(-\mathbf{H}) \\ \mathfrak{T}^a(\mathbf{H}) &= -\mathfrak{T}^a(-\mathbf{H}) \end{aligned} \quad \Rightarrow \quad \mathfrak{T} = \begin{pmatrix} T_{11} & T_{12} & 0 \\ -T_{12} & T_{11} & 0 \\ 0 & 0 & T_{33} \end{pmatrix}, \quad (13.55)$$

so that $\mathfrak{T}^a$ is an axial tensor.

- (iii) **Axial second-rank tensors** Two second-rank axial tensors may be mentioned here, the *magnetoelectric* tensor, which is a *c*-tensor, and the *optical gyration* symmetric tensor associated with optical activity. These tensors will be described in Section 13.3.3.

A list of matter tensors of rank 2 is given in Table 13.7.

13.3.2 Elasticity tensors

Definition of stress and strain field tensors

A body is said to be in a state of stress when one part exerts a force on its neighboring parts. When the forces acting on an arbitrary surface element dS in the body are the same irrespective of the position of dS , provided that its orientation is fixed, then the body is said to be under *homogeneous stress*.

In order to describe the stress forces acting on an arbitrary surface element in a body, it is necessary to identify the direction of force as well as the surface orientation, which is defined by its surface normal. Since both the force and surface normal are polar-vector

quantities, we need two indices to describe the stress, which implies that the stress is represented by a second-rank polar tensor; as a matter of fact it is a polar i -tensor. Thus, with respect to the axes OX_1, OX_2, OX_3 , shown in Figure 13.2, we denote by

$$\sigma_{\alpha\beta}, \quad (\alpha, \beta = 1, 2, 3) \quad (13.56)$$

the force along the $+\alpha$ direction (that is, along OX_α) transmitted across the face whose normal is along the OX_β direction by the medium on the $+$ side of the face.

The quantities $\sigma_{\alpha\beta}$ are called stress components, and, as we mentioned above, form a second-rank tensor σ .

By decomposing the general second-rank stress tensor into its irreducible spherical tensors, we may identify them as

$$\begin{aligned} {}^{(0)}\Gamma^+ &\Rightarrow \frac{1}{3} (\sigma_{11} + \sigma_{22} + \sigma_{33}) = P \text{ (hydrostatic pressure),} \\ {}^{(1)}\Gamma^+ &\Rightarrow \frac{1}{2} (\sigma_{ij} - \sigma_{ji}) = \text{stress moments about O,} \\ {}^{(0)}\Gamma^+ + {}^{(2)}\Gamma^+ &\Rightarrow \frac{1}{2} (\sigma_{ij} + \sigma_{ji}) = \text{symmetric stress tensor.} \end{aligned} \quad (13.57)$$

Since the cube of Figure 13.2 is by assumption in static equilibrium, the moments about OX_1, OX_2 , and OX_3 vanish, and we obtain

$$\sigma_{\alpha\beta} = \sigma_{\beta\alpha}, \quad (13.58)$$

in other words, the stress tensor is *symmetric*.

A body subjected to stress in general undergoes a deformation. The components $u_{\alpha\beta}$ of the *strain field tensor* $\mathbf{u}$ are defined by the derivative

$$u_{\alpha\beta} = \frac{\partial u_\alpha}{\partial x_\beta}, \quad (13.59)$$

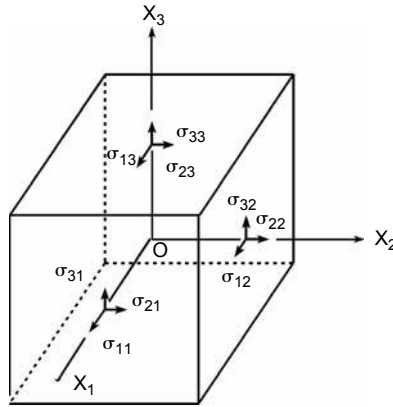


Fig. 13.2. Forces on the face of a unit cube in a homogeneously stressed body.

where $\mathbf{u}$ denotes the displacement of a point around which the strain is being examined. Notice that the strain parameters are *dimensionless*. Again, we decompose the strain tensor into its irreducible spherical components, and identify them as

$$\begin{aligned} {}^{(1)}\Gamma^+ &\Rightarrow \frac{1}{2} (u_{ij} - u_{ji}) = \text{rotation about O}, \\ {}^{(0)}\Gamma^+ + {}^{(2)}\Gamma^+ &\Rightarrow \frac{1}{2} (u_{ij} + u_{ji}) = \text{symmetric strain tensor}. \end{aligned} \quad (13.60)$$

Since we are interested in the strains within the body, we exclude displacements that lead to a rigid rotation of the body, namely the antisymmetric part of the displacement tensor $\mathbf{u}$, with terms

$$\frac{1}{2} (u_{\alpha\beta} - u_{\beta\alpha}) = \{u_{\alpha\beta}, u_{\beta\alpha}\}. \quad (13.61)$$

This leaves the symmetric strain tensor ε , where

$$\varepsilon_{\alpha\beta} = \frac{1}{2} (u_{\alpha\beta} + u_{\beta\alpha}) = [u_{\alpha\beta}, u_{\beta\alpha}], \quad (13.62)$$

where we introduced the convention that the curly and square brackets represent the anti-symmetrized and symmetrized components of the strain tensor, respectively. The strain tensor involves the outer-product of two polar i -vectors, and therefore it is a polar i -tensor. It has six independent components: $\varepsilon_{11}, \varepsilon_{22}, \varepsilon_{33}, \varepsilon_{12}, \varepsilon_{23}, \varepsilon_{31}$. Linear combinations of these Cartesian components provide bases for spherical tensors:

$${}^{(1)}\Gamma^+ \Rightarrow \frac{1}{3} (\varepsilon_{11} + \varepsilon_{22} + \varepsilon_{33}) = \varepsilon_B; \quad {}^{(2)}\Gamma^+ \Rightarrow \begin{cases} \frac{\sqrt{3}}{6} (3\varepsilon_{33} - \varepsilon_B) = \eta, \\ \frac{1}{2} (\varepsilon_{11} - \varepsilon_{22}) = \xi, \\ \varepsilon_{12}, \varepsilon_{23}, \varepsilon_{31}. \end{cases} \quad (13.63)$$

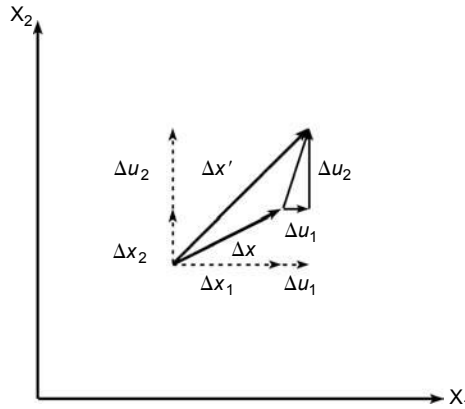


Fig. 13.3. A two-dimensional example illustrating the meaning of the strain components.

The five-dimensional Irrep $^{(2)}\Gamma^+$ is reducible with respect to point-groups of all crystallographic classes, as shown in Table 13.8. In all, we find that the 32 crystallographic point-groups classify into 11 distinct symmetry types. We also find that for all cases other than cubic symmetries, the dimensions of the relevant Irreps are $d \leq 2$. We also find that in some cases there is more than one independent basis for the same Irrep.

Table 13.8. *Irrep decomposition of strain tensor components for the 32 point-groups.*

Crystal class	Point-group	Irrep (dimension)	Basis	Number of constants	
				Irrep	Total
Cubic	(1) $m\bar{3}m, \bar{4}3m, 432$	$^{(1)}\Gamma(1)$	ε_B	1	3
		$^{(12)}\Gamma(2)$	η, ξ	1	
		$^{(25')}\Gamma(3)$	$\varepsilon_{12}, \varepsilon_{23}, \varepsilon_{31}$	1	
Tetrahedral	(2) $23, m\bar{3}$	$^{(1)}\Gamma(1)$	ε_B	1	3
		$^{(2)}\Gamma(1)$	$\left. \varepsilon_{12}, \varepsilon_{23}, \varepsilon_{31} \right\}$	1	
		$^{(3)}\Gamma(1)$		1	
		$^{(4)}\Gamma(3)$	$\varepsilon_{12}, \varepsilon_{23}, \varepsilon_{31}$	1	
Hexagonal	(3) $6mm, \bar{6}m2, 622, \frac{6}{mmm}$	$^{(1)}\Gamma(1)$	η, ε_B	3	5
		$^{(5)}\Gamma(2)$	$\varepsilon_{23}, \varepsilon_{31}$	1	
	(4) $6, \bar{6}, \frac{6}{m}$	$^{(6)}\Gamma(2)$	ε_{12}, ξ	1	5
		$^{(1)}\Gamma(1)$	η, ε_B	3	
		$^{(3)}\Gamma(1)$	$\left. \begin{aligned} \xi + i\varepsilon_{12} &= \varepsilon e^{i2\phi} \\ \xi - i\varepsilon_{12} &= \varepsilon e^{-i2\phi} \end{aligned} \right\}$	1	
		$^{(4)}\Gamma(1)$		1	
		$^{(5)}\Gamma(1)$	$\left. \begin{aligned} \varepsilon_{23} + i\varepsilon_{31} &= \varepsilon' e^{i\phi} \\ \varepsilon_{23} - i\varepsilon_{31} &= \varepsilon' e^{-i\phi} \end{aligned} \right\}$	1	
		$^{(6)}\Gamma(1)$		1	
Trigonal	(5) $32, 3m, \bar{3}m$	$^{(1)}\Gamma(1)$	η, ε_B	3	6
		$^{(3)}\Gamma(2)$	$\left\{ \begin{aligned} \varepsilon_{23}, \varepsilon_{31} \\ \varepsilon_{12}, \xi \end{aligned} \right.$	3	
	(6) $3, \bar{3}$	$^{(1)}\Gamma(1)$	η, ε_B	3	7
		$^{(2)}\Gamma(1)$	$\left\{ \begin{aligned} \varepsilon_{23} + i\varepsilon_{31} \\ \varepsilon_{12} - i\xi \end{aligned} \right.$	2	
		$^{(3)}\Gamma(1)$	$\left\{ \begin{aligned} \varepsilon_{23} - i\varepsilon_{31} \\ \varepsilon_{12} + i\xi \end{aligned} \right.$	2	

Table 13.8. (cont.)

Crystal class	Point-group	Irrep (dimension)	Basis	Number of constants	
				Irrep	Total
Tetragonal	(7) $422, \frac{4}{mmm}, 4mm, \bar{4}2m$	$^{(1)}\Gamma(1)$	η, ε_B	3	6
		$^{(3)}\Gamma(1)$	ξ	1	
		$^{(4)}\Gamma(1)$	ε_{12}	1	
		$^{(5)}\Gamma(2)$	$\varepsilon_{23}, \varepsilon_{31}$	1	
	(8) $4, \bar{4}, \frac{4}{m}$	$^{(1)}\Gamma(1)$	η, ε_B	3	7
		$^{(2)}\Gamma(1)$	ε_{12}, ξ	3	
		$^{(3)}\Gamma(1)$	$\varepsilon_{23} + i\varepsilon_{31} = \varepsilon_0 e^{i\phi}$	1	
		$^{(4)}\Gamma(1)$	$\varepsilon_{23} - i\varepsilon_{31} = \varepsilon_0 e^{-i\phi}$	1	
Orthorhombic	(9) $222, mm2, mmm$	$^{(1)}\Gamma(1)$	$\varepsilon_{11}, \varepsilon_{22}, \varepsilon_{33}$	6	9
		$^{(4)}\Gamma(1)$		1	
		$^{(2)}\Gamma(1)$	ε_{23}	1	
		$^{(3)}\Gamma(1)$	ε_{31}	1	
Monoclinic	(10) $2, m, \frac{2}{m}$	$^{(1)}\Gamma(1)$	$\varepsilon_{11}, \varepsilon_{22}, \varepsilon_{33}, \varepsilon_{12}$	10	13
		$^{(2)}\Gamma(1)$	$\varepsilon_{23}, \varepsilon_{31}$	3	
Triclinic	(11) $1, \bar{1}$		$\{\varepsilon_{ij}\}, i, j = 1, 2, 3$	21	21

Example 13.4

Strain in type (3) hexagonal systems

$$\begin{aligned} \frac{1}{3} (\varepsilon_{11} + \varepsilon_{22} + \varepsilon_{33}) &= \varepsilon_B \Rightarrow \text{represents a simple volume change} \\ \frac{\sqrt{3}}{6} (3\varepsilon_{33} - \varepsilon_B) &= \eta \Rightarrow \text{represents a change in } c/a \text{ ratio for fixed volume} \\ \varepsilon_{12}, \frac{1}{2} (\varepsilon_{11} - \varepsilon_{22}) &= \xi \Rightarrow \text{represent shear within the basal plane} \\ \varepsilon_{23}, \varepsilon_{31} &\Rightarrow \text{represent shear in a plane containing the } c\text{-axis.} \end{aligned}$$

Quadratic invariants It is useful to construct quadratic invariant products of symmetrized strains, since they are necessary in the construction of the corresponding potential energy expressions. First, we consider an Irrep $^{(\mu)}\Gamma$ with a single basis strain component

${}^\mu \varepsilon_i$, $i = 1, \dots, d_\mu$, then the corresponding quadratic invariant term is

$$\sum_i {}^\mu \varepsilon_i^* {}^\mu \varepsilon_i.$$

However, when there are $n_\mu > 1$ bases strain components corresponding to the same Irrep μ , then we have quadratic invariant terms of the form

$$\sum_i \frac{1}{2} ({}^\mu \varepsilon_i^{r*} {}^\mu \varepsilon_i^s + {}^\mu \varepsilon_i^r {}^\mu \varepsilon_i^{s*}),$$

where r, s label the bases. Thus, the total number of independent quadratic invariant terms is given by

$$\sum_\mu \frac{1}{2} n_\mu (n_\mu + 1). \quad (13.64)$$

The most general invariant takes the form

$$\sum_\mu \frac{1}{2} {}^{(\mu)} c_{rs} \sum_i {}^\mu \varepsilon_i^{r*} {}^\mu \varepsilon_i^s. \quad (13.65)$$

Case of complex Irreps We consider here the case where a two-dimensional real Rep is reducible to two one-dimensional complex Irreps. As an example, we consider the case of type (8) symmetry tetragonal systems, Table 13.8. We find that the one-dimensional Irreps ${}^{(4)}\Gamma$ and ${}^{(3)}\Gamma$ have bases $\varepsilon_0 e^{i\phi}$, giving rise to the same invariant term, namely, $\varepsilon_0^2 = \varepsilon_{13}^2 + \varepsilon_{23}^2$. Thus, there is only one phenomenological elastic constant associated with the two complex Irreps, and we should only consider a real two-dimensional Rep, with basis $[\varepsilon_{13}, \varepsilon_{23}]$. This argument also applies to symmetry types (4) hexagonal and (2) tetrahedral.

Example 13.5

Elastic Hamiltonian for type (3) hexagonal systems in the harmonic approximation.

According to Table 13.8, the strain in these systems transforms as ${}^{(1)}\Gamma$, ${}^{(5)}\Gamma$, and ${}^{(6)}\Gamma$. The elastic Hamiltonian in the harmonic approximation includes quadratic invariant terms: ε_B^2 , η^2 , $\varepsilon_B \eta$, ε_{23}^2 , ε_{31}^2 , ε_{12}^2 , and ξ^2 ; and we write the Hamiltonian as

$$\mathcal{H}_{\text{elast}} = \frac{1}{2} \left[c_{11}^{(1)} \varepsilon_B^2 + c_{12}^{(1)} \varepsilon_B \eta + c_{22}^{(1)} \eta^2 + c^{(5)} (\varepsilon_{23}^2 + \varepsilon_{31}^2) + c^{(6)} (\varepsilon_{12}^2 + \xi^2) \right],$$

where the five coefficients are expressed in terms of conventional elastic constants as

$$\begin{aligned} c_{11}^{(1)} &= \frac{1}{9} [2c_{11} + 2c_{12} + 4c_{13} + c_{33}] \\ c_{12}^{(1)} &= \frac{2}{3\sqrt{3}} [-c_{11} - c_{12} + c_{13} + c_{33}] \\ c_{22}^{(1)} &= \frac{1}{3} [2c_{11} + 2c_{12} - 8c_{13} + 4c_{33}] \\ c^{(5)} &= 2 [c_{11} - c_{12}] \\ c^{(6)} &= 4c_{44}. \end{aligned}$$

Elastic constants

For small stresses, the strain is proportional to the stress (Hooke's law). The reverse statement is also true and we may formally write

$$\begin{aligned} \sigma_{\alpha\gamma} &= \sum_{\beta=1}^3 \sum_{\lambda=1}^3 C_{\alpha\gamma,\beta\lambda} \varepsilon_{\beta\lambda}, \quad \alpha, \gamma = 1, 2, 3, \\ \varepsilon_{\alpha\gamma} &= \sum_{\beta=1}^3 \sum_{\lambda=1}^3 \mathfrak{S}_{\alpha\gamma,\beta\lambda} \sigma_{\beta\lambda}. \end{aligned} \quad (13.66)$$

The quantities $C_{\alpha\gamma,\beta\lambda}$ and $\mathfrak{S}_{\alpha\gamma,\beta\lambda}$ are called *elastic stiffness* and *compliance constants*, respectively; sometimes, without loss of meaning, we refer to either as elastic constants. The elastic stiffness constants are typically $\sim 10^{11}$ – 10^{12} dynes/cm².

In $\mathcal{E}(3)$ Euclidean space, the 81 elastic constants $\{C_{\alpha\gamma,\beta\lambda}\}$ form a fourth-rank tensor connecting the second-rank stress and strain tensors. They have the properties

$$C_{\alpha\gamma,\beta\lambda} = C_{\gamma\alpha,\beta\lambda}, \quad C_{\alpha\gamma,\beta\lambda} = C_{\alpha\gamma,\lambda\beta}. \quad (13.67)$$

These equalities are the result of the symmetric forms of the stress and strain components, respectively; they reduce the number of independent constants to 36.

The corresponding potential energy can be generalized in the form

$$\mathcal{V} = \mathcal{V}_0 + \frac{1}{2} \sum_{\alpha\beta\gamma\lambda} C_{\alpha\gamma,\beta\lambda} \varepsilon_{\alpha\gamma} \varepsilon_{\beta\lambda}, \quad (13.68)$$

which is valid only to first order. Equation (13.68) defines $C_{\alpha\gamma,\beta\lambda}$ as

$$C_{\alpha\gamma,\beta\lambda} = \left. \frac{\partial^2 \mathcal{V}}{\partial \varepsilon_{\alpha\gamma} \partial \varepsilon_{\beta\lambda}} \right|_0, \quad (13.69)$$

with $\mathcal{V}_0$ the energy density in the absence of strain. The definition of the elastic potential energy in (13.68) leads to further relations between the elastic constants,

$$C_{\alpha\gamma,\beta\lambda} = C_{\beta\lambda,\alpha\gamma}, \quad (13.70)$$

which reduces the number of independent constants from 36 to 21!

If the strain energy is to be in a form that is invariant with respect to rigid rotations, then the parameters that enter the energy expression are

$$\tilde{u}_{\alpha\beta} = \frac{1}{2} \left\{ u_{\alpha\beta} + u_{\beta\alpha} + \sum_{\gamma} u_{\gamma\alpha} u_{\gamma\beta} \right\}. \quad (13.71)$$

Crystal symmetry reduces the number even further, often causing many of the constants to vanish. For example, crystals with cubic symmetry have only 12 nonvanishing elastic constants, of which only 3 are independent.

It is customary to simplify the notation of the elastic constants by contracting pairs of indices into single indices, introduced by Voigt, where

$$\begin{array}{ccccccc} \alpha\gamma & 11 & 22 & 33 & (23, 32) & (31, 13) & (12, 21) \\ \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \\ i & 1 & 2 & 3 & 4 & 5 & 6. \end{array} \quad (13.72)$$

Based on the above scheme we define

$$\begin{aligned} \varepsilon_i &= (u_{\alpha\gamma} + u_{\gamma\alpha}) = 2\varepsilon_{\alpha\gamma} = 2\varepsilon_{\gamma\alpha}, & \alpha \neq \gamma, \\ \varepsilon_i &= u_{\alpha\gamma} = \varepsilon_{\alpha\gamma}, & \alpha = \gamma. \end{aligned} \quad (13.73)$$

Equations (13.66) and (13.68) become

$$\begin{aligned} \sigma_i &= \sum_{j=1}^6 c_{ij} \varepsilon_j, & i = 1, 2, \dots, 6, \\ \mathcal{V}_{\text{el}} &= \frac{1}{2} \sum_{ij} c_{ij} \varepsilon_i \varepsilon_j; \end{aligned} \quad (13.74)$$

and, according to (13.67) and (13.70), we have

$$c_{ij} = c_{ji}. \quad (13.75)$$

Example 13.6

Crystals with cubic symmetry

When we choose the coordinate axes to be parallel to the cube edges we find that they are equivalent, or that the crystal remains invariant with respect to exchanging axes. This immediately leads to

$$c_{11} = c_{22} = c_{33}; \quad c_{12} = c_{21} = c_{13} = c_{31} = c_{23} = c_{32}; \quad c_{44} = c_{55} = c_{66}. \quad (13.76)$$

In addition, there is a mirror plane normal to each axis; hence, reversing the direction of one of the coordinate axes must leave the stress unchanged. Another symmetry requirement is that, since the exchange of a pair of axes under four-fold rotation about the third axis leaves the crystal invariant, such operations should also leave the stress unaltered.

Applying these two restrictions and noting the further restriction imposed by (13.75), we have

$$\begin{aligned}
 c_{14} &= c_{25} = c_{36} = c_{63} = c_{52} = c_{41} = 0, \\
 c_{45} &= c_{56} = c_{64} = c_{46} = c_{65} = c_{54} = 0, \\
 c_{15} &= c_{26} = c_{34} = c_{43} = c_{62} = c_{51} \\
 &= c_{16} = c_{24} = c_{35} = c_{53} = c_{42} = c_{61} = 0.
 \end{aligned} \tag{13.77}$$

The array of values of the elastic constants is then reduced for a cubic crystal to the matrix

$$\mathbf{c} = \begin{bmatrix} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{12} & c_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{44} \end{bmatrix}. \tag{13.78}$$

The elastic energy can be expressed as

$$\begin{aligned}
 \mathcal{V}_{\text{el}} &= \frac{1}{2} c_{11} \left(\varepsilon_{xx}^2 + \varepsilon_{yy}^2 + \varepsilon_{zz}^2 \right) + c_{12} \left(\varepsilon_{xx} \varepsilon_{yy} + \varepsilon_{yy} \varepsilon_{zz} + \varepsilon_{zz} \varepsilon_{xx} \right) \\
 &+ \frac{1}{2} c_{44} \left(\varepsilon_{zy}^2 + \varepsilon_{zy}^2 + \varepsilon_{xy}^2 \right).
 \end{aligned} \tag{13.79}$$

Using the transformation $\begin{pmatrix} 1/\sqrt{3} & 1/\sqrt{2} & -1/\sqrt{6} \\ 1/\sqrt{3} & -1/\sqrt{2} & -1/\sqrt{6} \\ 1/\sqrt{3} & 0 & 2/\sqrt{6} \end{pmatrix}$ we obtain

$$\begin{aligned}
 \mathcal{V}_{\text{el}} &= \frac{1}{2} (c_{11} + 2c_{12}) \varepsilon_B^2 + \frac{1}{2} (c_{11} - c_{12}) (\eta^2 + \xi^2) \\
 &+ \frac{1}{2} c_{44} (\varepsilon_{zy}^2 + \varepsilon_{zy}^2 + \varepsilon_{xy}^2),
 \end{aligned} \tag{13.80}$$

where $\eta = \frac{\sqrt{3}}{6} (3\varepsilon_{33} - \varepsilon_B)$ and $\xi = \frac{1}{2} (\varepsilon_{11} - \varepsilon_{22})$.

Effect of symmetry We should note here that elasticity is a centrosymmetric property, i.e. the components of the elastic constant tensors remain invariant when the inversion operation is applied to the reference axes. This can be clearly demonstrated by noting that the elements of the inversion matrix are $-\delta_{\alpha\beta}$, and making use of (13.21) we obtain

$$C'_{\alpha\gamma, \beta\lambda} = \delta_{\alpha\mu} \delta_{\gamma\nu} \delta_{\beta\kappa} \delta_{\lambda\zeta} C_{\mu\nu, \kappa\zeta}. \tag{13.81}$$

The effect of other symmetry operations introduces relations among the elastic constants, expressed by (13.21). Since these symmetry operations depend on the symmetry point-group, the corresponding relations are system dependent.

The number of independent constants is given by (13.64), and the elastic potential energy is given by

$$\mathcal{V} = \sum_{\mu} \frac{1}{2} {}^{(\mu)}c_{rs} \sum_i {}^{\mu}\varepsilon_i^{r*} {}^{\mu}\varepsilon_i^s, \quad (13.82)$$

where the ${}^{(\mu)}c_{rs}$ are now symmetry-adapted elastic constants. The conditions of stability of the system are given by

$${}^{(\mu)}c_{rs} > 0; \quad \forall {}^{(\mu)}c_{rs}. \quad (13.83)$$

Thus, for the cubic system, the stability conditions are: $c_{11} + 2c_{12} > 0$, $c_{11} - c_{12} > 0$, $c_{44} > 0$.

The relation between ${}^{(\mu)}c_{rs}$ and the corresponding Cartesian components can be obtained by expanding the symmetry bases ${}^{(\mu)}\varepsilon_i$ in terms of the Cartesian components $\varepsilon_{\alpha\beta}$ in (13.82).

Finally, we present the typical forms of the elastic constant tensors for some crystal systems:

Hexagonal	Trigonal
$\begin{bmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{13} & 0 & 0 & 0 \\ c_{13} & c_{13} & c_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & 1/2(c_{11} - c_{12}) \end{bmatrix}$	$\begin{bmatrix} c_{11} & c_{12} & c_{13} & c_{14} & -c_{15}^* & 0 \\ c_{12} & c_{11} & c_{13} & -c_{14} & c_{15}^* & 0 \\ c_{13} & c_{13} & c_{33} & 0 & 0 & 0 \\ c_{14} & -c_{14} & 0 & c_{44} & 0 & c_{15}^* \\ 0 & 0 & 0 & 0 & c_{44} & c_{14} \\ 0 & 0 & 0 & c_{15}^* & c_{14} & 1/2(c_{11} - c_{12}) \end{bmatrix}$
Tetragonal	Orthorhombic
$\begin{bmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & c_{16}^* \\ c_{12} & c_{11} & c_{13} & 0 & 0 & -c_{16}^* \\ c_{13} & c_{13} & c_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ c_{16}^* & -c_{16}^* & 0 & 0 & 0 & c_{66} \end{bmatrix}$	$\begin{bmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{23} & 0 & 0 & 0 \\ c_{13} & c_{23} & c_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{66} \end{bmatrix}$

Asterisks indicate entries for the trigonal classes $3, \bar{3}$, and the tetragonal classes $4, \bar{4}$, $4/m$ only.

13.3.3 Tensors associated with electric and magnetic fields

Although there are many systems with symmetries that do not allow the presence of spontaneous electric or magnetic dipole moments, some of these systems may develop such moments when subjected to the influence an external field such as stress, electric, magnetic, or temperature change. In the following we will present related phenomena and the properties of their representative tensors. Alternative presenations may be found in references [83, 85, 73, 58, 82].

Tensors associated with optical properties of materials

General transformations of the dielectric tensor The usual description of the response of materials to electromagnetic fields, including their optical properties, is obtained by using Maxwell's equations and taking the constitutive relations between the complex amplitudes of the fields in the form

$$D_i = \sum_j \epsilon_{ij}(\omega, \mathbf{k}) E_j, \quad (13.84)$$

$$B_i = H_i, \quad (13.85)$$

where E_i , D_i , H_i , and B_i are the electric field, electric displacement, magnetic field, and magnetic induction, respectively; $\epsilon_{ij}(\omega, \mathbf{k})$ is the dielectric function tensor.

When the applied fields are weak, the response is assumed to be linear, and we obtain

$$D_i(\mathbf{r}, t) = \int_{-\infty}^t dt' \int d\mathbf{r}' \sum_j \epsilon_{ij}(\mathbf{r}, t; \mathbf{r}', t') E_j(\mathbf{r}', t'), \quad (13.86)$$

$$B_i = H_i, \quad \text{nonmagnetic system.} \quad (13.87)$$

The limits on the time integral are imposed by causality. Moreover, because the properties of materials are time-translation invariant, the kernel, i.e. the dielectric function, depends on the time difference $\tau = t - t'$. The kernel of the integration also satisfies the condition

$$\epsilon_{ij}(\mathbf{r}, \mathbf{r}'; t - t') = \epsilon_{ji}(\mathbf{r}', \mathbf{r}, t - t'). \quad (13.88)$$

For the case of a spatially homogeneous medium the kernel will, in addition, depend on $\boldsymbol{\rho} = \mathbf{r} - \mathbf{r}'$; in which case we write

$$\epsilon_{ij}(\omega, \mathbf{k}) = \int_0^\infty \int d\boldsymbol{\rho} \epsilon_{ij}(\tau, \boldsymbol{\rho}) \exp[i(\mathbf{k} \cdot \boldsymbol{\rho} - \omega\tau)]. \quad (13.89)$$

Since condition (13.88) becomes

$$\epsilon_{ij}(\tau, \boldsymbol{\rho}) = \epsilon_{ji}(\tau, -\boldsymbol{\rho}),$$

it leads to the relation

$$\epsilon_{ij}(\omega, -\mathbf{k}) = \epsilon_{ji}(\omega, \mathbf{k}). \quad (13.90)$$

We now wish to take into account that the system under consideration may be magnetic, and we have to consider the effect of time-reversal. For this case, we generalize (13.84) and (13.85) to

$$D_i = \sum_j [\epsilon_{ij}(\omega, \mathbf{k}) E_j + \alpha_{ij}(\omega, \mathbf{k}) H_j], \quad (13.91)$$

$$B_i = \sum_j [\beta_{ij}(\omega, \mathbf{k}) E_j + \mu_{ij}(\omega, \mathbf{k}) H_j]. \quad (13.92)$$

Transformation properties of physical fields The physical fields $x_i(\mathbf{r}, t)$ associated with the complex Fourier components $X_i(\mathbf{r}, t) = X_i^0 \exp[i(\mathbf{k} \cdot \boldsymbol{\rho} - \omega\tau)]$ are given by

$$x_i(\mathbf{r}, t) = \frac{1}{2} [X_i^0 \exp[i(\mathbf{k} \cdot \boldsymbol{\rho} - \omega\tau)] + X_i^{0*} \exp[i(\mathbf{k} \cdot \boldsymbol{\rho} - \omega\tau)],$$

where $X_i = E_i, D_i, B_i, H_i$; and $x_i = e_i, d_i, b_i, h_i$ are the corresponding physical fields. Under space and time inversion, we obtain

$$\Theta \begin{cases} e_i = e_i, \\ d_i = d_i, \\ h_i = -h_i, \\ b_i = -b_i, \end{cases} \quad I \begin{cases} e_i = -e_i, \\ d_i = -d_i, \\ h_i = h_i, \\ b_i = b_i, \end{cases} \quad \Theta \begin{cases} E_i = E_i^*, \\ D_i = D_i^*, \\ t = -t, \\ \mathbf{k} = -\mathbf{k}, \end{cases} \quad I \begin{cases} E_i = -E_i, \\ D_i = -D_i, \\ \mathbf{k} = -\mathbf{k}, \\ \mathbf{r} = -\mathbf{r}. \end{cases}, \quad (13.93)$$

Applying these transformations to (13.91) and (13.92) we obtain

$$\Theta \begin{cases} \epsilon_{ij}(\omega, \mathbf{k}) = \epsilon_{ij}^*(\omega, -\mathbf{k}), \\ \mu_{ij}(\omega, \mathbf{k}) = \mu_{ij}^*(\omega, -\mathbf{k}), \\ \alpha_{ij}(\omega, \mathbf{k}) = -\alpha_{ij}^*(\omega, -\mathbf{k}), \\ \beta_{ij}(\omega, \mathbf{k}) = -\beta_{ij}^*(\omega, -\mathbf{k}). \end{cases} \quad I \begin{cases} \epsilon_{ij}(\omega, \mathbf{k}) = \epsilon_{ij}(\omega, -\mathbf{k}), \\ \mu_{ij}(\omega, \mathbf{k}) = \mu_{ij}(\omega, -\mathbf{k}), \\ \alpha_{ij}(\omega, \mathbf{k}) = -\alpha_{ij}(\omega, -\mathbf{k}), \\ \beta_{ij}(\omega, \mathbf{k}) = -\beta_{ij}(\omega, -\mathbf{k}). \end{cases} \quad (13.94)$$

The dielectric tensor $\epsilon_{ij}(\omega, \mathbf{k})$ is symmetric with respect to the indices ij : The symmetry of the static, $\omega = 0$, tensor has been attributed earlier to the fact that the system is in equilibrium and, thus, the electrostatic energy is bilinear in the E -field. The symmetry at finite frequencies, where the system is out of thermodynamic equilibrium, is based on the Onsager theorem. In either case, because it is a symmetric second-rank tensor, it is associated with a *tensor ellipsoid* whose principal values are $\epsilon_x, \epsilon_y, \epsilon_z$ along the *principal dielectric axes* (PDAs).

Since it is natural to describe the optical properties of materials in terms of the electric field rather than the electric displacement, it is then convenient to use the relations

$$E_i = \sum_j \epsilon_{ij}^{-1} D_j,$$

which involve the *dielectric impermeability* tensor

$$\beta = \epsilon_0 [\epsilon]^{-1}, \quad (13.95)$$

whose principal values are

$$\beta_i = 1/n_i^2, \quad i = 1, 2, 3,$$

where the n_i s are the principal refractive indices. The corresponding tensor ellipsoid is called the *optical index ellipsoid* or *indicatrix*.

Optical birefringence We consider here a monochromatic electromagnetic wave propagating in an anisotropic nonmagnetic medium characterized by a dielectric tensor $\epsilon_{ij}(\omega, \mathbf{k})$; and we write Maxwell's equations as

$$\begin{aligned} \text{curl } \mathbf{E} &= i \frac{\omega}{c} \mathbf{H}, & \text{curl } \mathbf{H} &= -i \frac{\omega}{c} \mathbf{D}, \\ \mathbf{k} \times \mathbf{E} &= \frac{\omega}{c} \mathbf{H}, & \mathbf{k} \times \mathbf{H} &= -\frac{\omega}{c} \mathbf{D}. \end{aligned} \quad (13.96)$$

Equation (13.96) shows that $\mathbf{D} \perp \mathbf{k}$, $\mathbf{H}$ and $\mathbf{H} \perp \mathbf{k}$, but $\mathbf{E} \not\perp \mathbf{k}$.

We introduce an anisotropic refraction index by defining

$$\mathbf{k} = \frac{\omega}{c} \mathbf{n}. \quad (13.97)$$

Substitution in (13.96) gives

$$\begin{aligned}\mathbf{H} &= \mathbf{n} \times \mathbf{E}, & \mathbf{D} &= -\mathbf{n} \times \mathbf{H} \\ \mathbf{D} &= \mathbf{n} \times \mathbf{E} \times \mathbf{n} = \overbrace{n^2 \mathbf{E} - (\mathbf{n} \cdot \mathbf{E}) \mathbf{n}} \\ &= [\epsilon] \mathbf{E}.\end{aligned}\tag{13.98}$$

The last equation can be written in component form as

$$\left(n^2 \delta_{ij} - n_i n_j - \epsilon_{ij} \right) E_j = 0.\tag{13.99}$$

To obtain a geometric interpretation of (13.98) and (13.99) we rewrite (13.98) as

$$\frac{1}{n^2} \mathbf{D} = \mathbf{E} - (\hat{\mathbf{n}} \cdot \mathbf{E}) \hat{\mathbf{n}} = \mathbf{E}^\perp,\tag{13.100}$$

where $\mathbf{E}^\perp$ is perpendicular to $\hat{\mathbf{n}}$. By inverting (13.84) and choosing the 3-axis along an arbitrary $\hat{\mathbf{n}}$ we obtain

$$\mathbf{E}_i^\perp = \sum_{j=1}^2 \beta_{ij}^\perp \mathbf{D}_j,$$

and substituting in (13.100), we write

$$\sum_{j=1}^2 \left(\frac{1}{n^2} \delta_{ij} - \beta_{ij}^\perp \right) D_j = 0,\tag{13.101}$$

which defines a two-dimensional tensor ellipse perpendicular to $\hat{\mathbf{n}}$, having two unequal principal values corresponding to two values of n^2 (Figure 13.4), such that

$$E_i^\perp = \frac{1}{n_i^2} D_i, \quad i = 1, 2.$$

Thus, we have a situation where two linearly polarized waves traveling along the $\hat{\mathbf{n}}$ -direction, whose polarizations are mutually perpendicular and coinciding with the principal axes of the ellipse, will propagate with wave-velocities $v_1 = c/n_1$ and $v_2 = c/n_2$. This property is referred to as *optical birefringence* or *double-refraction*. Thus, when a ray of plane-polarized light is passed through such a material, it gets resolved along the two principal refraction directions and each of these components experiences a different refractive index. The difference in the refractive indices leads to a relative retardation between the two component waves.

We classify systems exhibiting birefringence into two categories, according to their dielectric tensors given in Table 13.1:

- (i) Biaxial crystal systems: Characterized by dielectric tensors with three distinct principal dielectric values:

Triclinic	Monoclinic	Orthorhombic
$\begin{pmatrix} \epsilon_{11} & \epsilon_{12} & \epsilon_{13} \\ \epsilon_{12} & \epsilon_{22} & \epsilon_{23} \\ \epsilon_{13} & \epsilon_{23} & \epsilon_{33} \end{pmatrix}$	$\begin{pmatrix} \epsilon_{11} & \epsilon_{12} & 0 \\ \epsilon_{12} & \epsilon_{22} & 0 \\ 0 & 0 & \epsilon_{33} \end{pmatrix}$	$\begin{pmatrix} \epsilon_{11} & 0 & 0 \\ 0 & \epsilon_{22} & 0 \\ 0 & 0 & \epsilon_{33} \end{pmatrix}$

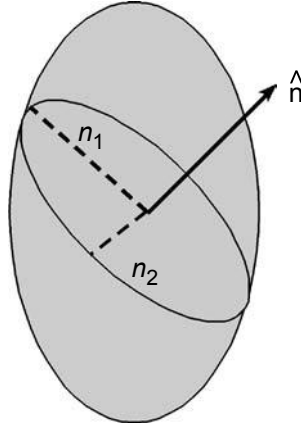


Fig. 13.4. Indicatrix ellipsoid showing the tensor ellipse of the index of refraction for waves propagating along $\hat{\mathbf{n}}$.

- (ii) Uniaxial crystal systems: Characterized by tensors with two principal dielectric values, they include tetragonal, trigonal, and hexagonal crystal systems.

$$\begin{pmatrix} \epsilon_{\perp} & 0 & 0 \\ 0 & \epsilon_{\perp} & 0 \\ 0 & 0 & \epsilon_{\parallel} \end{pmatrix}$$

Natural and induced optical activity: gyration tensor The phenomenon of optical activity of a medium is its ability to rotate the polarization plane of a linearly polarized wave as it propagates through it. This effect is a manifestation of *circular birefringence*, i.e. right- and left-circularly polarized light waves traveling in a given direction experience two different phase velocities, or indices of refraction, n_r and n_l , such that

$$\begin{aligned} \mathbf{D}_r &= \Re \left[D_0 (\hat{\mathbf{e}}_x + i\hat{\mathbf{e}}_y) e^{i\omega(t-n_r z/c)} \right], \\ \mathbf{D}_l &= \Re \left[D_0 (\hat{\mathbf{e}}_x - i\hat{\mathbf{e}}_y) e^{i\omega(t-n_l z/c)} \right]. \end{aligned}$$

Writing the plane-polarized wave, propagating along the z -axis, as a superposition of right and left circularly polarized waves

$$\begin{aligned} \mathbf{D} &= D_0 \exp \left[i\omega \left(t - \frac{1}{2}(n_r + n_l) \frac{z}{c} \right) \right] [(\hat{\mathbf{e}}_x + i\hat{\mathbf{e}}_y) e^{i\phi} + (\hat{\mathbf{e}}_x - i\hat{\mathbf{e}}_y) e^{-i\phi}] \\ &= 2D_0 e^{i\psi} (\cos \phi \hat{\mathbf{e}}_x - \sin \phi \hat{\mathbf{e}}_y), \\ \psi &= \omega \left(t - \frac{1}{2}(n_r + n_l) \frac{z}{c} \right), \quad \phi = \pi(n_r - n_l) \frac{z}{\lambda}, \quad \lambda = \frac{2\pi c}{\omega}, \end{aligned} \tag{13.102}$$

where $\phi = 0$ defines the incidence vacuum/medium interface where the wave is x -plane-polarized. At $\phi > 0$ the plane of polarization is turned by an angle ϕ .

Natural optical activity When an EM wave propagates in a medium its electric field induces a local response, which, because of the atomic environment, gives rise to inhomogeneities on the interatomic length scale. Thus, for an EM wave with wavelength λ , these inhomogeneities will be of the order of a/λ , where a is the interatomic length scale. The expansion of ϵ_{ij} to first order in a/λ gives rise to the natural optical activity. The corresponding tensor γ_{ijl} is then found by expanding $\epsilon_{ij}(\omega, \mathbf{k})$ to first order in $\mathbf{k}$; thus

$$\epsilon_{ij}(\omega, \mathbf{k}) = \epsilon_{ij}(\omega, 0) + i \sum_l \gamma_{ijl} k_l + \dots \quad (13.103)$$

Equation (13.90) then yields

$$\gamma_{ijl} = -\gamma_{jil}, \quad (13.104)$$

indicating that γ is antisymmetric with respect to ij , and we write

$$\rho_{ij} = \sum_l \gamma_{ijl} k_l = \sum_l \frac{\omega}{c} \gamma_{ijl} n_l = \sum_m e_{ijm} g_m, \quad (13.105)$$

where we used (13.97) and the fact that ρ_{ij} is a rank-2 axial tensor that can be expressed in terms of the *gyration vector* $\mathbf{g} = (g_1, g_2, g_3)$. We write the constitutive $\mathbf{D}/\mathbf{E}$ relations in the form

$$\begin{aligned} D_i &= \sum_j \epsilon_{ij}(\omega, 0) E_j + i (\mathbf{E} \times \mathbf{g})_i, \\ E_i &= \sum_j \beta_{ij}(\omega, 0) D_j + i (\mathbf{D} \times \mathbf{G})_i, \end{aligned} \quad (13.106)$$

where $\mathbf{G}$ is called the *optical activity vector*, and is given by

$$G_i = \sum_j \beta_{ij}(\omega, 0) g_j.$$

We now write (13.101), referred to its principal axes with $n = n_x, n_y$, and include the terms involving the optical activity vector, namely

$$\begin{aligned} \left(\frac{1}{n_x^2} - \frac{1}{n^2} \right) D_x + i G_z D_y &= 0, \\ -i G_z D_x + \left(\frac{1}{n_y^2} - \frac{1}{n^2} \right) D_y &= 0, \end{aligned} \Rightarrow \left(\frac{1}{n_x^2} - \frac{1}{n^2} \right) \left(\frac{1}{n_y^2} - \frac{1}{n^2} \right) = G_z^2. \quad (13.107)$$

To simplify the analysis we consider an isotropic medium with $n_x = n_y = n_0$ and obtain

$$\left. \begin{aligned} \frac{1}{n_r^2} &= \frac{1}{n_0^2} + G_z \Rightarrow \frac{D_y}{D_x} = +i, \\ \frac{1}{n_l^2} &= \frac{1}{n_0^2} - G_z \Rightarrow \frac{D_y}{D_x} = -i, \end{aligned} \right\} \quad \phi = \frac{\pi n_0^3 G_z}{\lambda} z,$$

which describe circularly polarized waves with $n_r \neq n_l$.

We use the linear dependence of g_m on n_l to write

$$g_m = \sum_s g_{ms} n_s, \quad \Rightarrow \quad \mathbf{n} \cdot \mathbf{g} = g_{ms} n_m n_s,$$

where g_{ms} is a symmetric rank-2 tensor; and substituting back in (13.105) we obtain the relation

$$\frac{\omega}{c} \gamma_{ijl} n_l = \sum_m e_{ijm} g_{ml} n_l \quad \Rightarrow \quad \frac{\omega}{c} \gamma_{ijl} = \sum_m e_{ijm} g_{ml}. \quad (13.108)$$

The corresponding relation between $\mathbf{D}$ and $\mathbf{E}$ is

$$D_i = \sum_j \left[\epsilon_{ij}(\omega, 0) E_j + \sum_l \gamma_{ijl} \frac{\partial E_j}{\partial x_l} \right]. \quad (13.109)$$

Since $\mathbf{D}$ and $\mathbf{E}$ are polar vectors, γ_{ijl} must be odd under inversion, and thus vanishes for centrosymmetric systems.

Faraday and MOKE (magneto-optic Kerr effect) rotations We consider the propagation of a plane-polarized EM wave through an isotropic medium in the presence of an external or internal magnetic field along the z -direction. Since the conductivity, $[\boldsymbol{\sigma}]$, and polarizability, $[\boldsymbol{\alpha}]$, tensors satisfy the Onsager relation, we use (13.54) and (13.55) to write

$$[\boldsymbol{\sigma}] = \begin{pmatrix} \sigma_{11} & \sigma_{12} & 0 \\ -\sigma_{12} & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{pmatrix}, \quad [\boldsymbol{\alpha}] = \begin{pmatrix} \alpha_{11} & \alpha_{12} & 0 \\ -\alpha_{12} & \alpha_{22} & 0 \\ 0 & 0 & \alpha_{33} \end{pmatrix}.$$

We write Maxwell's equations as

$$\begin{aligned} \text{curl } \mathbf{E} &= -\frac{1}{c} \frac{\partial \mathbf{H}}{\partial t} \\ \text{curl } \mathbf{H} &= -\frac{1}{c} \frac{\partial \mathbf{E}}{\partial t} + \frac{4\pi}{c} \mathbf{J}_{\text{total}} \\ \mathbf{J}_{\text{total}} &= \boldsymbol{\sigma} \cdot \mathbf{E} + \boldsymbol{\alpha} \cdot \frac{\partial \mathbf{E}}{\partial t}. \end{aligned}$$

Expressing the plane-wave fields as

$$\mathbf{E} = \mathbf{E}_0 e^{i\omega(t-nz/c)}, \quad \mathbf{H} = \mathbf{H}_0 e^{i\omega(t-nz/c)},$$

we obtain

$$\left. \begin{aligned} n(\mathbf{E} \times \hat{\mathbf{e}}_z) &= -\mathbf{H} \\ n(\mathbf{H} \times \hat{\mathbf{e}}_z) &= \mathfrak{N} \cdot \mathbf{E} \end{aligned} \right\} \Rightarrow \mathfrak{N} \cdot \mathbf{E} = n^2 [\mathbf{E} - E_z \hat{\mathbf{e}}_z], \quad (13.110)$$

where

$$\mathfrak{N} = \left(1 + 4\pi \boldsymbol{\alpha} + \frac{4\pi}{i\omega} \boldsymbol{\sigma} \right) = \begin{pmatrix} a_0 & -a_1 & 0 \\ a_1 & a_0 & 0 \\ 0 & 0 & a_3 \end{pmatrix}.$$

Substituting for $\mathfrak{N}$ in (13.110) we get

$$\left. \begin{aligned} (a_0 - n^2) E_x - a_1 E_y &= 0 \\ a_1 E_x + (a_0 - n^2) E_y &= 0 \\ a_3 E_z &= 0 \end{aligned} \right\} (a_0 - n^2)^2 + a_1^2 = 0 \text{ (secular determinant),}$$

which has circularly polarized solutions

$$\begin{aligned} n_+^2 = a_0 - ia_1 &\Rightarrow E_y^+ = iE_x^+ \text{ (right-handed), } v^+ = \frac{c}{n_+}, \\ n_-^2 = a_0 + ia_1 &\Rightarrow E_y^- = -iE_x^- \text{ (left-handed), } v^- = \frac{c}{n_-}. \end{aligned} \quad (13.111)$$

The rotation of the plane of polarization of a transmitted (refracted) plane-wave is known as the *Faraday effect*. A plane-wave reflected at vacuum/medium interface and normal incidence will suffer a rotation of

$$\phi = -\Im \frac{n_+ - n_-}{n_+ n_- - 1},$$

a phenomenon known as the magneto-optic Kerr effect or MOKE.

Photoelastic effects The transmission properties of optical waves through transparent (ionic or covalent) crystals is determined by the energy gaps in their electronic energy-bands, as will be explained in Chapter 14. These gaps undergo anisotropic changes when the crystal is subjected to external directional stress. Thus, optically isotropic materials become birefringent under anisotropic stress, while the birefringence properties of anisotropic systems may change under such stress. This property is known as *photoelasticity*.

It is convenient here to use the tensor β rather than ϵ . This phenomenon then involves the dependence of the components β_{ij} on either an applied stress σ_{kl} or on the presence of a strain ε_{kl} ; in either case we deal with the dependence of a symmetric rank-2 tensor, β_{ij} , on another symmetric rank-2 tensor $\sigma_{kl}(\varepsilon_{kl})$. Denoting the resulting changes in β_{ij} as $\Delta\beta_{ij}$ we write

$$\Delta\beta_{ij} = \begin{cases} \sum_{kl} p_{ijkl} \varepsilon_{kl}, \\ \sum_{kl} q_{ijkl} \sigma_{kl}. \end{cases} \quad (13.112)$$

We may adopt the Voigt notation and write

$$\Delta\beta_\alpha = \begin{cases} \sum_{\gamma=1}^6 p_{\alpha\gamma} \varepsilon_\gamma, \\ \sum_{\gamma=1}^6 q_{\alpha\gamma} \sigma_\gamma, \end{cases} \quad (13.113)$$

$\alpha = \{ij\}$, $\gamma = \{kl\}$. The intrinsic symmetry of the rank-4 tensors $[p]$ and $[q]$ involves index permutations of i, j and k, l , but not the permutations α, γ , namely

$$\mathcal{P} = \begin{pmatrix} 1 & 2 & 3 & 4 \\ 1 & 2 & 3 & 4 \end{pmatrix}, \begin{pmatrix} 1 & 2 & 3 & 4 \\ 2 & 1 & 3 & 4 \end{pmatrix}, \begin{pmatrix} 1 & 2 & 3 & 4 \\ 1 & 2 & 4 & 3 \end{pmatrix}, \begin{pmatrix} 1 & 2 & 3 & 4 \\ 2 & 1 & 4 & 3 \end{pmatrix}.$$

Thus, the general tensors $[p]$ and $[q]$ have 36 independent components each. The stress-optic and strain-optic coefficients are related via the elastic and stiffness constants as

$$q_{ik} = \sum_{j=1}^6 p_{ij} s_{jk}, \quad p_{ik} = \sum_{j=1}^6 q_{ij} c_{jk}.$$

Pyroelectricity and pyromagnetism

Some of the systems that do not possess spontaneous dipole moments may develop such moments when heated; such systems are labeled *pyroelectric* or *pyromagnetic*, depending on the type of induced moment. Since the temperature T is a scalar, the pyroeffects are characterized by either a polar i -vector for the case of electric moments, or by an axial

c -vector for magnetic moments. The relation between temperature and the induced moment is expressed as

$$M_i = q_i T, \quad (13.114)$$

$$P_i = q_i T.$$

It is obvious from the outset that centrosymmetric systems cannot support the presence of pyroeffects. It is also important to stress the fact that once a dipole moment develops it cannot be reversed. This constraint leads to the further requirement that the direction of the axis of polarization remains invariant under all symmetry operations of the associated point-group. Thus, pyroelectricity is manifest in only 10 of the 22 classes of noncentrosymmetric point-groups:

$$1, 2, m, mm2, 4, 4mm, 3, 3m, 6, 6mm.$$

Since the pyromagnetic tensor is an axial c -tensor, from the outset it is a null tensor for systems belonging to the 32 type I groups and to the 21 type III groups containing ΘI . Moreover, the irreversible directionality further limits its manifestation to only 31 of the 69 magnetic point-groups:

$$\begin{aligned} &1, \bar{1}, 2, \underline{2}, \mathbf{m}, \underline{m}, 2/\mathbf{m}, \underline{2}/\underline{m}, 222, 2mm, \underline{m}m\underline{2}, \\ &m\underline{m}m, 4, \bar{4}, 4/\mathbf{m}, 422, 4mm, \bar{4}2m, 4/m\underline{m}m, 3, \bar{3}, \\ &3\underline{2}, 3\underline{m}, \bar{3}m, 6, \bar{6}, 6/\mathbf{m}, 622, 6mm, \bar{6}m\underline{2}, 6/m\underline{m}m. \end{aligned}$$

Magnetoelectric effect

This effect is manifest in systems which develop magnetic moments when acted upon by an electric field, or vice versa. A system exhibiting such a phenomenon is termed a magnetoelectric medium. Although this effect was predicted by Pierre Curie in 1894, the conclusive evidence of its presence was reported by Astrov only in 1960, using the antiferromagnet Cr_2O_3 . The induced moments can be expressed in terms of the applied fields as

$$M_i = \sum_j m_{ij} E_j, \quad (13.115)$$

$$P_i = \sum_j (m^{-1})_{ij} B_j,$$

$$\Phi_{\text{ME}} = - \sum_{ij} m_{ij} E_i B_j, \quad (13.116)$$

where M_i, P_i are the induced magnetic and electric moments, respectively, and E_i, B_i the corresponding inducing external fields. Φ_{ME} is the contribution of the magnetoelectric effect to the thermodynamic potential. It is obvious from the structure of Φ_{ME} that the tensor $\mathbf{m}$ does not exhibit intrinsic symmetry. Moreover, $\mathbf{m}$ is of rank 2, and is an axial c -tensor, since $\mathbf{M}(\mathbf{B})$ is an axial c -vector, while $\mathbf{E}(\mathbf{P})$ is a polar i -vector. Consequently, from the outset, it is a null tensor for any systems belonging to type I and II Shubnikov groups.

Piezoelectricity and piezomagnetism

Pierre and Jacques Curie discovered in 1880 that when certain ionic crystals were subjected to mechanical stress electric charges appeared on their surfaces, positive charge on one side and negative charge on another. They also showed that the converse is true: when an electric voltage was applied across such a crystal it displayed a change in shape or a strain. It is clear that this effect involves a relation between a developed electric moment and the causing strain, or vice versa. Such macroscopic electromechanical phenomena can be described as

$$d\epsilon_{ij} = \sum_{kl} \left(\frac{\partial \epsilon_{ij}}{\partial S_{kl}} \right)_{\mathbf{E}} dS_{kl} + \sum_k \left(\frac{\partial \epsilon_{ij}}{\partial E_k} \right)_{\mathbf{S}} dE_k, \quad (13.117)$$

$$dP_i = \sum_{jk} \left(\frac{\partial P_i}{\partial S_{jk}} \right)_{\mathbf{E}} dS_{jk} + \sum_j \left(\frac{\partial P_i}{\partial E_j} \right)_{\mathbf{S}} dE_j, \quad (13.118)$$

where

$$\begin{aligned} \left(\frac{\partial \epsilon_{ij}}{\partial S_{kl}} \right)_{\mathbf{E}} &= C_{ij,kl}^{\mathbf{E}}, & \left(\frac{\partial P_i}{\partial E_j} \right)_{\mathbf{S}} &= \chi_{ij} \\ \left(\frac{\partial \epsilon_{ij}}{\partial E_k} \right)_{\mathbf{S}} &= p_{k,ij}, & \left(\frac{\partial P_i}{\partial S_{jk}} \right)_{\mathbf{E}} &= p_{i,jk}. \end{aligned} \quad (13.119)$$

Since stress and strain tensors are symmetric second-rank polar i -tensors, while the electric moment is a first-rank polar i -tensor, then $p_{i,jk}$ has to be a third-rank polar i -tensor, symmetric with respect to jk ; and we write

$$\begin{aligned} P_i &= \sum_j p_{i,jk} S_{jk}, \\ \epsilon_{jk} &= \sum_i p_{i,jk} E_i, \end{aligned} \quad (13.120)$$

where P_i, E_i are electric polarization and field, respectively, and the components of the tensor $p_{i,jk}$ are called piezoelectric moduli. Piezoelectricity contributes terms to a thermodynamic potential, of the form

$$\Phi = - \sum_{i,jk} p_{i,jk} E_i S_{jk}. \quad (13.121)$$

The 27 components of a general third-rank tensor can be reduced by intrinsic symmetries. The symmetry in the elastic indices reduces the number of independent components to $6 \times 3 = 18$. The tensor $p_{i,jk}$ may also be written in the Voigt notation as $p_{i,l}$, where l now runs from 1 to 6, and we can express the tensor as a 3×6 matrix.

Since $p_{i,l}$ is a polar i -tensor of odd rank, it becomes a null tensor for centrosymmetric systems. Conversely, we ascertain that systems exhibiting piezoelectricity must be non-centrosymmetric.

Further reduction in the number of independent components is possible, and depends on the symmetry of a system exhibiting the piezoelectric effect. Because of the jk -index

symmetry, the number of independent components for a crystal invariant under $\mathcal{G}$ is

$$\begin{aligned} \mathcal{N} &= \frac{1}{g} \sum_{R \in \mathcal{G}} \left[{}^{(v)}\chi^2(R) \right] {}^{(v)}\chi(R) \\ &= \frac{1}{g} \sum_{R \in \mathcal{G}} \frac{1}{2} \left({}^{(v)}\chi^2(R) + {}^{(v)}\chi(R^2) \right) {}^{(v)}\chi(R). \end{aligned} \quad (13.122)$$

Example 13.7

Piezoelectric tensor for systems with $\mathcal{C}_{3v}$ symmetry

Using (13.122), we find

$$\mathcal{N} = \frac{1}{6} \left[\frac{(9+3)}{2} \times 3 + 2 \times 0 + 3 \times \frac{(1+3)}{2} \times 1 \right] = 4.$$

Using the spherical tensor notation of (13.63) for the strain, we obtain the following subduction in terms of the Irreps of $\mathcal{C}_{3v}$:

$$\left. \begin{aligned} [\epsilon] &\rightarrow 2A_1(\epsilon_B, \eta) \oplus 2E \begin{pmatrix} \xi, \epsilon_{12} \\ \epsilon_{23}, \epsilon_{31} \end{pmatrix} \\ \mathbf{E} &\rightarrow A_1(E_3) \oplus E(E_1, E_2) \end{aligned} \right\} \Rightarrow \langle [\epsilon] \otimes \mathbf{E} | A_1 \rangle = (2A_1 \otimes A_1) \oplus (2E \otimes E).$$

This shows that we have two independent terms in the potential energy associated with $2A_1 \otimes A_1$ and two more associated with $2E \otimes E$. We write

$$\Phi = - \left[p_1 E_3 \epsilon_B + p_2 E_3 \eta + p_3 \sum_{i=1}^2 E_i \epsilon_{i3} + p_4 (E_1 \epsilon_{12} + E_2 \xi) \right].$$

Transforming to the Voigt notation, we obtain

$$\begin{aligned} \Phi = - & \left[p_{15} E_1 \epsilon_5 + p_{16} E_1 \epsilon_6 + p_{21} E_2 \epsilon_1 + p_{22} E_2 \epsilon_2 + p_{24} E_2 \epsilon_4 \right. \\ & \left. + p_{31} E_3 \epsilon_1 + p_{32} E_3 \epsilon_2 + p_{33} E_3 \epsilon_3 \right], \end{aligned}$$

where

$$\begin{aligned} p_{33} &= \frac{1}{3} (p_1 - 2p_2), & p_{31} &= p_{32} = (p_1 - p_2), \\ p_{24} &= p_{15} = p_3, & 2p_{21} &= -2p_{22} = p_{16} = p_4. \end{aligned}$$

The polarization vector is then given by

$$\mathbf{P} = - \frac{\partial \Phi}{\partial E_i} = \begin{bmatrix} 0 & 0 & 0 & 0 & p_{15} & -2p_{22} \\ -p_{22} & p_{22} & 0 & p_{15} & 0 & 0 \\ p_{31} & p_{31} & p_{33} & 0 & 0 & 0 \end{bmatrix} [\mathbf{S}],$$

and the strain vector (in the Voigt notation) is

$$\epsilon = -\frac{\partial \Phi}{\partial \epsilon_i} = \begin{bmatrix} 0 & -p_{22} & p_{31} \\ 0 & p_{22} & p_{31} \\ 0 & 0 & p_{33} \\ 0 & p_{15} & 0 \\ p_{15} & 0 & 0 \\ -p_{22} & 0 & 0 \end{bmatrix} \mathbf{E}.$$

We now list the forms of the piezoelectric tensors for most of the 32 crystallographic point-groups in Table 13.9. We omit the triclinic classes since they involve 18 independent constants.

Similarly, some crystals develop a magnetic moment when subjected to stress; such systems, by analogy, are termed piezomagnetic. Thus, the components of the induced

Table 13.9. *Piezoelectric tensors.*

Hex – 6, Tet – 4 (4*)	Hex – 6mm, Tet – 4mm (3*)
$\begin{bmatrix} 0 & 0 & 0 & p_{14} & p_{15} & 0 \\ 0 & 0 & 0 & p_{15} & -p_{14} & 0 \\ p_{13} & p_{13} & p_{33} & 0 & 0 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & 0 & 0 & 0 & p_{15} & 0 \\ 0 & 0 & 0 & p_{15} & 0 & 0 \\ p_{31} & p_{31} & p_{33} & 0 & 0 & 0 \end{bmatrix}$
Hex – 622, Tet – 422 (1*)	Hex – $\bar{6}$ (2*)
$\begin{bmatrix} 0 & 0 & 0 & p_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -p_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$	$\begin{bmatrix} p_{11} & -p_{11} & 0 & 0 & 0 & -2p_{21} \\ -p_{21} & p_{21} & 0 & 0 & 0 & -2p_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$
Hex – $\bar{6}m2$, $[m \perp x_1]$ (1*)	Hex – $\bar{6}m2$, $[m \perp x_2]$ (1*)
$\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & -2p_{22} \\ -p_{22} & p_{22} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$	$\begin{bmatrix} p_{11} & -p_{11} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -2p_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$
Tet – $\bar{4}$ (4*)	Tet – $\bar{4}2m$ (2*)
$\begin{bmatrix} 0 & 0 & 0 & p_{14} & p_{15} & 0 \\ 0 & 0 & 0 & -p_{15} & p_{14} & 0 \\ p_{13} & -p_{13} & 0 & 0 & 0 & p_{36} \end{bmatrix}$	$\begin{bmatrix} 0 & 0 & 0 & p_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -p_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & p_{36} \end{bmatrix}$

Table 13.9. (cont.)

Trig - 3 (6*)	Trig - 32 (2*)
$\begin{bmatrix} p_{11} & -p_{11} & 0 & p_{14} & p_{15} & -2p_{22} \\ -p_{22} & p_{22} & 0 & p_{15} & -p_{14} & -2p_{11} \\ p_{31} & p_{31} & p_{33} & 0 & 0 & 0 \end{bmatrix}$	$\begin{bmatrix} p_{11} & -p_{11} & 0 & p_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -p_{14} & -2p_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$
Trig - 3m, $[m \perp x_1]$ (4*)	Trig - 3m, $[m \perp x_2]$ (4*)
$\begin{bmatrix} 0 & 0 & 0 & 0 & p_{15} & -2p_{22} \\ -p_{22} & p_{22} & 0 & p_{15} & 0 & 0 \\ p_{31} & p_{31} & p_{33} & 0 & 0 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & 0 & 0 & 0 & p_{15} & 0 \\ -p_{22} & p_{22} & 0 & p_{15} & 0 & -2p_{11} \\ p_{31} & p_{31} & p_{33} & 0 & 0 & 0 \end{bmatrix}$
Ortho - 222 (3*)	Ortho - mm2 (5*)
$\begin{bmatrix} 0 & 0 & 0 & p_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & p_{25} & 0 \\ 0 & 0 & 0 & 0 & 0 & p_{36} \end{bmatrix}$	$\begin{bmatrix} 0 & 0 & 0 & 0 & p_{15} & 0 \\ 0 & 0 & 0 & p_{24} & 0 & 0 \\ p_{31} & p_{32} & p_{33} & 0 & 0 & 0 \end{bmatrix}$
Mono - 2, $[m \perp x_2]$ (8*)	Mono - 2, $[m \perp x_3]$ (8*)
$\begin{bmatrix} 0 & 0 & 0 & p_{14} & 0 & p_{16} \\ p_{21} & p_{22} & p_{23} & 0 & p_{25} & 0 \\ 0 & 0 & 0 & p_{34} & 0 & p_{36} \end{bmatrix}$	$\begin{bmatrix} 0 & 0 & 0 & p_{14} & p_{15} & 0 \\ 0 & 0 & 0 & p_{24} & p_{25} & 0 \\ p_{31} & p_{32} & p_{33} & 0 & 0 & p_{36} \end{bmatrix}$
Mono - m, $[m \perp x_2]$ (10*)	Mono - m, $[m \perp x_3]$ (10*)
$\begin{bmatrix} p_{11} & p_{12} & p_{13} & 0 & p_{15} & 0 \\ 0 & 0 & 0 & p_{24} & 0 & p_{26} \\ p_{31} & p_{32} & p_{33} & 0 & p_{35} & 0 \end{bmatrix}$	$\begin{bmatrix} p_{11} & p_{12} & p_{13} & 0 & 0 & p_{16} \\ p_{21} & p_{22} & p_{23} & 0 & 0 & p_{26} \\ 0 & 0 & 0 & p_{34} & p_{35} & 0 \end{bmatrix}$

* Number of independent components.

magnetization M_i are related to the applied stress S_{jk} by

$$\begin{aligned}
 M_i &= \sum_{j,k=1}^3 q_{i,jk} S_{jk} \\
 &= \sum_{l=1}^6 q_{i,jk} S_l,
 \end{aligned} \tag{13.123}$$

where the third-rank tensor $q_{i,jk}$ is called the *piezomagnetic* tensor:

$$\begin{array}{ccc}
 \Theta & I & \Theta I \\
 -1 & +1 & -1
 \end{array}$$

It is an axial c -tensor, since $\mathbf{M}$ is an axial c -vector and $\mathbf{S}$ is a polar i -tensor, and therefore is null for systems that belong to type II Shubnikov groups. Moreover, from Table 13.3, we find that for the 21 type III Shubnikov groups that contain the operation ΘI , $q_{i,jk}$ is a null tensor. Finally, piezomagnetism is absent for the point-groups 432 , $\bar{4}3m$, $m3m$ due to the combination of geometric and intrinsic symmetry in the jk indices. Consequently, there are 29 type I and 47 type III point-groups exhibiting piezomagnetism.

Piezomagnetism contributes terms to the thermodynamic potential, of the form

$$\Phi = - \sum_{i,jk} q_{i,jk} B_i S_{jk}. \quad (13.124)$$

Many of the systems belonging to the 66 piezomagnetic point-groups are not ferromagnetic, but when a stress is applied it induces a magnetic moment in these systems, and the ensuing phase must belong to one of the 31 ferromagnetic point-groups.

With the character given by

$$\chi_T(R(\phi)) = [{}^{(v)}\chi^2(R(\phi))] {}^{(a)}\chi(R(\phi)) = (4 \cos^2 \phi \pm 2 \cos \phi)(1 \pm 2 \cos \phi), \quad (13.125)$$

$$\chi_T(R(\phi)) = [{}^{(v)}\chi^2(R(\phi))] {}^{(a)}\chi(R(\phi)) = -(4 \cos^2 \phi \pm 2 \cos \phi)(1 \pm 2 \cos \phi), \quad (13.126)$$

for this type of tensor, the number of independent components is given by

$$N = \frac{1}{m} \sum_{R \in \mathcal{M}} \chi_T(R).$$

Example 13.8

Piezomagnetic tensor for systems with $3m$ (C_{3v}) and $3m$ symmetry

(i) $3m$ (C_{3v}):

$$N = \frac{1}{6} (18 + 2 \times 0 - 3 \times 2) = 2.$$

We obtain the following subduction in terms of the Irreps of C_{3v} :

$$\left. \begin{array}{ll} [\epsilon] & \rightarrow 2A_1 (\epsilon_B, \eta) \oplus 2E \begin{pmatrix} (\xi, \epsilon_{12}) \\ (\epsilon_{23}, \epsilon_{31}) \end{pmatrix} \\ \mathbf{B} & \rightarrow A_2 (B_3) \oplus E (-B_1, B_2) \end{array} \right\} \Rightarrow \langle [\epsilon] \otimes \mathbf{B} | A_1 \rangle = (2E \otimes E).$$

This shows that we have two independent terms in the potential energy associated with $2E \otimes E$. We write

$$\begin{aligned} \Phi &= - \left[q_1 \sum_{i=1}^2 B_i \epsilon_{i3} + q_2 (B_1 \epsilon_{12} + B_2 \xi) \right] \\ &= - \left[q_{15} (-B_1 \epsilon_5 + B_2 \epsilon_4) + 2q_{22} \left(-B_1 \epsilon_6 + \frac{1}{2} B_2 (\epsilon_1 - \epsilon_2) \right) \right], \end{aligned}$$

where the second line is in the Voigt notation. The induced magnetization vector is given by

$$\mathbf{M} = -\frac{\partial \Phi}{\partial B_i} = \begin{bmatrix} 0 & 0 & 0 & 0 & -q_{15} & -2q_{22} \\ q_{22} & -q_{22} & 0 & q_{15} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} [\mathbf{S}],$$

(ii) $3m$:

$$\mathcal{N} = \frac{1}{6} (18 + 2 \times 0 + 3 \times 2) = 4.$$

We obtain the following subduction in terms of the Irreps of $3m$:

$$\left. \begin{array}{l} [\epsilon] \rightarrow 2A_1(\epsilon_B, \eta) \oplus 2E \begin{pmatrix} \xi, \epsilon_{12} \\ \epsilon_{23}, \epsilon_{31} \end{pmatrix} \\ \mathbf{B} \rightarrow A_1(B_3) \oplus E(B_1, B_2) \end{array} \right\} \Rightarrow \langle [\epsilon] \otimes \mathbf{B} | A_1 \rangle = (2A_1 \otimes A_1) \oplus (2E \otimes E).$$

This is exactly the expansion in the case of Example 13.7, and we obtain the same tensor form, namely,

$$\mathbf{M} = -\frac{\partial \Phi}{\partial B_i} = \begin{bmatrix} 0 & 0 & 0 & 0 & q_{15} & -2q_{22} \\ -q_{22} & q_{22} & 0 & q_{15} & 0 & 0 \\ q_{31} & q_{31} & q_{33} & 0 & 0 & 0 \end{bmatrix} [\mathbf{S}].$$

Table 13.10. *Piezomagnetic matrices.*

Cubic – 23, $m\bar{3}$, $\bar{4}32$, $\bar{4}3m$, $m\bar{3}m$ (1^*)	
$\begin{bmatrix} 0 & 0 & 0 & q_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & q_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & q_{14} \end{bmatrix}$	
Tet – 4, $\bar{4}$, $4/m$ (4^*)	Hex – $\bar{6}22$, $\bar{6}mm$, $\bar{6}m2$ (1^*)
Hex – 6, $\bar{6}$, $6/m$	$\bar{6}m2$, $\bar{6}/mmm$,
$\begin{bmatrix} 0 & 0 & 0 & q_{14} & q_{15} & 0 \\ 0 & 0 & 0 & q_{15} & -q_{14} & 0 \\ q_{31} & q_{31} & q_{33} & 0 & 0 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & 0 & 0 & 0 & q_{15} & 0 \\ 0 & 0 & 0 & q_{24} & 0 & 0 \\ q_{31} & q_{31} & q_{33} & 0 & 0 & 0 \end{bmatrix}$
Hex – 622 , $6mm$, $\bar{6}m2$, $6/mmm$ (1^*)	Hex – $\bar{6}$, $\bar{6}$, $\bar{6}/m$, (2^*)
Tet – 422 , $4mm$, $\bar{4}2m$, $4/mmm$,	
$\begin{bmatrix} 0 & 0 & 0 & q_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -q_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$	$\begin{bmatrix} q_{11} & -q_{11} & 0 & 0 & 0 & -2q_{22} \\ -q_{22} & q_{22} & 0 & 0 & 0 & -2q_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$

Table 13.10. (*cont.*)Hex – $\bar{6}22$, $6\bar{m}m$, $\bar{6}m2$, $6/m\bar{m}m$ (3^*)Tet – $\bar{4}22$, $4\bar{m}m$, $\bar{4}2m$, $4/m\bar{m}m$

$$\begin{bmatrix} 0 & 0 & 0 & 0 & q_{15} & 0 \\ 0 & 0 & 0 & q_{15} & 0 & 0 \\ q_{31} & q_{31} & q_{33} & 0 & 0 & 0 \end{bmatrix}$$

Tet – $\bar{4}$, $\bar{4}$, $\bar{4}/m$ (4^*)

$$\begin{bmatrix} 0 & 0 & 0 & q_{14} & q_{15} & 0 \\ 0 & 0 & 0 & -q_{15} & q_{14} & 0 \\ q_{31} & -q_{31} & 0 & 0 & 0 & q_{36} \end{bmatrix}$$

Trig – 32 , $3m$, $\bar{3}m$ (2^*)

$$\begin{bmatrix} 0 & 0 & 0 & q_{14} & 0 & -2q_{22} \\ -q_{22} & q_{22} & 0 & 0 & -q_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

Ortho – 222 , $mm2$, mmm (3^*)

$$\begin{bmatrix} 0 & 0 & 0 & q_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & q_{25} & 0 \\ 0 & 0 & 0 & 0 & 0 & q_{36} \end{bmatrix}$$

Mono – 2 , m , $2/m$, (8^*)

$$\begin{bmatrix} 0 & 0 & 0 & q_{14} & q_{15} & 0 \\ 0 & 0 & 0 & q_{24} & q_{25} & 0 \\ q_{31} & q_{32} & q_{33} & 0 & 0 & q_{36} \end{bmatrix}$$

Tet – $\bar{4}22$, $4\bar{m}m$, $\bar{4}2m$ (2^*) $\bar{4}2m$, $4/m\bar{m}m$

$$\begin{bmatrix} 0 & 0 & 0 & q_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & q_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & q_{36} \end{bmatrix}$$

Trig – 32 , $3m$, $\bar{3}m$ (4^*)

$$\begin{bmatrix} q_{11} & -q_{11} & 0 & 0 & q_{15} & 0 \\ 0 & 0 & 0 & q_{15} & 0 & -2q_{11} \\ q_{31} & q_{31} & q_{33} & 0 & 0 & 0 \end{bmatrix}$$

Trig – 3 , $\bar{3}$ (6^*)

$$\begin{bmatrix} q_{11} & -q_{11} & 0 & q_{14} & q_{15} & -2q_{22} \\ -q_{22} & q_{22} & 0 & q_{15} & -q_{14} & -2q_{11} \\ q_{31} & q_{31} & q_{33} & 0 & 0 & 0 \end{bmatrix}$$

Ortho – 222 , $mm2$ (5^*) $mm2$, mmm

$$\begin{bmatrix} 0 & 0 & 0 & 0 & q_{15} & 0 \\ 0 & 0 & 0 & q_{24} & 0 & 0 \\ q_{31} & q_{32} & q_{33} & 0 & 0 & 0 \end{bmatrix}$$

Mono – $\bar{2}$, $\bar{m}$, $2/\bar{m}$ (10^*)

$$\begin{bmatrix} q_{11} & q_{12} & q_{13} & 0 & 0 & q_{16} \\ q_{21} & q_{22} & q_{23} & 0 & 0 & q_{26} \\ 0 & 0 & 0 & q_{34} & q_{35} & 0 \end{bmatrix}$$

* Number of independent components.

Magnetoelastic effects and magnetostriction

Magnetic systems exhibit what are generally labeled magnetoelastic effects. These properties involve the appearance of magnetization upon the application of stress, or, conversely, lattice deformation in the presence of an external magnetic field or spontaneous magnetization. The latter is referred to as *magnetostriction*.

The conventional measures of magnetostriction are the *magnetostrictive coefficients*, λ , defined as the fractional change $\Delta \mathbf{u}$ in linear dimension of a crystal in the β -direction, when the magnetization (or sublattice magnetization) is in the α -direction, namely

$$\lambda = \frac{|\boldsymbol{\ell} + \mathbf{u}| - |\boldsymbol{\ell}|}{|\boldsymbol{\ell}|^2} = \frac{\sum_i u_i \ell_i}{\sum_i \ell_i^2} = \sum_{ij} \frac{\partial u_i}{\partial x_j} \frac{\ell_i \ell_j}{\sum_k \ell_k^2},$$

where $\boldsymbol{\ell}$ is the unperturbed linear extension in the β -direction, and

$$\Delta \mathbf{u} = \sum_i \Delta u_i \hat{\mathbf{e}}_i = \sum_i \left(\sum_j \frac{\partial u_i}{\partial x_j} \ell_j \right) \hat{\mathbf{e}}_i$$

is the change in $\boldsymbol{\ell}$ due to magnetostriction. With $\beta_i = \ell_i/|\boldsymbol{\ell}|$, and identifying the symmetric part of the deformation with the strain, we obtain

$$\lambda = \sum_{ij} \varepsilon_{ij} \beta_i \beta_j. \quad (13.127)$$

We may expand the magnetic energy E_M of a physical system as a Taylor series in the lattice strains about the equilibrium configuration,

$$E_M = E_M^0 + \sum_{ij} \frac{\partial E_M}{\partial \varepsilon_{ij}} \Big|_0 \varepsilon_{ij} + \cdots, \quad (13.128)$$

where the second term is the linear magnetoelastic energy, which is generally described by a fourth-rank tensor $\mathbf{B}$, of the form

$$E_{\text{me}} = - \sum_{ijkl} B_{ijkl} \alpha_i \alpha_j \varepsilon_{kl}, \quad (13.129)$$

where $\alpha_i = S_i/S$ the i directional-cosine of the magnetic moment $\mathbf{M} = N\langle \mathbf{S} \rangle$. The form of the tensor must be invariant under the operations of the point-symmetry group of the system. It also satisfies the intrinsic permutation symmetries of the strain tensor and the permutation symmetry of the directional-cosine components. This leads to a maximum number of independent constants of 36.

Fixing the direction of magnetization $\boldsymbol{\alpha}$ and including the elastic energy E_{elast} we obtain

$$E = E_M^0 - \sum_{ijkl} B_{ijkl} \alpha_i \alpha_j \varepsilon_{kl} + \frac{1}{2} \sum_{ijkl} c_{ijkl} \varepsilon_{ij} \varepsilon_{kl}.$$

Example 13.9

Cubic crystals

We use here the Voigt notation; we write

$$\begin{aligned} E = E_M^0 - B_{11} \left(\alpha_1^2 \varepsilon_{11} + \alpha_2^2 \varepsilon_{22} + \alpha_3^2 \varepsilon_{33} \right) - B_{44} \left(\alpha_1 \alpha_2 \varepsilon_{12} + \alpha_2 \alpha_3 \varepsilon_{23} + \alpha_3 \alpha_1 \varepsilon_{31} \right) \\ + \frac{1}{2} c_{11} \left(\varepsilon_{11}^2 + \varepsilon_{22}^2 + \varepsilon_{33}^2 \right) + c_{12} \left(\varepsilon_{11} \varepsilon_{22} + \varepsilon_{22} \varepsilon_{33} + \varepsilon_{33} \varepsilon_{11} \right) + c_{44} \left(\varepsilon_{12}^2 + \varepsilon_{23}^2 + \varepsilon_{31}^2 \right). \end{aligned}$$

Minimizing the energy with respect to strain we obtain

$$\begin{aligned}\frac{\partial E}{\partial \varepsilon_{ii}} &= -B_{11}\alpha_i^2 + c_{11}\varepsilon_{ii} + c_{12}(\varepsilon_{jj} + \varepsilon_{kk}) = 0, & i, j, k \text{ cyclic,} \\ \frac{\partial E}{\partial \varepsilon_{ij}} &= -B_{44}\alpha_i\alpha_j + c_{44}\varepsilon_{ij} = 0, & i \neq j,\end{aligned}$$

which give the magnetostriction strains as

$$\varepsilon_{ii}^m = \frac{\alpha_i^2(c_{11} + 2c_{12}) - c_{12}}{(c_{11} - c_{12})(c_{11} + 2c_{12})} B_{11}, \quad \varepsilon_{ij}^m = \frac{\alpha_i\alpha_j}{c_{44}} B_{44}.$$

Next, we determine the magnetostrictive coefficients as

$$\begin{aligned}\lambda &= \sum_i \varepsilon_{ii} \beta_i^2 + \sum_{i < j} \varepsilon_{ij} \beta_i \beta_j \\ &= \frac{B_{11}}{c_{11} - c_{12}} (\alpha_1^2 \beta_1^2 + \alpha_2^2 \beta_2^2 + \alpha_3^2 \beta_3^2) \\ &\quad + \frac{B_{44}}{c_{44}} (\alpha_1 \alpha_2 \beta_1 \beta_2 + \alpha_2 \alpha_3 \beta_2 \beta_3 + \alpha_3 \alpha_1 \beta_3 \beta_1) - \frac{3c_{12} B_{11}}{(c_{11} - c_{12})(c_{11} + 2c_{12})} \\ &= \lambda_{100} (\alpha_1^2 \beta_1^2 + \alpha_2^2 \beta_2^2 + \alpha_3^2 \beta_3^2) + \lambda_{111} (\alpha_1 \alpha_2 \beta_1 \beta_2 + \alpha_2 \alpha_3 \beta_2 \beta_3 + \alpha_3 \alpha_1 \beta_3 \beta_1).\end{aligned}$$

A microscopic perspective To reveal the microscopic origin of magnetoelastic phenomena we write the single-ion spin Hamiltonian, at a given site, in the molecular-field approximation as

$$\mathcal{H}_m = \mathbf{H}^o \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{H}^{\text{ex}} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S} + \text{terms in } S^4 S^6, \quad (13.130)$$

where $\mathbf{H}^o$ is an external magnetic field, $\mathbf{H}^{\text{ex}}$ is an effective combined exchange and dipolar field, and $\mathbf{g}$ is the spectroscopic splitting tensor. The third term represents the effect of the crystal field through spin-orbit coupling, referred to as the single-site anisotropy; it is given in terms of the tensor $\mathbf{D}$. The field $\mathbf{H}^{\text{ex}}$ is given in terms of the magnetization $\mathbf{M}$ as

$$\mathbf{H}^{\text{ex}} = \mathbf{M} \cdot \mathbf{\Lambda}$$

and we rewrite (13.130) as

$$\mathcal{H}_m = \mathbf{H}^o \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{M} \cdot \mathbf{g}^{\text{ex}} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S} + \text{terms in } S^4 S^6, \quad (13.131)$$

The tensors $\mathbf{g}$, $\mathbf{g}^{\text{ex}}$, and $\mathbf{D}$ are determined perturbatively in terms of the relevant electronic wavefunctions; consequently they depend on the geometric properties of the atomic site. By introducing strain deformations, we write the lowest-order magnetoelastic Hamiltonian in the form

$$\begin{aligned}\mathcal{H}_{\text{me}} &= \sum_{ijkl} \left[\left(\frac{\partial g_{ij}}{\partial \varepsilon_{kl}} \right) H_i^o S_j + \left(\frac{\partial g_{ij}^{\text{ex}}}{\partial \varepsilon_{kl}} \right) M_i S_j + \left(\frac{\partial D_{ij}}{\partial \varepsilon_{kl}} \right) S_i S_j \right] \varepsilon_{kl} \\ &= \sum_{ijkl} (F_{ijkl} H_i^o S_j + F_{ijkl}^{\text{ex}} M_i S_j + G_{\alpha\beta\gamma\lambda} S_j S_j) \varepsilon_{kl}.\end{aligned} \quad (13.132)$$

Terms with higher degree in the spin operators involve higher rank tensors. This analysis shows that magnetoelastic phenomena are manifestations of two mechanisms. The first, known as single-ion contributions, arises from the modulation of crystal-field energy splittings by phonons or strain, and the second, referred to as two-ion contributions, involves similar modulations of the exchange couplings.

Single-ion contribution to magnetoelastic energy When constructing a Hamiltonian term accounting for magnetoelastic effects, one notices that the requirement of time-reversal invariance of the spin operators rules out any linear terms in the spin variables. Thus, the lowest degree magnetoelastic terms should involve linear strain variables and quadratic spin variables. Spin is an axial vector, hence we find

$$^{(1)}\Gamma^+ \otimes ^{(1)}\Gamma^+ = ^{(0)}\Gamma^+ + ^{(1)}\Gamma^+ + ^{(2)}\Gamma^+,$$

where

$$\begin{aligned} ^{(0)}\Gamma^+ &\Rightarrow S_x^2 + S_y^2 + S_z^2 = S(S+1), \\ ^{(1)}\Gamma^+ &\Rightarrow [S_i S_j - S_j S_i] = i\varepsilon_{ijk} S_k, \quad \text{first-degree terms,} \\ ^{(2)}\Gamma^+ &\Rightarrow \frac{\sqrt{3}}{2} \left[S_z^2 - \frac{1}{3} S(S+1) \right], \quad \frac{1}{2} [S_x^2 - S_y^2], \quad \frac{1}{2} [S_i S_j + S_j S_i] = S_{ij}. \end{aligned}$$

We immediately notice that unlike the elastic case, the spin operator corresponding to $^{(0)}\Gamma^+$ is simply a constant. We also find that the basis of $^{(1)}\Gamma^+$ reduces to first-degree monomials in the spin operators, and must be discarded. This reduces the number of magnetoelastic coupling constants associated with fully symmetric Hamiltonian terms. For the surviving terms, only combinations of elastic and spin variables belonging to the same row of an Irrep can contribute.

We find the following transformation isomorphisms:

$$\frac{\sqrt{3}}{2} \left[S_z^2 - \frac{1}{3} S(S+1) \right] \leftrightarrow \eta, \quad \frac{1}{2} [S_x^2 - S_y^2] \leftrightarrow \xi, \quad S_{ij} \leftrightarrow \varepsilon_{ij}. \quad (13.133)$$

Thus, in the case of type (1) cubic systems, Table 13.11, the invariant terms are

$$\frac{\sqrt{3}}{2} \left[S_z^2 - \frac{1}{3} S(S+1) \right] \eta + \frac{1}{2} [S_x^2 - S_y^2] \xi, \quad \sum_{i < j} S_{ij} \varepsilon_{ij};$$

whereas for type (7) tetragonal systems we obtain the five terms

$$\begin{aligned} \frac{\sqrt{3}}{2} \left[S_z^2 - \frac{1}{3} S(S+1) \right] \epsilon_B, \quad \frac{\sqrt{3}}{2} \left[S_z^2 - \frac{1}{3} S(S+1) \right] \eta, \\ \frac{1}{2} [S_x^2 - S_y^2] \xi, \quad S_{12} \epsilon_{12}, \quad \sum_{i=1}^2 S_{i3} \epsilon_{i3}. \end{aligned}$$

Case of complex Irreps We revisit the case where a two-dimensional real Rep is reducible to two 1-dimensional complex Irreps. Unlike the case of elastic strain invariants, it is possible here to construct invariant magnetoelastic terms of the form $S_{23} + iS_{13}$ and $\varepsilon_{23} + i\varepsilon_{13}$ will form bases of a complex Irrep, while $S_{23} - iS_{13}$ and $\varepsilon_{23} - i\varepsilon_{13}$ will become bases for the conjugate Irrep. This would yield product invariants terms of the form

$$(\varepsilon_{23} + i\varepsilon_{13}) (S_{23} + iS_{13})^*, \quad (\varepsilon_{23} - i\varepsilon_{13}) (S_{23} - iS_{13})^*.$$

Although each of these terms can be multiplied by a complex constant, the hermiticity of the Hamiltonian would require that these constants be complex conjugates, leading to two independent real constants. Alternatively, we may take two real combinations

$$\left(\varepsilon_{23} \mathcal{S}_{23} + \varepsilon_{13} \mathcal{S}_{13} \right), \quad \left(\varepsilon_{23} \mathcal{S}_{23} - \varepsilon_{13} \mathcal{S}_{13} \right)$$

with real phenomenological constants. Hence, each complex Irrep contributes an independent contribution to the magnetoelastic Hamiltonian.

The single-ion magnetoelastic Hamiltonian can then be written as

$$\begin{aligned} \mathcal{H}_{\text{me}}^{\text{si}} &= - \sum_{\tau} \sum_{(\mu)} \sum_{r,s} B_{rs}^{(\mu)}(\tau) \sum_i \varepsilon_{ir}^{(\mu)}(\tau) \mathcal{S}_{is}^{(\mu)}(\tau), \\ &= \sum_{\mu} \mathcal{H}_{\mu}^{\text{si}} \end{aligned}$$

(13.134)

where τ indexes the magnetic ions, μ the Ireps and r, s the Irrep rows.

Table 13.11. *Irrep decomposition of magnetoelastic coefficients for the 32 point-groups.*

Symmetry type	Point-group	Irrep	Number of constants			
			Single-ion		Two-ion	
			Irrep	Total	Irrep	Total
(1)	$m3m, \bar{4}3m,$ 432	$^{(1)}\Gamma(1)$	0		1	
		$^{(12)}\Gamma(2)$	1	2	1	3
		$^{(25')}\Gamma(3)$	1		1	
(2)	$23, m3$	$^{(1)}\Gamma(1)$	0		1	
		$^{(2)}\Gamma(1)$	1	3	1	4
		$^{(3)}\Gamma(1)$	1		1	
		$^{(4)}\Gamma(3)$	1		1	
(3)	$6mm, \bar{6}m2,$ $622, \frac{6}{mmm}$	$^{(1)}\Gamma(1)$	2		4	
		$^{(5)}\Gamma(2)$	1	4	1	6
		$^{(6)}\Gamma(2)$	1		1	

Table 13.11. *cont.*

Symmetry type	Point-group	Irrep	Number of constants			
			Single-ion		Two-ion	
			Irrep	Total	Irrep	Total
(4)	$6, \bar{6}, \frac{6}{m}$	$^{(1)}\Gamma(1)$	2		4	
		$^{(3)}\Gamma(1)$	1		1	
		$^{(4)}\Gamma(1)$	1	6	1	8
		$^{(5)}\Gamma(1)$	1		1	
		$^{(6)}\Gamma(1)$	1		1	
(5)	$32, 3m, \bar{3}m$	$^{(1)}\Gamma(1)$	2	6	4	8
		$^{(3)}\Gamma(2)$	4		4	
(6)	$3, \bar{3}$	$^{(1)}\Gamma(1)$	2		4	
		$^{(2)}\Gamma(1)$	4	10	4	12
		$^{(3)}\Gamma(1)$	4		4	
(7)	$422, \frac{4}{mmm}, 4mm, \bar{4}2m$	$^{(1)}\Gamma(1)$	2		4	
		$^{(3)}\Gamma(1)$	1	5	1	7
		$^{(4)}\Gamma(1)$	1		1	
		$^{(5)}\Gamma(2)$	1		1	
(8)	$4, \bar{4}, \frac{4}{m}$	$^{(1)}\Gamma(1)$	2		4	
		$^{(2)}\Gamma(1)$	4	8	4	10
		$^{(3)}\Gamma(1)$	1		1	
		$^{(4)}\Gamma(1)$	1		1	
(9)	$222, mm2, mmm$	$^{(1)}\Gamma(1)$	6		9	
		$^{(4)}\Gamma(1)$	1	9	1	12
		$^{(2)}\Gamma(1)$	1		1	
		$^{(3)}\Gamma(1)$	1		1	

Table 13.11. (*cont.*)

Symmetry type	Point-group	Irrep	Number of constants			
			Single-ion		Two-ion	
			Irrep	Total	Irrep	Total
(10)	$2, m, \frac{2}{m}$	$^{(1)}\Gamma(1)$	12	16	16	20
		$^{(2)}\Gamma(1)$	4		4	
(11)	$1, \bar{1}$		30	30	36	36

Example 13.9

Magnetoelastic Hamiltonian for type (3) hexagonal symmetry

From Table 13.8 we identify the invariant monomials: $\varepsilon_B \frac{\sqrt{3}}{2} [S_z^2 - \frac{1}{3}S(S+1)]$, $\eta \frac{\sqrt{3}}{2} [S_z^2 - \frac{1}{3}S(S+1)]$, $\xi \frac{1}{2} [S_x^2 - S_y^2]$, $\varepsilon_{12} S_{12}$, $\varepsilon_{23} S_{23}$, $\varepsilon_{31} S_{31}$. The magnetoelastic Hamiltonian can be written as

$$\begin{aligned} \mathcal{H}_{\text{me}}^{\text{si}} = & -B_{12}^{(1)} \varepsilon_B \frac{\sqrt{3}}{2} \left[S_z^2 - \frac{1}{3}S(S+1) \right] - B_{22}^{(1)} \eta \frac{\sqrt{3}}{2} \left[S_z^2 - \frac{1}{3}S(S+1) \right] \\ & - B^{(5)} \{ \varepsilon_{23} S_{23} + \varepsilon_{31} S_{31} \} - B^{(6)} \left\{ \xi \frac{1}{2} [S_x^2 - S_y^2] + \varepsilon_{12} S_{12} \right\}. \end{aligned}$$

Two-ion contribution to magnetoelastic energy The case of two-ion magnetoelasticity is similar to the single-ion case. Here, we replace terms like $(S_i S_j + S_j S_i)/2 = S_{ij}$ by $(S_i^\alpha S_j^\beta + S_j^\alpha S_i^\beta)/2 = S_{ij}(\alpha\beta)$; the only difference is that $\sum_i S_i^\alpha S_i^\beta \neq \text{constant}$.

The two-ion magnetoelastic Hamiltonian can then be written as

$$\begin{aligned} \mathcal{H}_{\text{me}}^{\text{ti}} = & - \sum_{\tau, \tau'} \sum_{(\mu)} \sum_{r,s} D_{rs}^{(\mu)}(\tau, \tau') \sum_i \varepsilon_{ir}^{(\mu)}(\tau, \tau') S_{is}^{(\mu)}(\tau, \tau'), \\ = & \sum_{\mu} \mathcal{H}_{\mu}^{\text{ti}} \end{aligned}$$
(13.135)

For pedagogical simplicity let us neglect the two-ion contribution and the dependence on τ for the moment. The total Hamiltonian can be written as

$$\begin{aligned}\mathcal{H} &= \mathcal{H}_{\text{elast}} + \mathcal{H}_{\text{me}} \\ &= \sum_{\mu, i, rs} \left[\frac{1}{2} {}^{(\mu)}c_{rs} {}^{\mu}\varepsilon_i^{r*} {}^{\mu}\varepsilon_i^s - {}^{(\mu)}B_{rs} {}^{\mu}\varepsilon_i^r \langle {}^{\mu}\mathcal{S}_i^s \rangle \right] \\ &= \sum_{\mu} \mathcal{H}_{\mu, i},\end{aligned}\tag{13.136}$$

where we used the expression (13.65) for $\mathcal{H}_{\text{elast}}$. The values of the ${}^{\mu}\varepsilon_i^r$ s are obtained by minimizing each $\mathcal{H}_{\mu, i}$ with respect to the set ${}^{\mu}\varepsilon_i^r$.

Example 13.10

Type (3) hexagonal symmetry

$$\begin{aligned}{}^{(1)}\Gamma \Rightarrow \mathcal{H}_1 &= \frac{1}{2} {}^1c_{11} \varepsilon_B^2 + {}^1c_{12} \varepsilon_B \eta + \frac{1}{2} {}^1c_{22} \eta^2 \\ &\quad - {}^{(1)}B_{12} \varepsilon_B \frac{\sqrt{3}}{2} \left[S_z^2 - \frac{1}{3} S(S+1) \right] - {}^{(1)}B_{22} \eta \frac{\sqrt{3}}{2} \left[S_z^2 - \frac{1}{3} S(S+1) \right]\end{aligned}$$

and we obtain

$$\begin{aligned}{}^1c_{11} \varepsilon_B + {}^1c_{12} \eta &= {}^{(1)}B_{12} \frac{\sqrt{3}}{2} \left[\langle S_z^2 \rangle - \frac{1}{3} S(S+1) \right], \\ {}^1c_{12} \varepsilon_B + \frac{1}{2} {}^1c_{22} \eta &= {}^{(1)}B_{22} \frac{\sqrt{3}}{2} \left[\langle S_z^2 \rangle - \frac{1}{3} S(S+1) \right],\end{aligned}$$

which yield

$$\varepsilon_B = \frac{{}^1c_{22} {}^{(1)}B_{12} - {}^1c_{12} {}^{(1)}B_{22}}{{}^1c_{11} {}^1c_{22} - {}^1c_{12}^2} \frac{\sqrt{3}}{2} \left[\langle S_z^2 \rangle - \frac{1}{3} S(S+1) \right].$$

Galvanomagnetic effects: the Hall effect

The presence of a magnetic field radically modifies the electrical transport properties of materials. By writing the Onsager relation for the resistivity tensor in the presence of a magnetic field, namely

$$\rho_{ij}(\mathbf{B}) = \rho_{ji}(-\mathbf{B}),$$

we realize that tensor $\boldsymbol{\rho}$ is not symmetric. We write $\boldsymbol{\rho}$ as

$$\boldsymbol{\rho} = \boldsymbol{\rho}^s + \boldsymbol{\rho}^a,$$

where $\boldsymbol{\rho}^s$ and $\boldsymbol{\rho}^a$ are symmetric and antisymmetric tensors of rank 2, respectively. We then find:

$$\begin{aligned}\rho_{ij}^s(\mathbf{B}) &= \rho_{ji}^s(\mathbf{B}) & \rho_{ij}^a(\mathbf{B}) &= -\rho_{ji}^a(\mathbf{B}) \\ \rho_{ij}^s(\mathbf{B}) &= \rho_{ji}^s(-\mathbf{B}) = \rho_{ij}^s(-\mathbf{B}) & \rho_{ij}^a(\mathbf{B}) &= \rho_{ji}^a(-\mathbf{B}) = -\rho_{ij}^a(-\mathbf{B}) \\ \rho_{ij}^s(\mathbf{B}) &\text{ is an even function of } \mathbf{B} & \rho_{ij}^a(\mathbf{B}) &\text{ is an odd function of } \mathbf{B}\end{aligned}$$

We express the relation between the electric field and current density vectors as

$$E_i = \sum_k \rho_{ik} J_k = \sum_k \left(\rho_{ik}^s J_k + \rho_{ik}^a J_k \right),$$

and writing $\boldsymbol{\rho}^a$ as an axial vector, $\boldsymbol{\rho}^A$, we obtain

$$E_i = \sum_k \rho_{ik}^s J_k + (\mathbf{J} \times \boldsymbol{\rho}^A)_i.$$

This last expression shows that energy dissipation, or Joule heating

$$\mathbf{J} \cdot \mathbf{E} = \sum_{ik} \rho_{ik}^s J_i J_k$$

is only associated with $\boldsymbol{\rho}^s$.

Expanding $\boldsymbol{\rho}(\mathbf{B})$ in powers of B_i , we obtain

$$\rho_{ik}^s(\mathbf{B}) = \rho_{ik}^0 + \rho_{iklm}^s B_l B_m, \quad (13.137)$$

$$\rho_{ik}^a(\mathbf{B}) = \rho_{ikl}^a B_l. \quad (13.138)$$

The tensor ρ_{ikl}^a is known as the *Hall tensor*; it relates an antisymmetric rank-2 tensor (axial vector) to another axial vector $\mathbf{B}$. It is therefore equivalent to a rank-2 polar tensor. The tensor ρ_{iklm}^s is known as the *magnetoresistance tensor*. It may be considered as relating two symmetric tensors, each of rank 2.

Thermoelectricity

Thermoelectric effects are phenomena associated with the simultaneous flow of electric and heat currents in a system. They may be viewed as the result of mutual interference between heat flow and electric current flow in a system. Relationships among various such phenomena were proposed in 1854 by Lord Kelvin. Here, we follow H. Callen's approach [76] in deriving the relations appropriate for each of the thermoelectric phenomena and how they influence each other. We consider the thermoelectric effects in the light of the Onsager reciprocity theorem, noting that the number of particles, the total internal energy, and the entropy are locally definable thermodynamic variables, in the manner adopted in Section 12.7. Thus, we define the particle current density $\mathbf{J}$, the energy current density $\mathbf{W}$, and the heat current density $T\mathbf{S}$, where $\mathbf{S}$ is the entropy current density. We use (13.129) to obtain a relation among the three currents, namely

$$T\mathbf{S} = \mathbf{Q} = \mathbf{W} - \mu \mathbf{J}, \quad (13.139)$$

where we used $F_W = 1/T$, $F_e = -\mu/T$, and μ is the electrochemical potential. Next, we obtain from (13.134) the relation

$$\begin{aligned}\dot{S} &= \nabla \cdot \mathbf{S} = \nabla \frac{1}{T} \cdot \mathbf{W} - \nabla \frac{\mu}{T} \cdot \mathbf{J} \\ &= \nabla \frac{1}{T} \cdot \mathbf{Q} - \frac{1}{T} \nabla \mu \cdot \mathbf{J}.\end{aligned}\quad (13.140)$$

Now, if we identify $\mathfrak{F}_Q = \nabla \frac{1}{T}$, $\mathfrak{F}_e = \frac{1}{T} \nabla \mu$, we may write (13.135) as

$$\begin{aligned}-\mathbf{J} &= L_{11} \frac{1}{T} \nabla \mu + L_{12} \nabla \frac{1}{T}, \\ \mathbf{Q} &= L_{21} \frac{1}{T} \nabla \mu + L_{22} \nabla \frac{1}{T}.\end{aligned}\quad (13.141)$$

Eliminating $\nabla \mu$ from (13.141) and using $\mathbf{Q} = T\mathbf{S}$, we obtain

$$\mathbf{S} = -\frac{L_{12}}{TL_{11}} \mathbf{J} + \frac{D}{TL_{11}} \nabla \frac{1}{T}.\quad (13.142)$$

The first term in (13.142) represents the contribution to the entropy current from the flow of an electric current; it shows that for a given temperature distribution in the system, the electric current carries with it an entropy of

$$S_J = -L_{12}/TL_{11}\quad (13.143)$$

per particle, in addition to the entropy flow due to the temperature gradient across the system.

We are now in a position to define the thermal and electrical conductivities in terms of the kinetic coefficients L , as

$$\begin{aligned}\kappa &= -\frac{\mathbf{Q}}{\nabla T} \Big|_{\mathbf{J}=0} \\ &= \frac{1}{T^2 L_{11}} (L_{11} L_{22} - L_{12}^2) = \frac{D}{T^2 L_{11}},\end{aligned}\quad (13.144)$$

$$\sigma = \frac{-e\mathbf{J}}{\nabla \mu/e} \Big|_{\nabla T=0} = \frac{e^2 L_{11}}{T},\quad (13.145)$$

and conversely, write the kinetic coefficients in terms of these measurable quantities

$$\begin{aligned}L_{11} &= \frac{T}{e^2} \sigma, \\ L_{12} &= -\frac{T^2}{e^2} \sigma S_J, \\ L_{22} &= \frac{T^3}{e^2} \sigma S_J^2 + T^2 \kappa.\end{aligned}\quad (13.146)$$

With the aid of these relationships we now consider the three thermoelectric effects:

- (i) **The Thomson effect** This effect is manifest when an electric current traverses a temperature gradient in a material.
- (ii) **The thermoelectric e.m.f. (Seebeck effect)** This effect furnishes the operating principle behind thermocouples. When a circuit is made of two different metals, and the junctions are maintained at two different temperatures, an e.m.f. develops

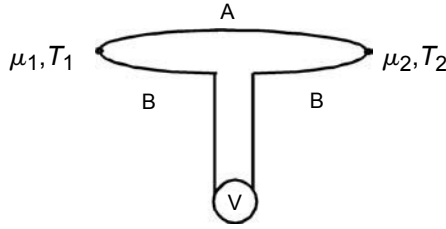


Fig. 13.5. Thermocouple configuration for the Seebeck effect.

across the circuit under condition of zero current. We consider such a circuit, shown in Figure 13.5, where the thermocouple comprises two different metal strips, A and B, and the e.m.f. is measured by the voltmeter V. At $J = 0$, we obtain from (13.141) for either conductor,

$$\nabla \mu = \frac{L_{12}}{TL_{11}} \nabla T. \quad (13.147)$$

- (iii) **The Peltier effect** When current is allowed to flow across a junction between two different metals, it is found that heat must be continuously added or subtracted at the junction in order to maintain its temperature constant. The heat is proportional to the current flowing and changes sign when the current is reversed.

13.4 Tensor field representations

Many problems in condensed matter, atomic, and molecular physics involve the construction of a set of basis functions that span the relevant Hilbert space. Such a set is referred to as a *tensor field* basis $\mathfrak{T}$ [86]; its components are suitably chosen to describe whatever physical property is being considered. For example, in the case of vibrational properties, the basis set comprises the displacement vectors of the constituent particles; each vector being a three-component first-rank tensor. In the case of magnetic properties, the basis set comprises the spin manifolds of the constituent particles.

The components of the basis set can be assigned two main labels: the first label, (μ) , identifies a particular site or particle of the system; for example, in the case of crystalline solids this label identifies the unit cell l and the sublattice κ to which the atom belongs, thus $(\mu) \rightarrow (l\kappa)$. The second label identifies the component of the physical tensor or manifold $\mathcal{T}_{\alpha\beta\dots}$ describing the physical property associated with the site or particle, be it displacement, spin, electron orbital, or any other physical quantity. The overall basis can then be written as $\mathfrak{T}_{\alpha\beta\dots}(\mu)$. It is just the direct outer-product of the site or particle position space $\delta(\mu' - \mu)$ and the tensor field $\mathcal{T}$, namely

$$\mathfrak{T} = \delta \otimes \mathcal{T}. \quad (13.148)$$

A very useful Rep of the symmetry group $\mathcal{G}$ associated with the system can be engendered by the action of group elements on the tensor field basis. This Rep depicts the symmetry of the physical property under consideration, and is often referred to as the

tensor field representation $\mathfrak{F}$. It is then obvious that we would be interested in determining its decomposition over the Irreps of the space or point-group $\mathcal{G}$.

We can engender separate Reps through the action of the group elements on the spaces δ and $\mathcal{T}$. The Rep $\Gamma^{\mathcal{P}}$, engendered on δ , describes how the sites or particles of the system permute among themselves under the action of the operations of the covering group $\mathcal{G}$; we will call it the *permutation* Rep. The tensor Rep, $\Gamma^{\mathcal{T}}$, engendered on $\mathcal{T}$, describes the transformation properties of the physical tensor basis assigned to a given site or atom, under the group operations. It is straightforward to discern that the $\mathfrak{F}$ is the direct product of these two Reps, namely,

$$\mathfrak{F} = \Gamma^{\mathcal{T}} \otimes \Gamma^{\mathcal{P}}. \quad (13.149)$$

13.4.1 The tensor representation $\Gamma^{\mathcal{T}}$

A tensor representation of the operation $(R|\boldsymbol{\tau} + \mathbf{t}) \in \mathbb{S}$ is generated by

$$R\mathcal{T} = \mathcal{T} \Gamma^{\mathcal{T}}(R), \quad R \in \mathbf{P} \subset \mathcal{O}(3), \quad (13.150)$$

where $\mathbf{P}$ is the point-group of $\mathbb{S}$. The basis functions of $\mathcal{T}$ are the tensor components defined on the atomic constituents of the system. $\Gamma^{\mathcal{T}}$ is usually reducible.

It is convenient to begin with defining the Reps classified under the group $\mathcal{O}(3)$ and then restrict our definition to particular site-symmetry subgroups $\mathbf{P}$. Let us start with the case of the physical tensor representing lattice displacements, encountered in lattice vibrational problems. Here, the functions of the basis tensor comprise vectors $\mathbf{u}$, each defines the displacement of a particular atomic-site of the system. The components of a displacement vector $\mathbf{u}$ transform according to the polar vector Rep of $\mathcal{O}(3)$. Thus, we find that for $R \in \mathcal{O}(3)$

$$R u_{\alpha} = \sum_{\beta} u_{\beta} {}^{\vee}\Gamma, \quad (13.151)$$

where ${}^{\vee}\Gamma \equiv ({}^1)\Gamma^{-}$ is the polar vector Rep of $\mathcal{O}(3)$.

In the case of magnetic, or spin, systems the basis tensor comprises magnetic moments, or classical spins $\mathbf{S}_{\mu}$, associated with site μ of the system. Accordingly, we obtain

$$R S_{\alpha} = \sum_{\beta} S_{\beta} {}^{\text{a}}\Gamma, \quad (13.152)$$

where ${}^{\text{a}}\Gamma \equiv ({}^1)\Gamma^{+}$ is the axial vector Rep of $\mathcal{O}(3)$.

As a further example, we find that for phenomena related to magnetoelastic effects, the basis tensor comprises outer-products of axial and polar vectors at each atomic-site of the system, namely, for site μ we obtain $\mathcal{T}(\mu) = {}^{\vee}\Gamma(\mu) \otimes {}^{\text{a}}\Gamma(\mu)$.

Once we have constructed the basis tensor $\mathcal{T}$, we restrict symmetry operations of $\mathcal{O}(3)$ to those belonging to a point-group $\mathbf{P}$, associated with a particular system; i.e. we subduce the Reps ${}^{\vee}\Gamma$, ${}^{\text{a}}\Gamma$, or ${}^{\vee}\Gamma \otimes {}^{\text{a}}\Gamma$, onto $\mathbf{P}$.

13.4.2 The permutation representation $\Gamma^{\mathcal{P}}$

The action of $R \in \mathcal{O}(3)$ on the δ basis results in a permutation among the atomic-sites. We notice that these permutations do not depend on the nature of the physical tensor basis $\mathcal{T}(\mu)$. Thus, it is a feature common to all possible physical tensor bases describing different physical aspects of a given system:

$$\boxed{\begin{array}{l} \textit{The permutation Rep is the same} \\ \textit{for all tensor representations of a system.} \end{array}} \quad (13.153)$$

13.4.3 Simple system decomposition

The constituent atoms of a system can be differentiated (or partitioned), according to species or site symmetry, into simpler subsystems. We refer to the original system as composite and label its distinct constituent subsystems as *simple systems*. Each simple system consists of all atoms whose position vectors can be obtained by applying all the elements of $\mathcal{G}$ to any position vector of one of its constituents. No two simple systems have atoms in common, and the elements of $\mathcal{G}$ permute the atoms of each simple system among themselves.

One of the simplest composite systems is H_2O : It comprises two simple systems, one contains O and the other contains H(1) and H(2). The $\mathcal{C}_{2v}$ group permutes the Hs. Consequently, we can associate a simple permutation Rep $\Gamma^{\mathcal{P}}(i)$ with each simple system i . This allows us to decompose $\Gamma^{\mathcal{P}}$ of a composite system into the direct sum of m simple permutation Reps of its m constituent simple systems, namely,

$$\Gamma^{\mathcal{P}} = \sum_{i=1}^m \oplus \Gamma^{\mathcal{P}}(i). \quad (13.154)$$

Thus, we find that *the permutation representation of the atoms of the composite system is the direct sum of the permutation representations $\Gamma^{\mathcal{P}}(i)$ of each of its m simple systems.*

Substituting in (13.149), we can write the tensor field Rep as

$$\begin{aligned} \mathfrak{F} &= \left(\sum_{i=1}^m \oplus \Gamma^{\mathcal{P}}(i) \right) \otimes \Gamma^{\mathcal{T}} \\ &= \sum_{i=1}^m \oplus \mathfrak{F}(i), \end{aligned} \quad (13.155)$$

where $\mathfrak{F}(j)$, the tensor field Rep of simple system j , is defined as

$$\mathfrak{F}(j) = \Gamma^{\mathcal{P}}(j) \otimes \Gamma^{\mathcal{T}}. \quad (13.156)$$

Thus, we are able to reduce the problem of constructing a tensor field Rep of a system to that of constructing the constituent tensor field Reps associated with its constituent simple systems.

13.4.4 Simple system tensor field Rep

We now consider the case of a single simple system generated by $\mathbb{S}$ from the atomic position vector $\mathbf{r}$, and its tensor field Rep

$$\mathfrak{F}(\mathbf{r}) = \Gamma^{\mathcal{P}}(\mathbf{r}) \otimes \Gamma^{\mathcal{T}}. \quad (13.157)$$

Since $\Gamma^{\mathcal{P}}(\mathbf{r})$ is common to all tensor fields associated with the simple crystal, we start by discussing its properties and methods for its construction.

The permutation representation $\Gamma^{\mathcal{P}}(\mathbf{r})$

As we mentioned above, $\Gamma^{\mathcal{P}}(\mathbf{r})$ is intimately associated with the site-symmetry of the position vector $\mathbf{r}$. The concept of site-symmetry is most general when we consider space-groups, in which case the composite and simple systems become composite and simple crystals, respectively. We direct our analysis to this general and more complicated case. It is then straightforward to simplify the procedures involved to the case of molecules and finite systems.

Site-symmetry subgroup

In Chapter 10 we discussed, at length, the idea of site-symmetries, orbits, equivalent positions, etc. It is now time to make use of these concepts.

First, we recall that applying all the operations of a space-group $\mathbb{S}$ to a given position vector $\mathbf{r}$ generates an orbit of $\mathbf{r}$, which here we can identify with a simple crystal, which is not necessarily a Bravais lattice. Next, we consider operations $K \in \mathbb{S}$ that transform $\mathbf{r}$ to

$$(K|\boldsymbol{\tau} + \mathbf{t})\mathbf{r} = \mathbf{r} + \mathbf{t}', \quad (13.158)$$

where $\mathbf{t}' \in \mathbb{T}$ is a lattice vector. The operations K form a subgroup $\mathbb{K} \subset \mathbb{S}$. One can expand $\mathbb{S}$ as

$$\mathbb{S} = \sum_{j=1}^{g/k} R_j \mathbb{K}. \quad (13.159)$$

The point-group $\mathbb{K}(\mathbf{r})$ of $\mathbb{K}$ is called the *site-symmetry point-group*. In Chapter 10, we described these point-groups in conjunction with the Wyckoff positions, and noted that these positions and their corresponding point-symmetry groups are listed in the *International Tables*.

Finally, we define a *site-symmetry subgroup*, or the subgroup of $\mathbf{r}$, $\mathbb{H}(\mathbf{r}) \subset \mathbb{K} \subset \mathbb{S}$, more restricted than $\mathbb{K}$ such that, for $H \in \mathbb{H}(\mathbf{r})$, we have

$$H\mathbf{r} = \mathbf{r}. \quad (13.160)$$

Elements of the subgroup $\mathbb{H}(\mathbf{r})$ are, in general, of the form $(R|\boldsymbol{\tau} + \mathbf{t}(R))$, where $\mathbf{t}(R) \in \mathbb{T}$ is a specific lattice translation vector that is required to restore $\mathbf{r}$. The site subgroup $\mathbb{H}(\mathbf{r})$ is isomorphic to the site point-group $\mathbb{K}(\mathbf{r})$. In general, the latter is not necessarily a subgroup of $\mathbb{S}$.

Induction of $\Gamma^{\mathcal{P}}(\mathbf{r})$

To determine the structure of the permutation $\text{Rep } \Gamma^{\mathcal{P}}(\mathbf{r})$ we expand $\mathbb{S}$ into the left cosets

$$\mathbb{S} = \sum_{i=1}^{g/h} R_i \mathbb{H}(\mathbf{r}). \quad (13.161)$$

Since all the elements of $\mathbb{H}(\mathbf{r})$ leave $\mathbf{r}$ invariant, the atomic position vectors of the simple crystal generated by $\mathbb{S}$ from $\mathbf{r}$ bear a one-to-one correspondence with the cosets in (13.161). That is, the atomic position vectors of the simple crystal can be obtained as

$$\mathbf{r}_j = (R_j | \boldsymbol{\tau}(j) + \mathbf{t}(j)) \mathbf{r}, \quad j = 1, \dots, m, \quad (13.162)$$

where

$$\mathbf{t}(j) = \mathbf{r}_j - R_j \mathbf{r} - \boldsymbol{\tau}(j) \quad (13.163)$$

is uniquely defined. In cases where the physical tensor basis comprises a manifold of functions centered at position vector $\mathbf{r}$, the engendered permutations are defined as

$$\begin{aligned} \mathbf{r}_j &= (R_j | \boldsymbol{\tau}(j) + \mathbf{t}(j))^{-1} \mathbf{r}, \\ \mathbf{t}(j) &= \mathbf{r} - R_j^{-1} \mathbf{r}_j - \boldsymbol{\tau}(j). \end{aligned} \quad (13.164)$$

The conjugate subgroup

$$\mathbb{H}(\mathbf{r}_j) = (R_j | \boldsymbol{\tau}(j))^{-1} (H)(\mathbf{r}) (R_j | \boldsymbol{\tau}(j)) \quad (13.165)$$

leaves $\mathbf{r}_j$ invariant.

Since $\Gamma^{\mathcal{P}}(\mathbf{r})$ is a Rep of $\mathbb{S}$ whose basis functions are the atomic positions $\mathbf{r}_i = R_i \mathbf{r}$, the (i, j) th element of the matrix $\Gamma^{\mathcal{P}}(R, \mathbf{r})$ is one if $R\mathbf{r}_j = \mathbf{r}_i$, or zero if $R\mathbf{r}_j \neq \mathbf{r}_i$. Consequently, the matrices of $\Gamma^{\mathcal{P}}(R, \mathbf{r})$ are defined as

$$\Gamma^{\mathcal{P}}(R, \mathbf{r})_{ij} = \begin{cases} 1 & \text{if } R_i^{-1} R R_j \in \mathbb{H}(\mathbf{r}), \\ 0 & \text{otherwise.} \end{cases} \quad (13.166)$$

It follows from (13.166) that the permutation $\text{Rep } \Gamma^{\mathcal{P}}(\mathbf{r})$ is just the ground Rep of $\mathbb{S}$ in $\mathbb{H}(\mathbf{r})$, or the Rep of $\mathbb{S}$ induced by the identity $\text{Irrep}^{(1)} \Sigma$ of the site subgroup $\mathbb{H}(\mathbf{r})$, namely,

$$\Gamma^{\mathcal{P}}(\mathbf{r}) = {}^{(1)} \Sigma \left(\mathbb{H}(\mathbf{r}) \right) \uparrow \mathbb{S}. \quad (13.167)$$

A program to generate the permutation Rep for a crystalline system

This program performs the following steps:

- (i) It converts all vectors and point-group matrices in terms of the lattice basis vectors (a-holohedry). This is very convenient when determining equivalent atomic positions. The resulting atomic-basis vectors are stored in **RATL**, and rotation a-matrices in **Rota**.
- (ii) The site-symmetry subgroups $\mathcal{G}_i$ are stored in **Atomsym**. The equivalent Wyckoff positions are identified with the aid of coset representatives of $\mathcal{G}_i$ in the crystallographic point-group $\mathcal{G}$.
- (iii) The site-permutation matrices are generated and stored in **PERMA**.

1. Express atomic position vectors in lattice-vector basis

```
RATC = RR;
RATL = {};
Do[B = Transpose[RATC[[i, j]]]·RL; AppendTo[RATL, B],
  {i, 1, NCEL}, {j, 1, NSP[[i]]}
]
Print["Atomic positions in Lattice Coordinates :
      ",MatrixForm[RATL]]
Do[
Rota[i] = Transpose[RL]·Rot[i]·G, {i, 1, g}
];
```

2. Determine the symmetry of atomic positions

```
Print["Atomic positions in Cartesian Coordinates
      and Their Symmetries : "];
Do[
  Atomsym = {}; PRT = 0;
  RRK = RATL[[ik, jk]]; LK = {}; Ltmp = {};
  Cosrep = {}; gr = 0;
  Switch[RRK == {0, 0, 0},
    True,
    gr = g; AppendTo[Atomsym, Range[g]]; PRT = 1;
    Print["(", ELMNT[[ik]], ", ", " ", jk,") Position at = ",
          RATC[[ik, jk]],", its group is the Full
          Point Group,"],
    False,
    Do[
      RK1 = RotG[Inv[[i]]]·(RRK + Tau[[i]]);
      RK1 = RK1 - RRK;
```

```

Switch[And[Mod[RK1[[1]],1] == 0,
          Mod[RK1[[2]],1] == 0,
          Mod[RK1[[3]],1] == 0,FreeQ[LK, i]],
      True, gr++; AppendTo[LK, i]
      ], {i, 1, g}
]; AppendTo[Atomsym, LK];
];
indeks = g/gr; Icoset = 1;
Acosrep = {1}; jj = 1; Lttmp = LK;

3. Generate coset Reps of site-symmetry subgroups

While[And[Icoset < indeks, jj < g], jj++;
      Switch[FreeQ[Lttmp, jj], True,
            Icoset++;AppendTo[Acosrep, jj];
            Do[cst = LK[[ij]];
              AppendTo[Lttmp,m[[1, jj, cst]]],
              {ij, 1, Length[LK]}
            ]
      ]
];
Switch[PRT == 0, True,
      Print["", ELMNT[[ik]], ", ", jk, "] Position at = ",
            RATC[[ik, jk]],", its group of Order ",
            gr, ", is ", LK, ", and its Coset Reps
            are ", Acosrep];
      Print["it has ", indeks, " equivalent
            Wyckoff positions."];
      ], {ik, 1, NCEL}, {jk, 1, NSP[[ik]]}
];

```

4. Generate site-permutations by rotations

```

NSP2 = {}; Do[AppendTo[NSP2,NSP[[ii]]2,{ii,1,NCEL}];
nrr = Apply[plus,NSP2];
PERMA = {Range[NAT]};NPER = {};tr = {};

```

```

Do[AppendTo[tr,{0,0,0}],{i,1,nrr}];
Do[
  NP = 0;
  Do[RP = RotG[Inv[[kk]]]·(RATL[[ik,jk]]+Tau[[kk]]);
    kx = 0; park = 0;
    While[And[kx < NSP[[ik]],park == 0],kx++;
      RDF = RP - RATL[[ik, kx]];
      Switch[And[Mod[RDF[[1]],1] == 0.,
        Mod[RDF[[2]],1] == 0.,
        Mod[RDF[[3]],1] == 0.],
        True,
        AppendTo[tr,RDF];
        Switch[Or[VectorNorm[RDF] == 0.,
          RDF[[1]]2 + RDF[[2]]2 +
          RDF[[3]]2 > 2],
          True,
          lx = NP + kx;
          AppendTo[NPER, lx]; park = 1
        ]
      ]
    ], {jk, 1, NSP[[ik]]}
  ]; NP += NSP[[ik]], {ik, 1, NCEL}
]; AppendTo[PERMA, NPER]; NPER = {}, {kk, 2, g}
];
Print[MatrixForm[Partition[PERMA, 8]]];

```

Reduction of $\Gamma^{\mathcal{P}}(\mathbf{r})$ with respect to Irreps of $\mathbb{S}$

When the symmetry of a system coincides with one of the point-groups, i.e. $\mathbb{G} \equiv \mathcal{G}$, as in the case of a molecule, the reduction in terms of the Irreps $^{(\mu)}\Gamma$ of $\mathcal{G}$ is straightforward

$$\Gamma^{\mathcal{P}}(\mathbf{r}) = \sum_{\mu} \langle \Gamma^{\mathcal{P}}(\mathbf{r}) | \mu \rangle^{(\mu)} \Gamma. \quad (13.168)$$

However, in the case of space-groups, i.e. $\mathbb{G} \equiv \mathbb{S}$, the reduction relation requires a bit of development.

We know that the Irreps of the space-group $\mathbb{S}$ are of the form $^{(*)\mathbf{k},\mu}\Gamma$; and that they are derived through induction from the allowable Irreps $^{(\mathbf{k},\mu)}\Omega$ of the group of the wavevector $\mathbb{S}_{\mathbf{k}}$, namely

$$^{(*)\mathbf{k},\mu}\Gamma = ^{(\mathbf{k},\mu)}\Omega \uparrow \mathbb{S}, \quad (13.169)$$

The subduction of $\Gamma^{\mathcal{P}}(\mathbf{r})$ onto the Irreps $^{(*)\mathbf{k},\mu}\Gamma$ then amounts to

$$\Gamma^{\mathcal{P}}(\mathbf{r}) = \sum_{*\mathbf{k},\mu}^{\oplus} \langle \Gamma^{\mathcal{P}}(\mathbf{r}) \mid *\mathbf{k},\mu \rangle ^{(*)\mathbf{k},\mu}\Gamma. \quad (13.170)$$

But $\Gamma^{\mathcal{P}}(\mathbf{r})$ itself is, in fact, an induced Rep defined by (13.167). We are thus faced with the need to determine how a Rep of $\mathbb{S}$, induced from one of its subgroups, $\mathbb{H}(\mathbf{r})$, can be expressed in terms of Irreps of $\mathbb{S}$, which themselves are induced from the allowable Irreps of $\mathbb{S}_{\mathbf{k}} \subset \mathbb{S}$. With the aid of (13.167) and (13.169), this can be expressed as

$$\begin{aligned} {}^{(1)}\Sigma \uparrow \mathbb{S} &= \sum_{*\mathbf{k},\mu}^{\oplus} \langle \Gamma^{\mathcal{P}}(\mathbf{r}) \mid *\mathbf{k},\mu \rangle ^{(\mathbf{k},\mu)}\Omega \uparrow \mathbb{S} \\ &= \sum_{*\mathbf{k},\mu}^{\oplus} \langle {}^{(1)}\Sigma \uparrow \mathbb{S} \mid ^{(\mathbf{k},\mu)}\Omega \uparrow \mathbb{S} \rangle ^{(\mathbf{k},\mu)}\Omega \uparrow \mathbb{S}, \end{aligned} \quad (13.171)$$

where ${}^{(1)}\Sigma \equiv {}^{(1)}\Sigma(\mathbb{H}(\mathbf{r}))$. $\langle {}^{(1)}\Sigma \uparrow \mathbb{S} \mid ^{(\mathbf{k},\mu)}\Omega \uparrow \mathbb{S} \rangle$ is called the intertwining number, denoted by $I[{}^{(1)}\Sigma \uparrow \mathbb{S} \mid ^{(\mathbf{k},\mu)}\Omega \uparrow \mathbb{S}]$. The determination of I requires the introduction of some new concepts and techniques which we have tried to avoid, so far. Since both $\mathbb{H}$ and $\mathbb{S}_{\mathbf{k}}$ are subgroups of $\mathbb{S}$, we expand $\mathbb{S}$ in terms of *double cosets* [12, 87], namely

$$\mathbb{S} = \sum_i \mathbb{H} S_i \mathbb{S}_{\mathbf{k}}, \quad (13.172)$$

where the $S_i = (R_i | v_i) \notin \mathbb{S}_{\mathbf{k}}$ and $\mathbb{H}$, is a *double coset representative*, and

$$S_i \mathbb{S}_{\mathbf{k}} S_i^{-1} = \mathbb{S}_{\mathbf{k}_i},$$

the subgroup of the wavevector $\mathbf{k}_i$, conjugate to $\mathbb{S}_{\mathbf{k}}$. The Irreps of $\mathbb{S}_{\mathbf{k}_i}$ are given by

$$^{(\mathbf{k}_i,\mu)}\Omega(S_i S \mathbb{S}_{\mathbf{k}} S_i^{-1}) = ^{(\mathbf{k},\mu)}\Omega(S). \quad (13.173)$$

Next, we define the subgroups

$$\mathbb{L}_i = \mathbb{H}(\mathbf{r}) \cap \mathbb{S}_{\mathbf{k}_i}. \quad (13.174)$$

These definitions, together with the intertwining number theorem [12, 87], allow us to express $I[{}^{(1)}\Sigma \uparrow \mathbb{S} \mid ^{(\mathbf{k},\mu)}\Omega \uparrow \mathbb{S}]$ as

$$\begin{aligned} I[{}^{(1)}\Sigma \uparrow \mathbb{S} \mid ^{(\mathbf{k},\mu)}\Omega \uparrow \mathbb{S}] &= \sum_i I[{}^{(1)}\Sigma \downarrow \mathbb{L}_i \mid ^{(\mathbf{k}_i,\mu)}\Omega \downarrow \mathbb{L}_i] \\ &= \sum_i I[{}^{(i,1)}\Lambda \mid ^{(\mathbf{k}_i,\mu)}\Omega \downarrow \mathbb{L}_i] \\ &= \sum_i \frac{1}{l_i} \sum_{L_i \in \mathbb{L}_i} ^{(\mathbf{k}_i,\mu)}\chi(L_i) \\ &= \sum_i \frac{1}{l_i} \sum_{L_i \in \mathbb{L}_i} ^{(\mathbf{k},\mu)}\chi(S_i^{-1} L_i S_i), \end{aligned} \quad (13.175)$$

where the summation is over all i in (13.172), and $^{(i,1)}\Lambda$ is the identity Irrep of $\mathbb{L}_i$. The second line of (13.175) is obtained because

$$^{(1)}\Sigma \downarrow \mathbb{L}_i = ^{(i,1)}\Lambda. \quad (13.176)$$

Reduction procedure

When we consider an element $(R|\boldsymbol{\tau} + \mathbf{t}) \in \mathbb{L}_i = H \cap \mathbb{S}_{\mathbf{k}_i}$, and write the double coset representative $S_i = (R_i|\boldsymbol{\tau}_i)$, we obtain the two conditions

$$\boldsymbol{\tau} + \mathbf{t} = \mathbf{r} - R\mathbf{r}, \quad (R|\boldsymbol{\tau} + \mathbf{t}) \in H(\mathbf{r}), \quad (13.177)$$

$$(R_i^{-1} R R_i) \mathbf{k} = \mathbf{k} + \mathbf{G}(R_i^{-1} R R_i), \quad (R|\boldsymbol{\tau} + \mathbf{t}) \in R_i \mathbb{S}_{\mathbf{k}} R_i^{-1}. \quad (13.178)$$

Two situations now arise:

- (i) **k inside the Brillouin zone** In this case, $\mathbf{G} = \mathbf{0}$, and the subduced Rep $^{(\mathbf{k},\mu)}\Omega(S_i^{-1} \mathbb{L}_i S_i)$ is written, according to (42), as

$$\begin{aligned} ^{(\mathbf{k},\mu)}\Omega(S_i^{-1} \mathbb{L}_i S_i) &= e^{i\mathbf{k} \cdot R_i^{-1}(\boldsymbol{\tau} + \mathbf{t} - \boldsymbol{\tau}_i + R\boldsymbol{\tau}_i)} ^{(\mu)}\Omega_{\mathbb{P}_{\mathbf{k}}} (R_i^{-1} R R_i) \\ &= ^{(\mu)}\Omega_{\mathbb{P}_{\mathbf{k}}} (R_i^{-1} R R_i), \end{aligned} \quad (13.179)$$

since, according to (13.177),

$$\boldsymbol{\tau} + \mathbf{t} = \boldsymbol{\tau}_i - R\boldsymbol{\tau}_i.$$

$^{(\mu)}\Omega_{\mathbb{P}_{\mathbf{k}}} (R_i^{-1} R R_i)$ is an Irrep of $\mathbb{P}_{\mathbf{k}}$, the point-group of the wavevector. Consequently, the procedure is confined to point-groups:

- (a) We expand the point-group $\mathbb{P}$ of $\mathbb{S}$ as

$$\mathbb{P} = \sum_i \mathbb{P}(\mathbf{r}) R_i \mathbb{P}_{\mathbf{k}}, \quad (13.180)$$

where $\mathbb{P}(\mathbf{r})$ is the point-group of $\mathbb{H}(\mathbf{r})$.

- (b) We then determine, for each double coset representative, the subgroup $R_i^{-1} \mathbb{P}(\mathbb{L}_i) R_i$ of $\mathbb{P}_{\mathbf{k}}$,

$$R_i^{-1} \mathbb{P}(\mathbb{L}_i) R_i = R_i^{-1} \mathbb{P}(\mathbf{r}) R_i \cap \mathbb{P}_{\mathbf{k}}. \quad (13.181)$$

- (c) Finally, we obtain

$$I = \sum_{R \in \mathbb{P}(\mathbb{L}_i)} \frac{1}{l_i} ^{(\mu)}\chi_{\mathbb{P}_{\mathbf{k}}} (R_i^{-1} R R_i). \quad (13.182)$$

A special situation arises when $\mathbf{k} = \mathbf{0}$, where the problem is simplified because $\mathbb{P}_0 = \mathbb{P} \supset \mathbb{P}(\mathbf{r})$, and procedure reduces to a subduction of the Irreps of $\mathbb{P}$ onto Irreps of its subgroup $\mathbb{P}(\mathbf{r})$.

Example 13.9

Intertwining number along the Λ -direction for the diamond structure

The diamond structure has the space-group $F_{\frac{41}{d}^3} \frac{2}{m} \sim \mathbb{O}_h^7$. We consider here the simple crystal associated with site $\mathbf{r} = \left(\frac{1}{8}, \frac{1}{8}, \frac{1}{8}\right)$, Wyckoff position (c).

The point-group symmetries are

$$\begin{aligned} \mathbb{P}_\Lambda &= \mathcal{C}_{3v}^{(xyz)} = (E|\mathbf{0}), 2(\mathcal{C}_3^{(xyz)}|\mathbf{0}), (\sigma_{\bar{x}y}|\mathbf{0}), (\sigma_{\bar{y}z}|\mathbf{0}), (\sigma_{\bar{z}x}|\mathbf{0}), \\ \mathbb{P}(\mathbf{r}) &= \mathcal{D}_{3d}^{(xyz)} = \mathcal{C}_{3v}^{(xyz)} \otimes ((E|\mathbf{0}), (I|\boldsymbol{\tau})) \\ &= \mathcal{C}_{3v}^{(xyz)} \oplus (I|\boldsymbol{\tau}), 2(S_6|\boldsymbol{\tau}), (C_{2\bar{x}y}|\boldsymbol{\tau}), (C_{2\bar{y}z}|\boldsymbol{\tau}), (C_{2\bar{z}x}|\boldsymbol{\tau}), \end{aligned}$$

where $S_6 = IC_3$, $XYZ \rightarrow \bar{Z}\bar{X}\bar{Y}$, and $\boldsymbol{\tau} = (1/4, 1/4, 1/4)$.

Notice that $\mathbb{P}_\Lambda \subset \mathbb{P}(\mathbf{r})$. These point subgroups give the following double coset expansion for $\mathcal{O}_h$

$$\mathcal{O}_h = \mathcal{D}_{3d}^{(xyz)} E \mathcal{C}_{3v}^{(xyz)} + \mathcal{D}_{3d}^{(xyz)} C_{2y} \mathcal{C}_{3v}^{(xyz)}.$$

The conjugate subgroups of $\mathbb{P}_\Lambda$ are:

$$\mathcal{C}_{3v}^{(xyz)}, \quad \text{and} \quad C_{2y} \mathcal{C}_{3v}^{(xyz)} C_{2y} = \mathcal{C}_{3v}^{(x\bar{y}\bar{z})},$$

which yield

$$\begin{aligned} \mathbb{L}_1 &= \mathcal{C}_{3v}^{(xyz)}, \\ \mathbb{L}_2 &= \mathcal{D}_{3d}^{(xyz)} \cap \mathcal{C}_{3v}^{(x\bar{y}\bar{z})} = \mathcal{C}_2^{(x\bar{z})} \end{aligned}$$

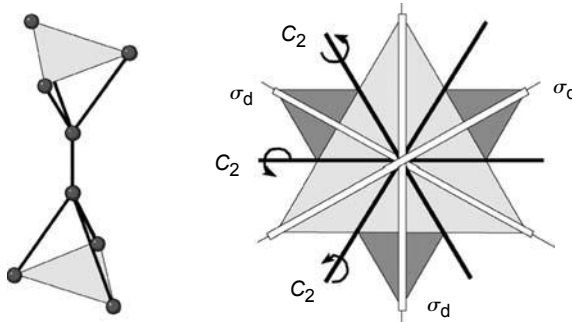


Fig. 13.6. (Left) Staggered configuration of the diamond structure with $\mathcal{D}_{3d}$ symmetry, (right) projection showing the C_2 and σ_d operations.

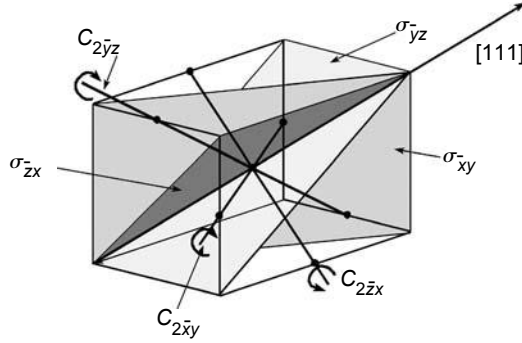


Fig. 13.7. Symmetry operations relative to the cubic unit cell.

and

$$R_1^{-1} \mathbb{P}(\mathbb{L}_1) R_1 = \mathcal{C}_{3v}^{(xyz)},$$

$$R_2^{-1} \mathbb{P}(\mathbb{L}_2) R_2 = \mathcal{C}_2^{(xz)}.$$

We then find that the only surviving intertwining numbers are

$$I\left({}^{(1)}\Lambda(\mathcal{C}_{3v}) \middle| {}^{(\Lambda,1)}\Omega(\mathcal{C}_{3v}) \downarrow \mathcal{C}_{3v}\right) = 1,$$

$$I\left({}^{(1)}\Lambda(\mathcal{C}_2) \middle| {}^{(\Lambda,1)}\Omega(\mathcal{C}_{3v}) \downarrow \mathcal{C}_2\right) = 1,$$

$$I\left({}^{(1)}\Lambda(\mathcal{C}_2) \middle| {}^{(\Lambda,3)}\Omega(\mathcal{C}_{3v}) \downarrow \mathcal{C}_2\right) = 1.$$

and finally obtain

$$\left\langle \Gamma^{\mathcal{P}} \left(\frac{1}{8}, \frac{1}{8}, \frac{1}{8} \right) \middle| * \Lambda, 1 \right\rangle = 2,$$

$$\left\langle \Gamma^{\mathcal{P}} \left(\frac{1}{8}, \frac{1}{8}, \frac{1}{8} \right) \middle| * \Lambda, 2 \right\rangle = 0,$$

$$\left\langle \Gamma^{\mathcal{P}} \left(\frac{1}{8}, \frac{1}{8}, \frac{1}{8} \right) \middle| * \Lambda, 3 \right\rangle = 1.$$

- (ii) **k on the Brillouin zone boundary** When **k** falls on the BZ boundary, the expression of $\text{Irrep}^{(\mathbf{k},\mu)} \Omega(S_i^{-1} L_i S_i)$ has to be modified to

$${}^{(\mathbf{k},\mu)} \Omega(S_i^{-1} L_i S_i) = e^{i\mathbf{k} \cdot \mathbf{t}(R_i^{-1} R R_i)} {}^{(\mu)} \widehat{\Omega}_{\mathbb{P}_{\mathbf{k}}} \left(R_i^{-1} R R_i \right). \quad (13.183)$$

where ${}^{(\mu)} \widehat{\Omega}_{\mathbb{P}_{\mathbf{k}}} \left(R_i^{-1} R R_i \right)$ is a multiplier Irrep of $\mathbb{P}_{\mathbf{k}}$, and $\mathbf{t}(R_i^{-1} R R_i)$ is defined, according to (34), as

$$S_i^{-1} L_i S_i = (E \mid \mathbf{t}(R_i^{-1} R R_i)) \left(R_i^{-1} R R_i \mid \boldsymbol{\tau}(R_i^{-1} R R_i) \right). \quad (13.184)$$

The procedure described in (i) is slightly modified here.

- Step (a) is identical here to that of (i).
- Step (b) of (i) is augmented by the additional computation of $\mathbf{t}(\mathcal{R})$, $\boldsymbol{\tau}(\mathcal{R})$ and $\mathbf{G}(\mathcal{R})$, where $\mathcal{R} = R_i^{-1} R R_i$, with the aid of (13.177) and (13.184).
- In step (c) of (i), we use (13.182) instead of (13.183), and obtain

$$I = \sum_{\substack{i \\ R \in \mathbb{L}_i}} \frac{1}{l_i} e^{i\mathbf{k} \cdot \mathbf{t}(\mathcal{R})} e^{i\mathbf{G}(\mathcal{R}) \cdot \boldsymbol{\tau}(\mathcal{R})} \chi_{\mathbb{P}_{\mathbf{k}}}(\mathcal{R}). \quad (13.185)$$

Example 13.10

Intertwining number at the K -point for $\mathbb{O}_h^7$

The K -point has $\mathbf{k} = (\frac{3\pi}{2a}, \frac{3\pi}{2a}, 0)$, and the corresponding subgroups are

$$\begin{aligned} \mathbb{P}_K &= \mathbb{C}_{2v}^{(xy, \bar{x}y, z)} = (E|\mathbf{0}), (C_2^{(xy)}|\mathbf{0}), (\sigma_z|\boldsymbol{\tau}), (\sigma_{\bar{x}y}|\mathbf{0}), \\ \mathbb{P}(\mathbf{r}) &= \mathbb{D}_{3d}^{(xyz)} = \mathbb{C}_{3v}^{(xyz)} \otimes \mathcal{C}_i \\ &= (E|\mathbf{0}), 2(C_3^{(xyz)}|\mathbf{0}), 3(C_2|\boldsymbol{\tau}), (I|\boldsymbol{\tau}), 2(S_6|\boldsymbol{\tau}), 3(\sigma_d|\mathbf{0}). \end{aligned}$$

The double coset expansion is then given by

$$\mathbb{O}_h = \mathbb{D}_{3d}^{(xyz)} E \mathbb{C}_{2v}^{(xy, \bar{x}y, z)} + \mathbb{D}_{3d}^{(xyz)} C_{2x} \mathbb{C}_{2v}^{(xy, \bar{x}y, z)},$$

with double coset representatives $(E|\mathbf{0})$, $(C_{2x}|\mathbf{0})$. The conjugate subgroups of $\mathbb{P}_K$ and the corresponding $\mathbb{L}_i$ s are

$$\begin{aligned} E \mathbb{C}_{2v}^{(xy, \bar{x}y, z)} E &= \mathbb{C}_{2v}^{(xy, \bar{x}y, z)} \Rightarrow \mathbb{L}_1 = \mathbb{C}_s^{(\bar{x}y)}, \\ C_{2x} \mathbb{C}_{2v}^{(xy, \bar{x}y, z)} C_{2x} &= \mathbb{C}_{2v}^{(x\bar{y}, xy, z)} \Rightarrow \mathbb{L}_2 = \mathbb{C}_2^{(\bar{x}y)}, \end{aligned}$$

which yields for $\mathcal{R}$ and $\mathbf{t}(\mathcal{R})$

$$\begin{aligned} R_1^{-1} \mathbb{L}_1 R_1 &= \mathbb{C}_s^{(\bar{x}y)} \rightarrow (E|\mathbf{t} = \mathbf{0}), \quad \sigma_{\bar{x}y}|\mathbf{t} = \mathbf{0}, \\ R_2^{-1} \mathbb{L}_2 R_2 &= \mathbb{C}_2^{(xy)} \rightarrow (E|\mathbf{t} = \mathbf{0}), \quad C_2^{(xy)}|\mathbf{t} = 0, -\frac{1}{2}, -\frac{1}{2}. \end{aligned}$$

Using Table 13.12 for the multiplier Irrep of K , we find that the only surviving intertwining numbers are

$$\begin{aligned} I\left({}^{(1)}\Lambda(\mathbb{C}_s^{(\bar{x}y)}) \middle| {}^{(K,1)}\Omega(\mathbb{C}_{2v}) \downarrow \mathbb{C}_s^{(\bar{x}y)} \right) &= 1, \\ I\left({}^{(1)}\Lambda(\mathbb{C}_2) \middle| {}^{(K,1)}\Omega(\mathbb{C}_{2v}) \downarrow \mathbb{C}_2 \right) &= 1, \\ I\left({}^{(1)}\Lambda(\mathbb{C}_2) \middle| {}^{(K,3)}\Omega(\mathbb{C}_{2v}) \downarrow \mathbb{C}_2 \right) &= 1, \\ I\left({}^{(1)}\Lambda(\mathbb{C}_2) \middle| {}^{(K,4)}\Omega(\mathbb{C}_{2v}) \downarrow \mathbb{C}_2 \right) &= 1. \end{aligned}$$

Table 13.12. *Multiplier Irreps for K-point* ($\alpha = \exp[i3\pi/4]$).

	E	$\sigma_{\bar{x}y}$	σ_z	C_2
$^{(K,1)}\Omega$	1	1	α	α
$^{(K,2)}\Omega$	1	-1	$-\alpha$	α
$^{(K,3)}\Omega$	1	1	$-\alpha$	$-\alpha$
$^{(K,4)}\Omega$	1	-1	α	$-\alpha$

As an example, we present the computation

$$\begin{aligned}
 I\left(^{(1)}\Lambda(\mathbb{C}_2) \middle| ^{(K,1)}\Omega(\mathbb{C}_{2v}) \downarrow \mathbb{C}_2\right) &= \frac{1}{2} \left[e^{i\left(\frac{3\pi}{2}, \frac{3\pi}{2}, 0\right) \cdot \mathbf{t}(E)} {}^{(\mu)}\widehat{\chi}_{\mathbb{P}_K}(E) \right. \\
 &\quad \left. + e^{i\left(\frac{3\pi}{2}, \frac{3\pi}{2}, 0\right) \cdot \mathbf{t}(C_2)} {}^{(\mu)}\widehat{\chi}_{\mathbb{P}_K}(C_2) \right] \\
 &= \frac{1}{2} \left[1 \times 1 + \exp\left[-i\frac{3\pi}{4}\right] \times \exp\left[-i\frac{3\pi}{4}\right] \right] \\
 &= 1,
 \end{aligned}$$

and finally obtain

$$\begin{aligned}
 \left\langle \Gamma^{\mathcal{P}}\left(\frac{1}{8}, \frac{1}{8}, \frac{1}{8}\right) \middle| *K, 1 \right\rangle &= 2, \\
 \left\langle \Gamma^{\mathcal{P}}\left(\frac{1}{8}, \frac{1}{8}, \frac{1}{8}\right) \middle| *K, 2 \right\rangle &= 0, \\
 \left\langle \Gamma^{\mathcal{P}}\left(\frac{1}{8}, \frac{1}{8}, \frac{1}{8}\right) \middle| *K, 3 \right\rangle &= 1, \\
 \left\langle \Gamma^{\mathcal{P}}\left(\frac{1}{8}, \frac{1}{8}, \frac{1}{8}\right) \middle| *K, 4 \right\rangle &= 1.
 \end{aligned}$$

Reduction of the tensor field Rep

Having obtained the reduction of $\Gamma^{\mathcal{P}}(\mathbf{r})$, we substitute back in (13.157) to obtain

$$\mathfrak{F}^{\text{TF}}(\mathbf{r}) = \Gamma^{\mathcal{P}}(\mathbf{r}) \otimes \Gamma^{\mathcal{T}} \quad (13.186)$$

$$= \sum_{*\mathbf{k}, \mu}^{\oplus} \langle \Gamma^{\mathcal{P}}(\mathbf{r}) \mid *\mathbf{k}, \mu \rangle [{}^{(*\mathbf{k}, \mu)}\Gamma \otimes \Gamma^{\mathcal{T}}]. \quad (13.187)$$

We must now reduce the direct outer-product

$$[{}^{(*\mathbf{k}, \mu)}\Gamma \otimes \Gamma^{\mathcal{T}}] = \sum_{(*\mathbf{k}', \nu)} \langle {}^{(*\mathbf{k}, \mu)}\Gamma \otimes \Gamma^{\mathcal{T}} \mid *\mathbf{k}', \nu \rangle {}^{(*\mathbf{k}', \nu)}\Gamma \quad (13.188)$$

and obtain

$$\begin{aligned} \mathfrak{F}^{\text{TF}}(\mathbf{r}) &= \sum_{*\mathbf{k}, \mu}^{\oplus} \langle \Gamma^{\text{TF}}(\mathbf{r}) \mid *\mathbf{k}, \mu \rangle (*\mathbf{k}', \nu) \Gamma, \\ \langle \Gamma^{\text{TF}}(\mathbf{r}) \mid *\mathbf{k}, \mu \rangle &= \sum_{(\mathbf{k}', \nu)} \langle \Gamma^{\mathcal{P}}(\mathbf{r}) \mid *\mathbf{k}', \nu \rangle \\ &\quad \times \langle (*\mathbf{k}', \nu) \Gamma \otimes \Gamma^{\mathcal{T}} \mid *\mathbf{k}, \mu \rangle. \end{aligned} \quad (13.189)$$

For tensor fields belonging to $\mathbf{k} = \mathbf{0}$, i.e. $\Gamma^{\mathcal{T}} = {}^{(0, \sigma)}\Gamma$, we have

$$\begin{aligned} \langle \Gamma^{\text{TF}}(\mathbf{r}) \mid *\mathbf{k}, \mu \rangle &= \sum_{\nu} \langle \Gamma^{\mathcal{P}}(\mathbf{r}) \mid *\mathbf{k}, \nu \rangle \\ &\quad \times \langle (*\mathbf{k}, \nu) \Gamma \otimes {}^{(0, \sigma)}\Gamma \mid *\mathbf{k}, \mu \rangle. \end{aligned} \quad (13.190)$$

Such cases are found in problems concerning lattice vibrations (${}^{(0, \sigma)}\Gamma = \Gamma^{\nu}$), lattice spin excitations (${}^{(0, \sigma)}\Gamma = \Gamma^{\text{a}}$), etc.

We described above the method for calculating the intertwining number $I({}^{(1)}\Sigma \uparrow \mathbb{S} \mid {}^{(\mathbf{k}, \mu)}\Omega \uparrow \mathbb{S}) = \langle \Gamma^{\mathcal{P}}(\mathbf{r}) \mid *\mathbf{k}, \nu \rangle$, it then remains here to compute the intertwining number $I(*\mathbf{k}, \nu \otimes (\mathbf{0}, \sigma) \mid *\mathbf{k}, \mu)$, which can be written as

$$I(*\mathbf{k}, \nu \otimes (\mathbf{0}, \sigma) \mid *\mathbf{k}, \mu) = I({}^{(\mathbf{k}, \nu)}\Omega \otimes {}^{(0, \sigma)}\Gamma \downarrow \mathbb{P}_{\mathbf{k}} \mid {}^{(\mathbf{k}, \mu)}\Omega). \quad (13.191)$$

Example 13.11

Intertwining number for the Λ -point of $\mathbb{O}_h^7$ and for $\Gamma^{\mathcal{T}} = \Gamma^{\nu}$

The group of the Λ -wavevector, $\mathbb{C}_{3v}$, has the three Irreps:

	E	$2C_3$	3σ
${}^{(1)}\Lambda$	1	1	1
${}^{(2)}\Lambda$	1	1	-1
${}^{(3)}\Lambda$	2	-1	0
Γ^{ν}	3	0	1

$$I({}^{(1)}\Lambda \otimes \Gamma^{\nu} \downarrow \mathbb{P}_{\mathbf{k}} \mid {}^{(1)}\Lambda) = \frac{1}{6} [1 \times 3 + 2 \times 1 \times 0 + 3 \times 1 \times 1] = 1,$$

$$I({}^{(1)}\Lambda \otimes \Gamma^{\nu} \downarrow \mathbb{P}_{\mathbf{k}} \mid {}^{(2)}\Lambda) = 0, \quad I({}^{(1)}\Lambda \otimes \Gamma^{\nu} \downarrow \mathbb{P}_{\mathbf{k}} \mid {}^{(3)}\Lambda) = 1,$$

$$I({}^{(2)}\Lambda \otimes \Gamma^{\nu} \downarrow \mathbb{P}_{\mathbf{k}} \mid {}^{(1)}\Lambda) = 0, \quad I({}^{(2)}\Lambda \otimes \Gamma^{\nu} \downarrow \mathbb{P}_{\mathbf{k}} \mid {}^{(2)}\Lambda) = 1,$$

$$\begin{aligned}
I\left({}^{(2)}\Lambda \otimes \Gamma^v \downarrow \mathbb{P}_{\mathbf{k}} \middle| {}^{(3)}\Lambda\right) &= 1, & I\left({}^{(3)}\Lambda \otimes \Gamma^v \downarrow \mathbb{P}_{\mathbf{k}} \middle| {}^{(1)}\Lambda\right) &= 1, \\
I\left({}^{(3)}\Lambda \otimes \Gamma^v \downarrow \mathbb{P}_{\mathbf{k}} \middle| {}^{(2)}\Lambda\right) &= 1, & I\left({}^{(3)}\Lambda \otimes \Gamma^v \downarrow \mathbb{P}_{\mathbf{k}} \middle| {}^{(3)}\Lambda\right) &= 2.
\end{aligned}$$

Finally, we use (13.190) and the results of Example 13.9 to obtain

$$\begin{aligned}
\left\langle \Gamma^{\text{TF}} \left(\frac{1}{8}, \frac{1}{8}, \frac{1}{8} \right) \middle| * \Lambda, 1 \right\rangle &= 2 \times 1 + 0 \times 0 + 1 \times 1 = 3, \\
\left\langle \Gamma^{\text{TF}} \left(\frac{1}{8}, \frac{1}{8}, \frac{1}{8} \right) \middle| * \Lambda, 2 \right\rangle &= 2 \times 0 + 0 \times 1 + 1 \times 1 = 1, \\
\left\langle \Gamma^{\text{TF}} \left(\frac{1}{8}, \frac{1}{8}, \frac{1}{8} \right) \middle| * \Lambda, 3 \right\rangle &= 2 \times 1 + 0 \times 1 + 1 \times 2 = 4.
\end{aligned}$$

Exercises

- 13.1 Consider the case where the symmetry point-group of a system possesses two conjugate inequivalent Irreps ${}^1E$ and ${}^2E$. A basis for such a pair is usually given in the form $x_1 \pm ix_2$. Now, suppose that the system exhibits a phenomenon where two of its physical properties, (x_1, x_2) and (y_1, y_2) , form two bases for such a pair of Irreps, namely, $x_1 \pm ix_2$ and $y_1 \pm iy_2$, which in turn are related by tensors

$$y_1 + iy_2 = \mathfrak{T}(x_1 + ix_2), \quad y_1 - iy_2 = \mathfrak{T}^*(x_1 - ix_2).$$

- (i) Determine the tensor that relates the physical vectors $\mathbf{X} = [x_1, x_2]$ and $\mathbf{Y} = [y_1, y_2]$.
 - (ii) What happens when that tensor is intrinsically symmetric?
- 13.2 Consider the wurtzite structure with $6mm$ ($\mathcal{C}_{6v}$) point-group symmetry. Determine the number of independent parameters in:
- (i) the polarization tensor,
 - (ii) the piezoelectric tensor,
 - (iii) the Hall tensor,
 - (iv) the elasticity tensor.
- 13.3 Determine the nonvanishing components of the piezoelectric tensor for a crystal with point-group symmetry 2 ($\mathcal{C}_2$). How would you extrapolate your results to crystals with $\mathbb{P} = 222$ ($\mathcal{D}_2$)?
- 13.4 Quartz crystals are commonly used as piezoelectric transducers. Quartz has $\mathbb{P} = 32$ ($\mathcal{D}_3$).

- (i) Follow the procedure of Example 13.7 to show that its piezoelectric tensor has the form

$$\begin{bmatrix} p_{11} & -p_{11} & 0 & p_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -p_{14} & -2p_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}.$$

- (ii) Determine the electric field orientation that can produce expansion/contraction along the x_1 -axis.

14

Electronic properties of solids

14.1 Introduction

Information regarding the electronic structure of a condensed matter system provides the basis for understanding the myriad of its physical properties: optical, mechanical, magnetic, electrical, etc. There are two main hurdles, however, that seriously hamper any attempt to derive the electronic states of condensed matter systems: The first arises from the gigantic difference in the time scales associated with the motions of electrons and nuclei, or ions, which can be in the order of 10^3 – 10^5 . The second difficulty concerns the numbers of particles involved, which are at least of the order of Avogadro's number of $\sim 10^{24}$. In order to overcome the first hurdle, we invoke the adiabatic, or Born–Oppenheimer, approximation, which we will discuss in the following chapter. The only impact of this approximation here is that we treat the ions classically and fix all the ionic positions, $\{\mathbf{R}\}$; we introduce their interactions with the electron system as an external potential, $V(\mathbf{r}, \{\mathbf{R}\})$. For simplicity, we drop $\{\mathbf{R}\}$ from the notation in the remainder of the chapter.

14.2 The one-electron approximations and self-consistent-field theories

Similar presentations to the content of this section can be found in references [88, 89, 90].

14.2.1 The many-body problem

Our objective here is to determine the ground-state properties of an interacting many-electron system subject to an external potential $V(\mathbf{r})$, representing the interaction with the frozen ions. The many-electron wavefunction satisfies the Schrödinger equation:

$$\left[\sum_i \mathcal{H}_i + \frac{1}{2} \sum \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - E \right] \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = 0, \quad (14.1)$$

where

$$\mathcal{H}_i = -\frac{\hbar^2}{2m} \nabla_i^2 + V(\mathbf{r}_i) = T_i + V(\mathbf{r}_i).$$

We have omitted terms involving electron spin, such as spin-orbit coupling, and other

relativistic effects, as well as external magnetic fields, etc. Dirac is reported to have said that the Schrödinger equation (14.1) had, with one blow, taken care of all chemistry and, by implication, of the electronic structure of solids. In a formal sense this is, of course, true. Yet, due to the Coulomb repulsion between the electrons, this Hamiltonian is obviously not the sum of single-electron Hamiltonians $\mathcal{H}_i$. In principle this means that the total wavefunction depends on the positions of all the electrons, the coordinates of which are all correlated, so that an exact solution of (14.1) for a solid with $\sim 10^{24}$ variables is, practically speaking, meaningless since there is no way of recording the wavefunction. Fortunately, we are mainly interested in practical aspects, where we deal with physical quantities that involve a highly diminished number of variables, such as the one- and two-particle density matrices from which we can obtain, for example, the energy E , the particle density $n(r)$, particle-particle correlation functions, etc.

For most cases, therefore, the *one-electron approximation* is commonly used. In this approximation, the electron-electron interaction experienced by a particular electron at r_i is replaced by an averaged interaction with all other electrons, giving rise to some potential $V_e(r_i)$.

Validity of the one-particle approximation to the many-body problem

Three factors mainly determine the applicability of the one-particle approximation to a given many-body system:

- (i) The *range* of the interparticle interaction potential.
- (ii) The particle *density*.
- (iii) The degree of *localization* of the constituent particles.

The effect of the first factor may be demonstrated by considering the extreme case of a hard-wall-type interparticle interaction potential. It is obvious that in this case we cannot obtain an averaged effective potential that can account for the interaction of a test particle with the rest of the system, of similar particles, and thus allow us to compute an approximate trajectory, or a wavefunction, of the test particle that can describe its motion in the presence of the system's other particles. This severe restriction may be relaxed when the range of the potential becomes relatively long. An operational definition of a long-range potential, $v(\mathbf{r})$, is usually expressed in terms of the divergence of a particle's potential energy when the system's size tends to infinity, i.e., when we consider an infinite homogeneous system surrounding our test particle which is placed at the origin of our coordinate system. The total potential energy of our test particle is then

$$\begin{aligned} E_V &= \int d\mathbf{r} \, v(\mathbf{r}) n(\mathbf{r}) \\ &= 4\pi n \int v(r) r^2 dr, \end{aligned} \tag{14.2}$$

where we used the homogeneity of the system to set $n(\mathbf{r}) = n$; this integral diverges when $v(r) \propto (1/r^m)$ with $m \leq 2$. Consequently, interaction potentials satisfying the last condition are considered long-range.

The effect of the second factor is rather obvious, since if a system comprises, say, three particles, the interaction energy of our test particle will, no doubt, depend on the specific configuration of the three particles, and an averaged potential will introduce serious errors in the corresponding energies, trajectories, and wavefunctions.

The effect of localization can be illustrated by considering a system comprising a large number of particles, yet divided into a large number of spatial cells, each accommodating a small number of particles. Assuming the first two factors are satisfied, we find that we still have to consider the dwell-time of a given particle (our test particle in the present case) in each cell. Now, if the particle is completely delocalized, i.e. it is a free particle with almost zero dwell-time, our test particle will only feel a potential averaged over a large number of cells and, consequently, a one-particle effective potential can be, quite justifiably, constructed. However, if our test particle has an appreciable dwell-time in each cell, then its motion will be strongly correlated with the motions of the particles in the cell where it is temporarily located. In this case a simple one-particle averaged potential is inadequate.

Historically two physically different approaches to the one-electron approximation have been used to arrive at approximate solutions to (14.1), the Hartree–Fock and the density functional formalisms.

14.2.2 The Hartree–Fock approach

The Hartree model

If it were possible to write the Hamiltonian of a system of interacting electrons as a sum of single-particle Hamiltonians, it would be possible to write the many-electron wavefunction as a product of single-particle wavefunctions:

$$\Psi(r_1, r_2, \dots, r_N) = \prod_{i=1}^N \psi_i(r_i). \quad (14.3)$$

But, since the Hamiltonian (14.1) is not just a sum of single-particle Hamiltonians, the true wavefunctions cannot be written in the product form of (14.3), which, furthermore, does not have the *antisymmetry* property required for fermions.

We may argue, however, that in the case of interacting electrons, the long-range nature of the Coulomb potential and the high particle density mitigate omission of certain correlations that might be present, since these correlation effects are less serious when our test particle feels the effective sum of all the pair interactions with the particles of the system. The effective potential in this case does not exhibit significant abrupt changes similar to those which occur in the case of the short-range potentials. Consequently, in such cases the omission of correlations present in, for example, the two-particle and three-particle wavefunctions may lead to tolerable errors. It is then possible to construct our wavefunctions as products of single-particle wavefunctions.

Thus, in the case of a system of electrons, we may use the approximate form (14.3) for the wavefunction, within a variational principle framework:

$$E \leq E' \equiv \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}, \quad (14.4)$$

which for any state $|\Psi\rangle$ gives an upper bound E' for the exact ground-state energy E . This approximation of neglecting correlation effects present in the exact wavefunctions of two or more electrons is invoked in both the *Hartree* model, and in the *Hartree–Fock* model discussed below.

The normalization of the wavefunctions ψ_i is introduced as Lagrange multipliers ϵ_i . One then has to minimize the expression

$$\langle \psi_1(r_1) \dots \psi_N(r_N) | H | \psi_N(r_N) \dots \psi_1(r_1) \rangle - \sum_i \epsilon_i \langle \psi_i | \psi_i \rangle, \quad (14.5)$$

with respect to variations in the functions ψ_j . This approach is known as the *Hartree approximation* to the ground-state energy. It produces a system of coupled, nonlinear Hartree equations for the single-particle wavefunctions with the corresponding Hartree single-particle energies ϵ_i^H :

$$\left[T + v_H^i(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i^H \psi_i(\mathbf{r}), \quad (14.6)$$

where the effective, or Hartree, potential $v_H(\mathbf{r})$ is the mean-field function

$$\begin{aligned} v_H^i(\mathbf{r}) &= V(\mathbf{r}) + \int d\mathbf{r}' \frac{e^2 n_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ &= V(\mathbf{r}) + \mathcal{K}(\mathbf{r}), \end{aligned} \quad (14.7)$$

with

$$n_i(\mathbf{r}') = \sum_j \psi_j^*(\mathbf{r}') \psi_j(\mathbf{r}'),$$

where the prime indicates that the term $\psi_i^* \psi_i$ should be omitted in the summation. This obviously presents a mean-field theory: each electron is regarded as moving in the external potential plus the mean potential of all the electrons.

This set of equations is solved by iteration. For a system of N electrons, one solves the single-particle Schrödinger equation,

$$\left\{ -\frac{1}{2} \nabla^2 + v_H^i(r) \right\} \psi_i = \epsilon_i^H \psi_i, \quad (14.8)$$

for the N lowest eigenfunctions and then $n(\mathbf{r})$ is determined from the expression

$$n(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2. \quad (14.9)$$

The Hartree approximation for the total energy then gives:

$$E_H = \sum_i \langle \psi_i | T + v(\mathbf{r}) | \psi_i \rangle + \frac{1}{2} \sum_{i \neq j} \left\langle \psi_i \psi_j \left| \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \right| \psi_j \psi_i \right\rangle, \quad (14.10)$$

Equations (14.7)–(14.10) together constitute the *self-consistent Hartree equations*.

The Hartree approach can be dramatically improved by the inclusion of exchange effects which lead to the so-called Hartree–Fock equations.

The physical origin of the exchange energy The exchange energy has its origin in the antisymmetrization of the fermionic wavefunction, and, for electrons, it is derived from no other than the repulsive Coulomb potential. To understand this effect, let us first establish the symmetry of quantum mechanical wavefunctions of systems of identical particles. The term identical particles implies that the total energy of the system, and hence its associated Hamiltonian, remain invariant when two particles are exchanged. The process of the two-particle exchange is effected within the framework of quantum mechanics through a permutation, or a transposition, operator $\hat{P}$. *The invariance of the system's Hamiltonian* with respect to the operation of particle exchange means that $\hat{P}$ commutes with the Hamiltonian $\mathcal{H}$ since

$$\begin{aligned}\hat{P}\mathcal{H}\Psi &= \hat{P}\mathcal{H}\hat{P}^{-1}\hat{P}\Psi \\ &= \mathcal{H}\hat{P}\Psi = E\hat{P}\Psi,\end{aligned}\tag{14.11}$$

where

$$\mathcal{H}\Psi = E\Psi,\tag{14.12}$$

thus both operators share the same eigenfunctions. For the sake of simplicity, let us consider a two-particle system. The eigenfunctions of $\hat{P}$ satisfy the equation

$$\hat{P}\Psi(r_1, r_2) = \Psi'(r_2, r_1) = p\Psi(r_1, r_2),\tag{14.13}$$

where p is the corresponding eigenvalue. Repeating the permutation operation will take us back to the original wavefunction

$$\begin{aligned}\hat{P}^2\Psi(r_1, r_2) &= \hat{P}\Psi'(r_1, r_2) \\ &= p^2\Psi(r_1, r_2) = \Psi(r_1, r_2),\end{aligned}\tag{14.14}$$

which leads to two possible values for p , namely, $p = \pm 1$. Consequently, we have two types of classes of many-body wavefunctions under the operation of two-particle exchange, symmetric bosons with $p = 1$, and antisymmetric fermions with $p = -1$.

Now, let us consider the implication of antisymmetry of fermionic wavefunctions by considering the simple case of two spinless noninteracting particles. The condition of antisymmetry requires that

$$\Psi(r_2, r_1) = -\Psi(r_1, r_2).$$

It is quite illuminating, then, to describe this wavefunction in terms of the relative coordinate $\Delta r = r_2 - r_1$, in particular in the vicinity of $\Delta r = 0$, i.e. when the two particles occupy the same point in space, i.e. $r_1 = r_2 = r$.

The antisymmetry requirement leads to

$$\Psi(r, r) = -\Psi(r, r) \quad \Rightarrow \quad \Psi(r, r) = 0.$$

Moreover, the requirement that a quantum mechanical wavefunction should have a continuous magnitude and a continuous derivative will force a gradual, rather than an abrupt, or discontinuous, change in the magnitude of the wavefunction in the vicinity of $\Delta r = 0$ where it is required to vanish due to the antisymmetry. This may be regarded as an effective “hole” in the wavefunction in the vicinity of $\Delta r = 0$, which corresponds to a mutual

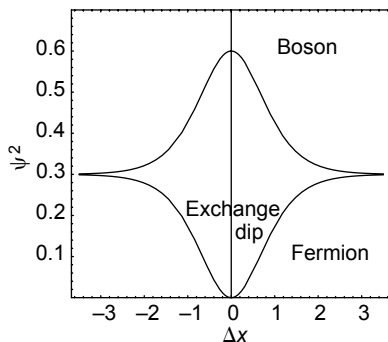


Fig. 14.1. A schematic of $\Psi^2(\Delta x)$ for a pair of fermions and a pair of bosons.

avoidance between the two particles *even when they are noninteracting*. This behavior is obviously absent in the classical analogue. When a repulsive Coulomb interaction between the two fermionic particles (electrons for example) is turned on, the mutual avoidance due to the *exchange hole* in the two-particle wavefunction will lead to a reduction of the Coulomb energy in the fermionic case relative to the classical case, which in turn has a lower energy than the bosonic symmetrized wavefunction. This reduction due to the antisymmetrization of the total wavefunction is referred to as the *exchange energy*.

Notice that in the case of a mutually attractive interaction potential, exemplified by the pairing mechanism in superconductivity, a symmetrized bosonic wavefunction will have a lower energy than both the classical case and the fermionic wavefunction. In Figure 14.1 we present a schematic of antisymmetrized fermion and symmetrized boson wavefunctions displaying exchange hole (fermion) and mound (boson).

Next let us consider the case of two electrons with spin. The total wavefunction is expressed as

$$\Psi(\mathbf{1}, \mathbf{2}) = \Phi(r_1, r_2) \chi(\sigma_1, \sigma_2), \quad (14.15)$$

where σ_i is the spin degree of freedom of electron i and χ is the total spin wavefunction. Now, the overall antisymmetry of the wavefunction Ψ is satisfied by the two combinations $\Phi_s \chi_a$, singlet spin state, or $\Phi_a \chi_s$, triplet spin state. Considerations of the spatial wavefunction in the previous example immediately indicate that in the absence of any other external interactions the triplet state, with antisymmetrized spatial wavefunction, will have lower energy than the singlet state. The difference in energy between the two configurations is still identified as due to *exchange effects*.

The Hartree–Fock model

In the Hartree model, discussed above, the trial many-electron wavefunction did not satisfy the required fermionic antisymmetry. Therefore, it seems logical to apply the Wigner antisymmetrizing projection operator

$$\mathfrak{A} = \frac{1}{(N!)^{1/2}} \sum_{\mathcal{P}_n} (-1)^n \mathcal{P}_n,$$

where $\mathcal{P}_n$ is a permutation operator involving n transpositions, to the Hartree trial wavefunction and obtain

$$\Psi = \mathfrak{A} \left[\phi_1(\mathbf{r}_1) \dots \phi_N(\mathbf{r}_N) \chi_1(\sigma_1) \dots \chi_N(\sigma_N) \right], \quad (14.16)$$

which can also be expressed as a Slater determinant of single-particle wavefunctions:

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_m, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{bmatrix} \psi_1(\mathbf{r}_1) & \dots & \psi_i(\mathbf{r}_1) & \dots & \psi_N(\mathbf{r}_1) \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \psi_1(\mathbf{r}_N) & \dots & \psi_i(\mathbf{r}_N) & \dots & \psi_N(\mathbf{r}_N) \end{bmatrix}, \quad (14.17)$$

where $\psi = \phi(\mathbf{r}) \chi(\sigma)$, is the product of spin and space wavefunctions. Each spatial wavefunction ϕ appears twice because of spin.

The orthonormalization conditions,

$$\int d\mathbf{r} \phi_i(\mathbf{r})^* \phi_j(\mathbf{r}) = \delta_{ij}, \quad (14.18)$$

are satisfied through Lagrange multipliers, as we have done above. The “best” single-particle orbitals ψ_i are obtained by varying the total energy with respect to the many-body wavefunction

$$\begin{aligned} \delta E &= \delta \int d\mathbf{r}^N \Psi^* \mathcal{H} \Psi \\ &= \int d\mathbf{r}^N \Psi^* \mathcal{H} \delta \Psi + \int d\mathbf{r}^N \delta \Psi^* \mathcal{H} \Psi. \end{aligned} \quad (14.19)$$

The variation of Ψ is expressed in terms of variations of the single-particle wavefunctions, so that

$$\delta \Psi(\mathbf{r}_1, \dots, \mathbf{r}_m, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \sum_i \begin{bmatrix} \psi_1(\mathbf{r}_1) & \dots & \delta \psi_i(\mathbf{r}_1) & \dots & \psi_N(\mathbf{r}_1) \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \psi_1(\mathbf{r}_N) & \dots & \psi_i(\mathbf{r}_N) & \dots & \psi_N(\mathbf{r}_N) \end{bmatrix}. \quad (14.20)$$

The resulting HF equations, derived in Appendix 14.A, are expressed as

$$\begin{aligned} & \left[\mathcal{H}(\mathbf{r}) + \sum_j e^2 \int d\mathbf{r}' \frac{|\psi_j(\mathbf{r}')|^2}{r_{12}} + \varepsilon_{ii} \right] \psi_i(\mathbf{r}) \\ & - \sum_{j:\uparrow\uparrow} \left[e^2 \int d\mathbf{r}' \frac{\psi_i^*(\mathbf{r}') \psi_j(\mathbf{r}')}{r_{12}} + \varepsilon_{ij} \right] \psi_j(\mathbf{r}) = 0, \end{aligned} \quad (14.21)$$

where $r_{12} = |\mathbf{r} - \mathbf{r}'|$. Equation (14.21) can be written in the compact notation

$$[\mathcal{H}(\mathbf{r}) + \mathcal{K}(\mathbf{r}) + \mathcal{J}(\mathbf{r}, \mathbf{r}') - E_{\text{HF}}] \phi(\mathbf{r}) = 0, \quad (14.22)$$

where we identify $\mathcal{K}(\mathbf{r})$ and $\mathcal{J}(\mathbf{r}, \mathbf{r}')$ as the Coulomb and exchange operators, respectively, the latter being nonlocal. This approximation is known as the *Hartree–Fock model*. The

resulting Hartree–Fock energy, E_{HF} , differs from the Hartree energy by an additional, negative exchange energy:

$$E_{\text{HF}} = E_{\text{H}} + E_{\text{exc}}, \quad (14.23)$$

$$E_{\text{exc}} = -\frac{1}{2} \sum_{i \neq j, \uparrow \uparrow} \iint d\mathbf{r}_1 d\mathbf{r}_2 \psi_i(\mathbf{r}_1)^* \psi_j^*(\mathbf{r}_2) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi_j(\mathbf{r}_1) \psi_i(\mathbf{r}_2), \quad (14.24)$$

where only electrons of the same spin are to be included in the sum.

Again, the solution is obtained via a self-consistent iteration method. However, the nonlocality contained in the Hartree–Fock potential makes it impossible to carry out full Hartree–Fock calculations for condensed matter systems without the introduction of local approximations. A frequently used form is the local exchange potential of Slater

$$\mathcal{J} \simeq -3\alpha \left[\frac{3}{4\pi} n^{1/3}(\mathbf{r}, \mathbf{r}) \right],$$

where α is an adjustable parameter.

14.2.3 Density functional formalisms

In presenting the above self-consistent models, we find that the density $n(\mathbf{r})$ plays a prominent role. This evokes the question as to whether there exists a formally *exact* theory for the ground state of electronic systems in terms of the density $n(\mathbf{r})$ of which these models and their refinements are just approximations. This question leads us to the *density functional theory* (DFT). We should, however, recognize at the outset that this formalism leads to a classical description of the sought-after ground state. Thus, we should always keep in mind that, in spite of the tempting similarities between the basis functions that will emerge in the DFT formalism and the wavefunctions of an HF formalism, their physical interpretations are dramatically different.

We start this presentation with the simplest and oldest version of the DFT formalism, the Thomas–Fermi model.

The Thomas–Fermi model

This model capitalizes on the properties of a uniform noninteracting electron gas system, which has the following connections between the Fermi momentum, k_{F} , Fermi energy, E_{F} , and the density, n :

$$E_{\text{F}} = \frac{1}{2} k_{\text{F}}^2, \quad (14.25)$$

$$n = \frac{1}{3\pi^2} k_{\text{F}}^3, \quad (14.26)$$

in atomic units, given in Table 14.1.

It extends these relations to a many-electron system, subject to external potentials, by breaking up the system into cells of suitable size such that, in each, the electrons can be regarded as a uniform electron gas having the local density $n(\mathbf{r})$, with $\mathbf{r}$ the center of the cell. Thus, for an external potential $V(\mathbf{r})$, we divide space into cells, Ω_j , and in each cell we visualize the electrons as having a uniform density in a constant potential, $v_{\text{eff}}(\mathbf{r}_j)$, with a Fermi energy $E_{\text{F},j}$. Obviously, $E_{\text{F},j}$ must be equal in all cells, since otherwise the

Table 14.1. *Atomic units.*

Quantity	Atomic unit	Equivalent
Length	$a_0 = \frac{\hbar^2}{me^2}$	0.529 Å
Energy	Hartree = $\frac{e^2}{a_0}$	27.2 eV
Time	$t_a = \frac{\hbar}{\text{Hartree}}$	2.419×10^{-17} s
Probability density	$ \psi ^2 = \frac{1}{a_0^3}$	6.75 Å^{-3}

energy could be lowered by transferring electrons from a cell of higher E_F to one of lower E_F . We call this common value of E_F the *chemical potential*, μ . Dropping the subscript j on r , and using (14.25) and (14.26), we obtain

$$n(\mathbf{r}) = \frac{1}{3\pi^2} [k_F(\mathbf{r})]^3 = \frac{1}{3\pi^2} \{2[\mu - v_{\text{eff}}(\mathbf{r})]\}^{3/2}, \quad (14.27)$$

$$v_{\text{eff}}(\mathbf{r}) = V(\mathbf{r}) + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (14.28)$$

where the second term in the effective potential $v_{\text{eff}}(\mathbf{r})$ is the mean electrostatic potential at the point $\mathbf{r}$ due to the electron charge distribution. Equations (14.27) and (14.28) represent the *Thomas–Fermi model*. They require a self-consistent solution for the quantities $v_{\text{eff}}(\mathbf{r})$ and $n(\mathbf{r})$.

A posteriori, we are alerted to the basic assumption that underlies this model: the system can be broken up into cells which must be small enough for $v_{\text{eff}}(\mathbf{r})$ to be effectively constant in each cell, and, at the same time, each cell must be large enough to contain many electrons ($N \gg 1$), so that the electron gas equations, (14.25) and (14.26), make sense.

Alternatively, the Thomas–Fermi model can be cast in the form of a variational principle for the total energy:

$$E_{\text{TF}}[n(\mathbf{r})] = \int d\mathbf{r} \left[V(\mathbf{r}) n(\mathbf{r}) + \frac{3}{10} (3\pi^2)^{2/3} n(\mathbf{r})^{5/3} \right] + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (14.29)$$

The first term describes, exactly, the interactions of the electrons with the external potential $V(\mathbf{r})$. The second term describes, approximately, their kinetic energy, since, for a free-electron gas of uniform density n occupying a volume Ω , the kinetic energy is given by

$$T = \Omega \frac{3}{10} (3\pi^2)^{2/3} n^{5/3}. \quad (14.30)$$

Finally, the last term in (14.29) describes the Coulomb-interaction energy in a mean-field approximation in which the correlation between the densities at two points $\mathbf{r}$ and $\mathbf{r}'$ is neglected.

The minimization of E_{TF} is subject to the constraint, i.e. a Lagrange multiplier, that the total number of electrons be N . This leads to

$$\delta \left[E_{\text{TF}}[n(\mathbf{r})] - \mu \int d\mathbf{r} n(\mathbf{r}) \right] = 0, \quad (14.31)$$

which is precisely equivalent to the coupled equations (14.27) and (14.28).

The basic Thomas–Fermi model, described above, can be further refined by the addition of exchange, gradient, and correlation corrections, which is the subject of the Hohenberg–Kohn–Sham density functional formalism.

The HKS density functional formalism

The density functional formalism was first introduced by Hohenberg, Kohn, and Sham [189, 190] as a general theory of inhomogeneous electron gases in their ground state. The central quantity in this theory is the electron density, whose basic role is established by the theorem that the properties of the system, in particular the ground-state energy, are functionals of this density. With the density as the varied function, a variational principle is established for the energy. The associated Euler equation is formulated in two ways, both in principle exact, which are particularly convenient for the study of strongly inhomogeneous systems. One formulation is similar to the Thomas–Fermi method, the other to the Hartree–Fock method; in their various approximate versions they represent systematic ways of extending the classic methods which they resemble.

Let us first examine the Hamiltonian of a many-particle system. First, it contains a sum of the kinetic energies of individual particles of the form $-(\hbar^2/2m)\nabla_i^2$, which depends only on the particle type through the mass m . Second, it contains a sum of interparticle interaction terms $\mathcal{V}$, which is also determined by the type of particles comprising the system, for example, for electrons, $\mathcal{V} = (1/2) \sum (e^2/r_{ij})$. Finally, it contains the energy of interaction with an external potential V , which distinguishes different systems that belong to the same particle type and the same particle number N . Notice that both the interparticle and/or the external potentials may be nonlocal or velocity-dependent.

The lemma of Hohenberg and Kohn The importance of the density, $n(\mathbf{r})$, which was prominent in the approximate theories just described, is greatly enhanced by a rigorous lemma which demonstrates that $V(\mathbf{r})$, ignoring additive constants, is a **unique functional of $n(\mathbf{r})$** . An important consequence of this fact is that the ground state Ψ is then such a functional, since $V(\mathbf{r})$ fixes $\mathcal{H}$, and $\mathcal{H}$, via the Schrödinger equation, determines Ψ .

The uniqueness demonstration proceeds by *reductio ad absurdum*: We assume that $V(\mathbf{r})$ is not unique; i.e. that there is another potential $V'(\mathbf{r})$, which differs from V by more than a constant, that gives rise to the same density $n(\mathbf{r})$. The ground state associated with V' is denoted by Ψ' , with energy E'_N . Since Ψ' satisfies a different Schrödinger equation it

must be different from Ψ , and we get

$$E_N = \langle \Psi | \mathcal{H} | \Psi \rangle < \langle \Psi' | \mathcal{H} | \Psi' \rangle = \langle \Psi' | \mathcal{H}' + V - V' | \Psi' \rangle; \quad (14.32)$$

and so (recalling the assumption $n = n'$),

$$E_N < E'_N + \int d\mathbf{r} \left[V(\mathbf{r}) - V'(\mathbf{r}) \right] n(\mathbf{r}). \quad (14.33)$$

Interchanging primed and unprimed quantities gives

$$E'_N < E_N + \int d\mathbf{r} \left[V'(\mathbf{r}) - V(\mathbf{r}) \right] n(\mathbf{r}). \quad (14.34)$$

and addition of (14.33) and (14.34) then leads to the inconsistency $E_N + E'_N < E_N + E'_N$. Hence it is seen that $V(\mathbf{r})$ must be a unique functional of $n(\mathbf{r})$.

Variational principle We define an energy functional

$$E_V[n(\mathbf{r})] = \int d(\mathbf{r}) V(\mathbf{r}) n(\mathbf{r}) + F[n(\mathbf{r})], \quad (14.35)$$

where

$$F[n(\mathbf{r})] \equiv \langle \Psi | T + \mathcal{V} | \Psi \rangle \quad (14.36)$$

is a universal functional of $n(\mathbf{r})$ for a given species of fermion. T depends on the mass of the fermion species, and $\mathcal{V}$ is the corresponding interaction between the species particles. Clearly, for the correct $n(\mathbf{r})$ associated with the potential $v(\mathbf{r})$ and having spatial integral

$$\int d\mathbf{r} n(\mathbf{r}) = N, \quad (14.37)$$

$E_v[n]$ is equal to the ground-state energy E_N . It may be seen also that E_N is the minimum value of $E_v[n]$ with respect to other density distributions corresponding to the same N . Consider a trial density distribution $n'(\mathbf{r}) \neq n(\mathbf{r})$ with the associated ground state $\Psi' \neq \Psi$. Then

$$\begin{aligned} E_N < \langle \Psi' | \mathcal{H} | \Psi' \rangle &= \int d(\mathbf{r}) v(\mathbf{r}) n'(\mathbf{r}) + \langle \Psi' | T + \mathcal{V} | \Psi' \rangle \\ &= E_v[n']. \end{aligned} \quad (14.38)$$

The vanishing of the first variation of $E_v[n']$ about the correct density may be expressed by writing

$$\delta E_v[n] = 0, \quad (14.39)$$

subject to the condition that all densities considered satisfy

$$\int d(\mathbf{r}) n(\mathbf{r}) = N. \quad (14.40)$$

Notice here that the energy of the ground state, regarded as a functional of the density, attains its minimum value with respect to *variation* of the *particle density* subject to

the normalization condition when the density has the correct value. This statement is in contrast with the usual minimum theorem for the ground-state energy, where the energy attains its minimum value with respect to *variation* of the *ground-state wavefunction when the wavefunction* is correct. The density $n(\mathbf{r})$ is a real, positive function of a single vector variable, whereas the wavefunction is a complex function of N vector variables, which must have nodes if there are three or more electrons. It is remarkable that it is, in principle, sufficient to vary the density. Notice also that up to this point the HK theorems involve a very significant restriction to spinless fermions, which do not exist. By replacing the density with a generalized four-current within a relativistic formalism, it has been possible to introduce particle spin. The ground-state energy is then a unique functional of the four-current density, and this quantity attains its minimum value with respect to variations that preserve the equation of continuity when the density is correct. As a result of these considerations, the ground-state energy becomes a functional of the spin densities, a statement generally abbreviated as

$$E_G \equiv E_G[n_\uparrow(r), n_\downarrow(r)]. \quad (14.41)$$

Separation of electrostatic terms: use of Lagrange multiplier Because of the long range of the Coulomb interaction, it is often convenient to separate from $F[n]$ the classical Coulomb self-energy of the electrons by writing

$$F[n] = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + G[n], \quad (14.42)$$

where $G[n]$ is a universal functional like $F[n]$, which contains the contributions of the kinetic, exchange, and correlation energies. The total energy functional then becomes

$$E_v[n] = \int d\mathbf{r} v(\mathbf{r}) n(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + G[n]. \quad (14.43)$$

The electrostatic potential in the system will be denoted by $\phi(\mathbf{r})$:

$$\phi(\mathbf{r}) = v(\mathbf{r}) + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (14.44)$$

If $v(\mathbf{r})$ is regarded as being due to a distribution of positive charge of number density $n_+(\mathbf{r})$, then this may be written in the form

$$\phi(\mathbf{r}) = \int d\mathbf{r}' \frac{n(\mathbf{r}') - n_+(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (14.45)$$

Note that (14.45) implies that

$$\nabla^2 \phi(\mathbf{r}) = -4\pi [n(\mathbf{r}) - n_+(\mathbf{r})]. \quad (14.46)$$

It is also frequently convenient to use a Lagrange multiplier μ to write the variational equation for $n(\mathbf{r})$ as

$$\delta \left\{ E_v[n] - \mu \int d\mathbf{r} n(\mathbf{r}) \right\} = 0, \quad (14.47)$$

with μ determined by (14.40). Equation (14.47) implies that, for the correct density,

$$\frac{\delta E_v[n]}{\delta n(\mathbf{r})} = \mu. \quad (14.48)$$

Using (14.43) and (14.44), this may be put in the form

$$\frac{\phi(\mathbf{r}) + \delta G[n]}{\delta n(\mathbf{r})} = \mu. \quad (14.49)$$

For large N , it is easily seen that μ is equal to the chemical potential $\partial E_N / \partial N$. We denote the correct densities corresponding to N and $N-1$ particles in the potential $v(\mathbf{r})$ by $n_N(\mathbf{r})$ and $n_{N-1}(\mathbf{r})$. Then

$$\begin{aligned} \left. \frac{\partial E_N}{\partial N} \right|_{v(\mathbf{r}); T=0K} &= E_v[n_N] - E_v[n_{N-1}] \\ &= \int d(\mathbf{r}) \left. \frac{\delta E_v[n]}{\delta n(\mathbf{r})} \right|_{n=n_N} [n_N(\mathbf{r}) - n_{N-1}(\mathbf{r})] = \mu, \end{aligned} \quad (14.50)$$

where (14.48) is used in the last step.

The method of Kohn and Sham Kohn and Sham introduced a recipe that is tantalizingly close to a HF approach, yet it is classical. They introduced a set of N orthonormal single-particle functions to define the particle density $n(r)$ as

$$n(r) = \sum_{i=1}^N u_i^*(r) u_i(r). \quad (14.51)$$

The variation of the density is effected by varying the functions $u_i^*(r)$ and $u_i(r)$,

$$\delta n(r) = \sum_{i=1}^N \{ \delta u_i^*(r) u_i(r) + u_i^*(r) \delta u_i(r) \}, \quad (14.52)$$

however, the symmetrical disposition of $u_i(\mathbf{r})$ and $u_i^*(\mathbf{r})$ allows the variation to be carried out with respect to $u_i^*(r)$ only. This process is quite straightforward except for the kinetic energy, which is written in the form

$$\begin{aligned} E_{\text{KE}}^s(n) &= \frac{\hbar^2}{2m} \sum_{i=1}^N \int d\mathbf{r} \nabla u_i^*(\mathbf{r}) \cdot \nabla u_i(\mathbf{r}) \\ &= \frac{\hbar^2}{2m} \sum_{i=1}^N \int d\mathbf{r} u_i^*(\mathbf{r}) (-\nabla^2) u_i(\mathbf{r}), \end{aligned} \quad (14.53)$$

where the N functions are the same as in (14.52). The superscript on E indicates a single-particle approximation. This step is an approximation, i.e. no proof has been given that (14.53) holds for the exact E_{KE} . Formally, the complication can be ignored because the difference between E_{KE} and E_{KE}^s can be absorbed in $G[n]$. Thus the variation may now

be performed on the functional

$$\begin{aligned} E_v[n] &= E_{\text{KE}}^s + \frac{e^2}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \int d\mathbf{r} \mathbf{v}(\mathbf{r}) n(\mathbf{r}) + G[n] \\ &= \sum_{i=1}^N \int d\mathbf{r} u_i^*(\mathbf{r}) \left[\frac{-\hbar^2}{2m} \nabla^2 + v(\mathbf{r}) + \frac{e^2}{2} \sum_{j=1}^N \frac{|u_j(\mathbf{r}')|^2}{|\mathbf{r}|} \right] u_i(\mathbf{r}) + G[n]. \end{aligned} \quad (14.54)$$

The variation will then lead to

$$\left[\frac{-\hbar^2}{2m} \nabla^2 + v(\mathbf{r}) + \frac{e^2}{2} \sum_{j=1}^N \frac{|u_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta G[n]}{\delta u_i^*(\mathbf{r})} \right] u_i(\mathbf{r}) = \epsilon_i u_i(\mathbf{r}), \quad (14.55)$$

where we can define

$$V_{\text{exc}} = \frac{\delta G[n]}{\delta u_i^*(r)}. \quad (14.56)$$

Another major difficulty with the density functional approach lies in our imperfect knowledge of the exchange-correlation potential. The only system for which there is reasonably complete understanding of E_{exc} is the free electron gas, for which E_{exc} is an ordinary function of n . In a free electron gas, however, the density is independent of position. In order to adapt these results to the case of an inhomogeneous electron gas, the *local density approximation* is introduced. In this approximation, as the density is a function of the position, $n \equiv n(\mathbf{r})$, it is assumed that E_{exc} has the same value at a point r that it would have in a free electron gas, namely,

$$E_{\text{exc}} \rightarrow E_{\text{exc}}[n(r)].$$

In the simplest approximation in which only the exchange is considered, we have seen that the exchange energy per unit volume, and not per electron, of a free electron gas is

$$E_{\text{exc}}[n] = \frac{-3}{2} e^2 \left(\frac{3n^4}{8\pi} \right)^{1/3}. \quad (14.57)$$

Hence, the exchange potential is

$$V_{\text{exc}} = \frac{dE_{\text{exc}}[n]}{dn} = -2e^2 \left(\frac{3n(r)}{8\pi} \right)^{1/3}, \quad (14.58)$$

where now $n(r)$ is given by (14.52).

These results have a simple generalization to the case of spin-polarized systems, by which is meant a system in which the densities of spin “up” and spin “down” electrons are not equal – either locally or, possibly, overall. In this case, as indicated in (14.56), the energy is to be regarded as a functional of $n_{\uparrow}$ and $n_{\downarrow}$, and we have for the exchange-correlation potentials,

$$V_{\text{exc}\sigma} = \frac{\delta E[n_{\uparrow}, n_{\downarrow}]}{\delta n_{\sigma}}. \quad (14.59)$$

There is a different exchange-correlation potential for electrons of each spin. In the *local spin density approximation* (LSDA), the free electron gas result for E_{exc} is used. In the exchange only case, this is

$$E_{\text{exc}} = \frac{-3}{2} e^2 \sum_{\sigma} n_{\sigma} \left(\frac{3n_{\sigma}(r)}{8\pi} \right)^{1/3}. \quad (14.60)$$

The spin densities are those obtained locally, i.e.

$$n_{\sigma} \rightarrow n_{\sigma}(r) = \sum_i |u_{i\sigma}(r)|^2. \quad (14.61)$$

Thus, the exchange potential is

$$V_{\text{exc}\sigma} = \frac{dE_{\text{exc}[n]}}{dn_{\sigma}} = -2e^2 \left(\frac{3n_{\sigma}(r)}{8\pi} \right)^{1/3}. \quad (14.62)$$

14.3 Methods and techniques for band structure calculations

Several methods for calculating the electronic structure of condensed matter systems have been developed over the past six or more decades. The distinguishing feature among the different methods is the type of basis function set employed. Group theoretical techniques are mainly applied to block-diagonalize the corresponding matrices, and thus allow the handling of large basis sets, which cannot be done otherwise. In the case of crystalline solids, this approach has the added advantage of elucidating the identification and symmetry-labeling of the different branches of the ensuing band structure.

14.3.1 Bloch and Wannier bases

Writing a Bloch function as

$$\Psi(\mathbf{k}, \mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u_{\mathbf{k}}(\mathbf{r}),$$

where $u_{\mathbf{k}}(\mathbf{r})$ has the lattice periodicity, we can classify $u_{\mathbf{k}}(\mathbf{r})$ into two main categories:

- (a) **Plane-waves or momentum eigenfunctions** $u(\mathbf{k}, \mathbf{r})$ can be expanded as a Fourier series of the periodic lattice,

$$u(\mathbf{k}, \mathbf{r}) = \sum_{\mathbf{G}} a_{\mathbf{k}}(\mathbf{G}) e^{i\mathbf{G} \cdot \mathbf{r}}, \quad (14.63)$$

where the $\mathbf{G}$ s are reciprocal lattice vectors. Consequently, we find

$$\Psi(\mathbf{k}, \mathbf{r}) = \sum_{\mathbf{G}} a_{\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}}. \quad (14.64)$$

The physical interpretation of this equation is that a Bloch electron with wavevector $\mathbf{k}$ can have momentum $\mathbf{k} + \mathbf{G}$; and the probability of finding momentum $\mathbf{k} + \mathbf{G}$ is simply $|a_{\mathbf{k}}(\mathbf{G})|^2$, apart from a normalization constant. Using the orthonormality of the functions $e^{i\mathbf{G} \cdot \mathbf{r}}$, we can express $a_{\mathbf{k}}(\mathbf{G})$ as

$$a_{\mathbf{k}}(\mathbf{G}) = \frac{1}{\Omega} \int d\mathbf{r} \Psi(\mathbf{k}, \mathbf{r}) e^{-i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}}. \quad (14.65)$$

The periodicity of the Bloch states in reciprocal space, $\Psi(\mathbf{k}, \mathbf{r}) = \Psi(\mathbf{k} + \mathbf{G}, \mathbf{r})$, requires that

$$a_{\mathbf{k}}(\mathbf{G}) = \frac{1}{\Omega} \int d\mathbf{r} \Psi(\mathbf{k} + \mathbf{G}, \mathbf{r}) e^{-i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}} = a(\mathbf{k} + \mathbf{G}). \quad (14.66)$$

- (b) **Localized Wannier functions** Another implication of the periodicity of the Bloch function in reciprocal space is that it can be expanded as a Fourier series in real space:

$$\Psi(\mathbf{k}, \mathbf{r}) = \sum_{\mathbf{t}} w(\mathbf{t}, \mathbf{r}) e^{i\mathbf{k} \cdot \mathbf{t}}, \quad (14.67)$$

$$w(\mathbf{t}, \mathbf{r}) = \frac{1}{\Omega_{\text{BZ}}} \int d\mathbf{k} \Psi(\mathbf{k}, \mathbf{r}) e^{-i\mathbf{k} \cdot \mathbf{t}}, \quad (14.68)$$

where Ω_{BZ} is BZ volume. Since $e^{-i\mathbf{k} \cdot \mathbf{t}} \Psi(\mathbf{k}, \mathbf{r}) = \Psi(\mathbf{k}, \mathbf{r} - \mathbf{t})$, we obtain

$$w(\mathbf{t}, \mathbf{r}) = \frac{1}{\Omega_{\text{BZ}}} \int_{\Omega_{\text{BZ}}} d\mathbf{k} \Psi(\mathbf{k}, \mathbf{r} - \mathbf{t}) \quad (14.69)$$

or

$$w(\mathbf{r} - \mathbf{t}) = \frac{1}{\Omega_{\text{BZ}}} \int_{\Omega_{\text{BZ}}} d\mathbf{k} \Psi(\mathbf{k}, \mathbf{r}). \quad (14.70)$$

Consequently,

$$\Psi(\mathbf{k}, \mathbf{r}) = \sum_{\mathbf{t}} w(\mathbf{r} - \mathbf{t}) e^{i\mathbf{k} \cdot \mathbf{t}}. \quad (14.71)$$

$w(\mathbf{r})$ is the Wannier function.

The orthonormality of the Bloch functions can be used to derive the orthonormality and completeness relations of the Wannier functions,

$$\int_{\text{all space}} w^*(\mathbf{r} - \mathbf{t}) w(\mathbf{r} - \mathbf{t}') d\mathbf{r} = \delta(\mathbf{t}, \mathbf{t}'), \quad (14.72)$$

and

$$\sum_{\mathbf{t}} w^*(\mathbf{r}' - \mathbf{t}) w(\mathbf{r} - \mathbf{t}) = \delta(\mathbf{r}' - \mathbf{r}). \quad (14.73)$$

The Wannier functions provide the basic justification for the application of the tight-binding method in electronic structure calculations, as we will discuss below.

14.3.2 Symmetries of the electron dispersion curves (bands) $E(\mathbf{k})$

We consider the behavior of the eigenvalue equation

$$\mathcal{H} \Psi_{\mathbf{k}} = E(\mathbf{k}) \Psi_{\mathbf{k}}, \quad (14.74)$$

under the action of $\mathbb{S}$, the symmetry space-group of $\mathcal{H}$. We examine the action of $S \in \mathbb{S}$, namely

$$S \mathcal{H} S^{-1} \Psi_{\mathbf{k}} = \mathcal{H} S \Psi_{\mathbf{k}} = E(\mathbf{k}) S \Psi_{\mathbf{k}}. \quad (14.75)$$

Equations (14.74) and (14.75) show that $S \Psi_{\mathbf{k}}$ has the same energy $E(\mathbf{k})$ as $\Psi_{\mathbf{k}}$. Two possibilities may now arise:

- (i) $S \in \mathbb{S}_{\mathbf{k}}$, then, for the basis $^{(\mathbf{k},\mu)}\Psi$ that transforms as the $(\mathbf{k},\mu)$ Irrep of $\mathbb{S}_{\mathbf{k}}$,

$$S^{(\mathbf{k},\mu)}\Psi \Rightarrow ^{(\mathbf{k},\mu)}\Psi;$$

- (ii) $S \notin \mathbb{S}_{\mathbf{k}}$, then,

$$S\Psi_{\mathbf{k}} = \Psi_{R\mathbf{k}}, \quad S = (R|\boldsymbol{\tau} + \mathbf{t}). \quad (14.76)$$

Thus, all the states belonging to $^*\mathbf{k}$ have the same energy $E(\mathbf{k})$. When we consider a general $\mathbf{k}$, such that $\mathbb{S}_{\mathbf{k}} = (E|\mathbf{0}) \otimes \mathbb{T}$, $^*\mathbf{k}$ contains g members, namely the order of the point-group of $\mathbb{S}$.

If we also consider the time-reversal symmetry of the Hamiltonian, we find that

$$\mathcal{H} \Theta \Psi_{\mathbf{k}} = \mathcal{H} \Psi_{-\mathbf{k}} = E(\mathbf{k}) \Psi_{-\mathbf{k}}, \quad (14.77)$$

since Θ reverses the momentum direction.

These observations lead us to conclude that an *irreducible zone* (IZ) of volume Ω_{BZ}/g contains all the eigenenergies of the electron system.

Now, we explore the translational properties of $E(\mathbf{k})$, by using (14.71) for $\Psi_{\mathbf{k}}$, to write

$$\Psi_{\mathbf{k}+\mathbf{G}} = \sum_{\mathbf{t}} w(\mathbf{r} - \mathbf{t}) e^{i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{t}} = \Psi_{\mathbf{k}}, \quad (14.78)$$

and thus establish the periodicity of $E(\mathbf{k})$ in reciprocal space.

The fact that the symmetries of $E(\mathbf{k})$ establish the IZ leads to the conclusion that $E(\mathbf{k})$ must assume optimum values at its boundaries, namely maxima or minima. Since the density of states is $\propto 1/|\nabla E(\mathbf{k})|$, it must have singularities at these boundaries. Hence, we further conclude that a majority of the electronic states are confined to high-symmetry planes, directions and points, and we need only focus our attention to these locations in the IZ.

Symmetry projection operators for space-groups

Calculations of the electronic structures are based on the application of variational techniques in the minimization of the functional

$$\frac{\langle \Psi_{\mathbf{k}} | \mathcal{H} | \Psi_{\mathbf{k}} \rangle}{\langle \Psi_{\mathbf{k}} | \Psi_{\mathbf{k}} \rangle}, \quad (14.79)$$

where

$$\mathcal{H} = T + U(\mathbf{r})$$

is a one-electron Hamiltonian, and

$$\Psi_{\mathbf{k}} = \sum_n C_{\mathbf{k}}(n) \phi_n(\mathbf{r})$$

is a trial wavefunction, and $\{\phi_n\}$ is a suitable basis set. The coefficients $C_{\mathbf{k}}(n)$ are treated variationally.

The step of block-diagonalizing the matrix associated with (14.79) involves the application of symmetry projection operators. It is worthwhile to review briefly their forms, especially for the case of space-groups.

The elements of the point-group of the wavevector $\mathbb{P}_{\mathbf{k}}$ commute with the translation projection operator $^{(\mathbf{k})}\mathcal{P}$. Hence, all the projection operators $^{(\mu)}\mathcal{P}(\mathbf{k})$ of the allowable

Irreps of $\mathbb{P}_{\mathbf{k}}$ commute with $^{(\mathbf{k})}\mathcal{P}$; and we can define a projection operator for each of the allowable Irreps of little-group $\mathbb{G}_{\mathbf{k}}$ as

$$\begin{aligned} ^{(\mathbf{k},\mu)}\mathcal{P}_{jj} &= ^{(\mu)}\mathcal{P}_{jj}(\mathbb{P}_{\mathbf{k}}) ^{(\mathbf{k})}\mathcal{P} \\ &= \left[\frac{d_{\mu}}{p_{\mathbf{k}}} \sum_{R \in \mathbb{P}_{\mathbf{k}}} ^{(\mathbf{k},\mu)}\varepsilon_{jj}^*(R|\boldsymbol{\tau}) \widehat{(R|\boldsymbol{\tau})} \right] \left[\frac{1}{N} \sum_{\mathbf{t}} ^{(\mathbf{k})}\Delta^*(\mathbf{t}) \right]. \end{aligned} \quad (14.80)$$

We may write

$$^{(\mathbf{k},\mu)}\varepsilon_{jj}^*(R|\boldsymbol{\tau}) = e^{-i\mathbf{k} \cdot \boldsymbol{\tau}} ^{(\mu)}\Omega^*(R)_{jj}, \quad (14.81)$$

when (i) $\mathbf{k}$ lies inside the BZ, (ii) $\mathbb{S}$ or $\mathbb{S}_{\mathbf{k}}$ are symmorphic; then, (14.80) reduces to

$$^{(\mathbf{k},\mu)}\mathcal{P}_{jj} = \left[\frac{d_{\mu}}{p_{\mathbf{k}}} \sum_{R \in \mathbb{P}_{\mathbf{k}}} ^{(\mu)}\Omega^*(R)_{jj} \widehat{(R|\mathbf{0})} \right] \left[\frac{1}{N} \sum_{\mathbf{t}} ^{(\mathbf{k})}\Delta^*(\mathbf{t}) \right] \quad (14.82)$$

since

$$\widehat{(R|\boldsymbol{\tau})} ^{(\mathbf{k})}\mathcal{P} = e^{-i\mathbf{k} \cdot \boldsymbol{\tau}} ^{(\mathbf{k})}\mathcal{P}.$$

The determination of the $(\mathbf{k}; (\mu, j))$ symmetrized manifold is obtained according to the projection

$$\left\langle \Psi_{\mathbf{k}} \left| ^{(\mathbf{k},\mu)}\mathcal{P}_{jj} \right. \right\rangle \left\langle ^{(\mathbf{k},\mu)}\mathcal{P}_{jj} \left| \mathcal{H} \right| ^{(\mathbf{k},\mu)}\mathcal{P}_{jj} \right\rangle \left\langle ^{(\mathbf{k},\mu)}\mathcal{P}_{jj} \left| \Psi_{\mathbf{k}} \right. \right\rangle. \quad (14.83)$$

14.3.3 Plane-wave methods

The simplest wavefunction basis available for band structure calculations is a complete, symmetry-adapted, set of $\mathbf{G}$ plane-waves. It is a direct manifestation of the periodic nature of a crystalline system, which allows the wavefunction expansion

$$\Psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{k}-\mathbf{G}) \cdot \mathbf{r}},$$

and the expansion of the crystal potential as

$$V(\mathbf{r}) = \sum'_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}},$$

where the prime indicates the omission of V_0 since it adds just a constant to the energy dispersion curves. Treating the coefficients $C_{\mathbf{k}}(\mathbf{G})$ as variational parameters, we obtain the set of coupled equations

$$(\varepsilon_{\mathbf{k}+\mathbf{G}} - E) C_{\mathbf{k}}(\mathbf{G}) + \sum_{\mathbf{G}'} V_{\mathbf{G}'} C_{\mathbf{k}}(\mathbf{G} - \mathbf{G}') = 0,$$

(14.84)

with free electron energy given by

$$\varepsilon_{\mathbf{k}+\mathbf{G}} = \frac{\hbar^2}{2m} (\mathbf{k} + \mathbf{G})^2. \quad (14.85)$$

Free and nearly free electron band structure

Free electron bands It will be useful to determine $E(\mathbf{k})$ in the absence of a potential. When $V(\mathbf{r}) = 0$, the energy is purely kinetic, and is given by

$$E(\mathbf{k}) = \frac{\hbar^2 \mathbf{k}^2}{2m}. \quad (14.86)$$

For pedagogical reasons, we also consider the case known as the *empty lattice* and write

$$E(\mathbf{k} + \mathbf{G}) = \frac{\hbar^2}{2m} (\mathbf{k} + \mathbf{G})^2, \quad (14.87)$$

with wavefunction

$$\Psi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) = e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}. \quad (14.88)$$

The free electron energy, given by (14.86), is shown as a dashed parabola in Figure 14.2 for a one-dimensional crystal.

It is customary, however, to choose to restrict $\mathbf{k}$ to the first Brillouin zone, each $\mathbf{G}$ -vector corresponds to a particular section of the parabolic curve $E(\mathbf{k} + \mathbf{G})$. For example, $G = 2\pi/a$ produces the section of $E(\mathbf{k} + \mathbf{G})$ extending from $k = \pi/a$ to $3\pi/a$.

If the various sections of $E(\mathbf{k} + \mathbf{G})$ in the extended zone scheme in Figure 14.2 are translated by $-\mathbf{G}$, we obtain the *reduced zone scheme*. This is permissible because both $E(\mathbf{k} + \mathbf{G})$ and $\Psi_{\mathbf{k}+\mathbf{G}}(\mathbf{r})$ are periodic in $\mathbf{G}$.

Thus we need only work in the first Brillouin zone.

For the sake of simplicity, we set lattice constants $a = b = c = 1$ in the following examples.

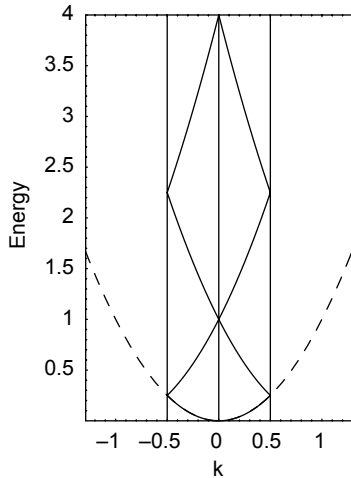


Fig. 14.2. One-dimensional free-electron bands in the reduced Brillouin zone (solid curves). The equivalent band in the extended zone (dashed curve). ($a = 1$)

*Example 14.1***Face-centered cubic free-electron band structure**

The face-centered cubic crystal structure and its associated Brillouin zone are illustrated in Figures 14.3 and 14.4, respectively. The symmetry lines and symmetry points are depicted using standard notation. It is usually convenient to present points K and U as symmetry points, but, in reality, they do not strictly satisfy the requirements of a symmetry point. They have each been chosen to be the midpoint of an edge of the Brillouin zone in order that the small region of the Brillouin zone, defined in Figure 14.4 by the symmetry points Γ , K , W , X , U , L and symmetry lines, is an irreducible zone. This wedge is 1/48th of the full Brillouin zone. The full Brillouin zone can be constructed by operating on the irreducible zone by all 48 elements of the holosymmetric point-group, the holohedry. In fact, point K has the same symmetry as any other point on the Σ -line. Thus,

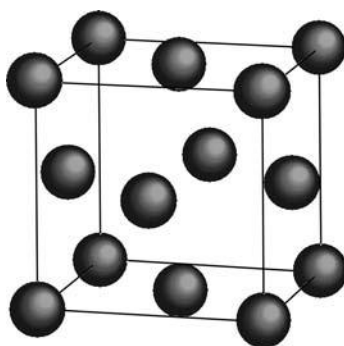


Fig. 14.3. Atomic positions in the f.c.c. structure. Al, Ca, Ni, and Cu are typical of this structure.

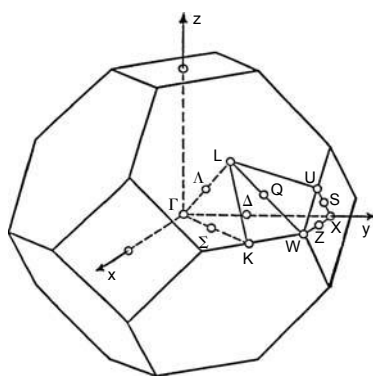


Fig. 14.4. The Brillouin zone for the f.c.c. structure.

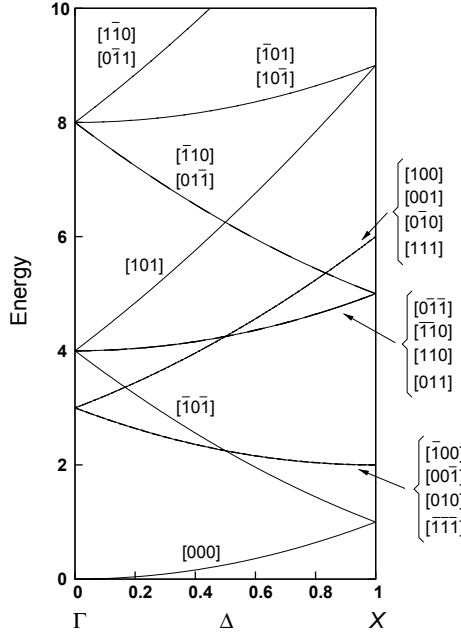


Fig. 14.5. Energy bands for the empty f.c.c. lattice along the Γ -X direction.

the point-group $\mathcal{P}_K$ does not satisfy the requirement that there exists a neighborhood of K in which no point has the symmetry $\mathcal{P}_K$ except K itself. A similar argument holds for U .

The free electron band structure for a face-centered cubic crystal is shown in Figure 14.5, along the Δ -symmetry direction. We discuss here how this free electron band structure is obtained. The reciprocal lattice for a face-centered cubic crystal is body-centered cubic, for which a general reciprocal lattice vector is given by

$$\begin{aligned} \mathbf{G} &= h \mathbf{b}_1 + k \mathbf{b}_2 + l \mathbf{b}_3 \\ &= \frac{2\pi}{a} [(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}})h + (-\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})k + (\hat{\mathbf{x}} - \hat{\mathbf{y}} + \hat{\mathbf{z}})l], \end{aligned} \quad (14.89)$$

where the Miller indices h, k, l label the components of $\mathbf{G}$ with respect to the reciprocal basis vectors of the body-centered cubic reciprocal lattice. Rearranging terms, we write

$$\begin{aligned} \mathbf{G} &= \frac{2\pi}{a} [(h - k + l)\hat{\mathbf{x}} + (h + k - l)\hat{\mathbf{y}} + (-h + k + l)\hat{\mathbf{z}}] \\ &= \frac{2\pi}{a} [H\hat{\mathbf{x}} + K\hat{\mathbf{y}} + L\hat{\mathbf{z}}], \end{aligned} \quad (14.90)$$

where H, K, L are integer indices that label vectors in $\mathbf{k}$ -space relative to the Cartesian coordinate system of Figure 14.4. It is often convenient to label vectors with respect to the Cartesian coordinate system, but it must be kept in mind that such vectors are not generally reciprocal lattice vectors $\mathbf{G}$, even when labeled by integers. In particular, the X point, denoted by $[HKL] = [100]$ is not a reciprocal lattice vector.

Suppose we wish to plot the free electron energy bands in the $\mathbf{k}_x$ -direction. We have

$$\begin{aligned} E(\mathbf{k}) &= \frac{\hbar^2}{2m} [(k_x + G_x)^2 + (k_y + G_y)^2 + (k_z + G_z)^2] \\ &= \frac{\hbar^2}{2m} [(k_x + G_x)^2 + G_y^2 + G_z^2], \quad \text{taking } k_y = k_z = 0 \\ &= \frac{\hbar^2}{2m} \left(\frac{2\pi}{a} \right)^2 [(u + h - k + l)^2 + (h + k - l)^2 + (-h + k + l)^2], \end{aligned} \quad (14.91)$$

where u is the fractional distance of $\mathbf{k}_x$ along the $[100]$ direction from the Γ point $(0, 0, 0)$ to the X point $(2\pi/a, 0, 0)$, and a is the lattice constant for the nonprimitive cubic unit cell of the face-centered cubic crystal.

For convenience, we normalize all energies by setting

$$\frac{\hbar^2}{2m} \left(\frac{2\pi}{a} \right)^2 \equiv 1. \quad (14.92)$$

We can now express the energy $E(\mathbf{k}_x)$ as a function of u as

$$E_u(hkl) = (u + h - k + l)^2 + (h + k - l)^2 + (-h + k + l)^2. \quad (14.93)$$

With $[hkl] = [000]$, we get $E_u = u^2$, which produces the lowest lying energy band in the panel of Figure 14.5 that extends between the Γ point and the X point.

Now consider the $\mathbf{G}$ -vectors corresponding to

$$[hkl] = [100], [010], [001], [\bar{1}00], [0\bar{1}0], [00\bar{1}].$$

We find

$$E_u(100) = E_u(001) = E_u(0\bar{1}0) = u^2 + 2u + 3,$$

which gives triply degenerate energy bands that run from $E = 3$ at the Γ point to $E = 6$ at the X point. The quadruple degeneracy shown for this band in Figure 14.5 arises because we also have

$$E_u(111) = u^2 + 2u + 3.$$

Similarly, we find

$$E_u(\bar{1}00) = E_u(00\bar{1}) = E_u(010) = u^2 - 2u + 3,$$

which gives rise to a triply degenerate band running from $E = 3$ at the Γ point to $E = 2$ at the X point. Here the degeneracy is increased to 4-fold by a contribution from

$$E_u(\bar{1}\bar{1}\bar{1}) = u^2 - 2u + 3.$$

The band from $E = 4$ at Γ down to $E = 1$ at X is given by

$$E_u(\bar{1}0\bar{1}) = (u - 2)^2.$$

Note that in this example, just considered, the $\mathbf{G}$ -vectors have been indexed with respect to the primitive lattice vectors, not the Cartesian coordinate system.

Nearly free electron energy bands In the presence of a nonzero crystal potential, the free electron bands are modified. Sometimes, for nearly free electron metals, such as aluminum, the modification is surprisingly little. Even for silicon, a semiconductor, the electron energy bands are highly reminiscent of the free electron band structure. Still, the differences, even when small, are important.

There are two aspects of the band structure affected by a nonzero potential. First, many of the degeneracies of the free electron band structure are removed. Second, bands may be prohibited from crossing in certain cases. What happens is dictated by symmetry arguments based on group theory. We first discuss these aspects for the one-dimensional case, which is shown in Figure 14.6.

Each pair of degenerate wavefunctions, $\exp[\pm iGx/2]$, on the free electron parabola of Figure 14.6, are coupled by a corresponding Fourier component V_G of the crystal potential. This can be represented in matrix form by the eigenvalue problem

$$\begin{vmatrix} (G/2)^2 - E & V_G \\ V_G^* & (G/2)^2 - E \end{vmatrix} \begin{bmatrix} \exp[iGx/2] \\ \exp[-iGx/2] \end{bmatrix} = 0.$$

This results in the new set

$$E_+ = (G/2)^2 + |V_G|, \quad \Psi_+ = \sin(Gx/2), \quad E_- = (G/2)^2 - |V_G|, \quad \Psi_- = \cos(Gx/2).$$

Thus, states bounded by $\frac{G}{2} \leq k \leq (\frac{G}{2} + \frac{\pi}{a})$ belong to a band, as indicated by the bold segments of Figure 14.6.

Hence, we note that the nearly free electron energies are distributed in *bands*. (These bands do not overlap in the one-dimensional case.) The bands are associated with

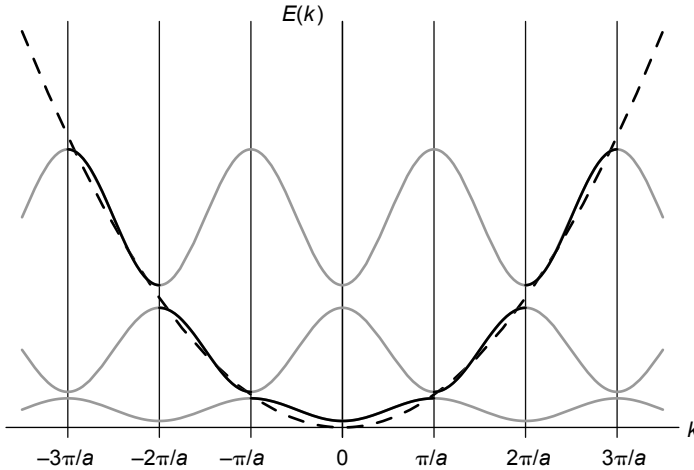


Fig. 14.6. The free electron band structure (dashed parabola) and the three lowest-lying nearly free electron energy bands for a one-dimensional crystal. The sinusoidal curves are the bands in the *repeated* zone scheme. The bold segments of the sinusoidal curves, adjacent to the free electron parabola, represent the band structure in the *extended* zone scheme.

particular $\mathbf{G}$ -vectors. However, when working in the first Brillouin zone, it is customary to use an integer index n as a band index, rather than $\mathbf{G}$, to provide a needed additional index to identify particular wavefunctions and eigenvalues. Thus we write

$$\Psi = \Psi_{n\mathbf{k}}(\mathbf{r}) \quad \text{and} \quad E = E_n(\mathbf{k}). \quad (14.94)$$

This is illustrated in Figure 14.7 in the reduced zone scheme.

We have found that when $\mathbf{k}$ is restricted to the first Brillouin zone, we may think of $\Psi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) = e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$ as being another solution to Schrödinger's equation that belongs to $\mathbf{k}$ rather than to $\mathbf{k} + \mathbf{G}$, but which corresponds to another energy eigenvalue that generally differs from that belonging to $\Psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}$. Thus, in the reduced zone scheme, there is an infinite number of solutions $E_n(\mathbf{k})$ and $\Psi_{n\mathbf{k}}(\mathbf{r})$ for each $\mathbf{k}$, which is why an additional band index is needed. Also, with $N \approx 10^{22}$ electrons/cm³, the discrete values of $\mathbf{k}$ are so densely packed in the Brillouin zone that $E(\mathbf{k})$ is a continuous function for all practical purposes.

Now we consider the case for which V_G is nonzero in higher dimensions. We write down (14.84) with particular values of $\mathbf{k}$ and $\mathbf{G}$. But $C_{\mathbf{k}}(\mathbf{G})$ is connected to all other coefficients $C_{\mathbf{k}}(\mathbf{G}')$, so we must write down still another version of (14.84) with a new value of $\mathbf{G}'$ in the term $C_{\mathbf{k}}(\mathbf{G}')$. In this way, an infinite set of equations is found, one equation for each $\mathbf{G}'$.

We select our first value of $\mathbf{G}$ to be $\mathbf{G} = 0$. A second equation can be written with $\mathbf{G}' = \mathbf{G}_1$, a third with $\mathbf{G}' = \mathbf{G}_2$, and so forth. Of course, in practice we have to truncate to some finite number of terms, but a representative portion of the set of equations looks like this:

$$\begin{aligned} (\varepsilon_{\mathbf{k}} - E) C_{\mathbf{k}}(\mathbf{0}) + V_{\mathbf{G}_1} C_{\mathbf{k}}(\mathbf{G}_1) + V_{\mathbf{G}_2} C_{\mathbf{k}}(\mathbf{G}_2) + V_{\mathbf{G}_3} C_{\mathbf{k}}(\mathbf{G}_3) + \cdots &= 0, \\ (\varepsilon_{\mathbf{k}+\mathbf{G}_1} - E) C_{\mathbf{k}}(\mathbf{G}_1) + V_{\mathbf{G}_1-\mathbf{G}_2} C_{\mathbf{k}}(\mathbf{G}_2) + V_{\mathbf{G}_1-\mathbf{G}_3} C_{\mathbf{k}}(\mathbf{G}_3) + \cdots &= 0, \\ (\varepsilon_{\mathbf{k}+\mathbf{G}_2} - E) C_{\mathbf{k}}(\mathbf{G}_2) + V_{\mathbf{G}_2-\mathbf{G}_1} C_{\mathbf{k}}(\mathbf{G}_1) + V_{\mathbf{G}_2-\mathbf{G}_3} C_{\mathbf{k}}(\mathbf{G}_3) + \cdots &= 0. \end{aligned} \quad (14.95)$$

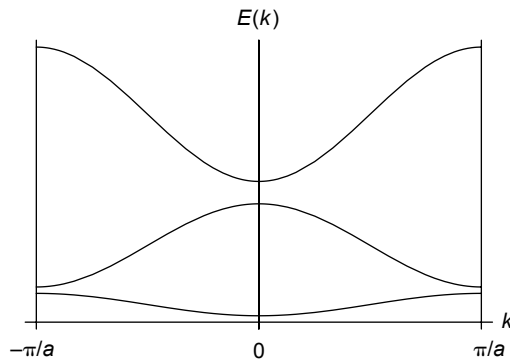


Fig. 14.7. Nearly free electron band structure of Figure 14.6 in the reduced zone scheme. This is obtained by translating the bold segments of Figure 14.6 by $\mathbf{G}$ -vectors to bring them into the first Brillouin zone.

We can gain some insight into the coefficients that must be included if we rewrite (14.84) as

$$C_{\mathbf{k}}(\mathbf{G}) = \frac{\sum_{\mathbf{G}'} V_{\mathbf{G}-\mathbf{G}'} C_{\mathbf{k}}(\mathbf{G}')}{(\varepsilon_{\mathbf{k}-\mathbf{G}'} - E)}. \quad (14.96)$$

The coefficient $C_{\mathbf{k}-\mathbf{G}'}$ will be large if $\varepsilon_{\mathbf{k}-\mathbf{G}'} \simeq E$. Thus, we find the condition for strong coupling of the coefficients is that $\varepsilon_{\mathbf{k}} = \varepsilon_{\mathbf{k}-\mathbf{G}'}$. Clearly, it is necessary, as a minimum, to include *all* values of $\mathbf{G}'$ such that $\mathbf{k}' = \mathbf{k} - \mathbf{G}'$ and for which $\varepsilon_{\mathbf{k}} = \varepsilon_{\mathbf{k}-\mathbf{G}'}$. We now illustrate this point by calculating the low-lying energy values for aluminum at the W point.

Example 14.2

The W point in aluminum

Aluminum is face-centered cubic. Its Brillouin zone is shown in Figure 14.4. We wish to determine the lowest-lying energy levels at the W point. We designate the wavevector of this point by $\mathbf{k}_W$,

$$\mathbf{k}_W = \frac{2\pi}{a} \begin{bmatrix} 1 & \frac{1}{2} & 0 \end{bmatrix}, \quad (14.97)$$

with respect to the Cartesian coordinate system of Figure 14.4, and we have just this one $\mathbf{k}$ -value in mind.

By inspection of the Brillouin zone it is clear that there are 24 equivalent W points on the surface of the Brillouin zone. These points are the corners of the six squares that make up part of the surface. Of these points, only three are connected to $\mathbf{k}_W$ by a $\mathbf{G}$ -vector. These are $\mathbf{G}$ -vectors that *must* be included in any calculation of the energies in the presence of a finite potential. They connect $\mathbf{k}_W$ to equivalent $\mathbf{k}$ -vectors, given by

$$\begin{aligned} \mathbf{k}_2 &= \frac{2\pi}{a} \begin{bmatrix} \bar{1} & \frac{1}{2} & 0 \end{bmatrix} = \mathbf{k}_W - \frac{2\pi}{a} [200] = \mathbf{k}_W - \mathbf{G}_{200}, \\ \mathbf{k}_3 &= \frac{2\pi}{a} \begin{bmatrix} 0 & \bar{1} & \bar{1} \end{bmatrix} = \mathbf{k}_W - \frac{2\pi}{a} [111] = \mathbf{k}_W - \mathbf{G}_{111}, \\ \mathbf{k}_4 &= \frac{2\pi}{a} \begin{bmatrix} 0 & \bar{1} & 1 \end{bmatrix} = \mathbf{k}_W - \frac{2\pi}{a} [11\bar{1}] = \mathbf{k}_W - \mathbf{G}_{11\bar{1}}, \end{aligned} \quad (14.98)$$

with $\mathbf{k}_1 = \mathbf{k}_W$. The relevant $\mathbf{G}$ -vectors can be found from inspection of Figure 14.4, for we observe that the planes bounding the Brillouin zone in the vicinity of $\mathbf{k}_W$ are the (200), (111), and (11 $\bar{1}$) planes. The $\mathbf{G}$ -vectors perpendicular to these planes enter into (14.95). Note that these planes and $\mathbf{G}$ -vectors are indexed with respect to the Cartesian coordinate system.

Basis functions chosen in this manner are generally not eigenfunctions. Indeed, the four basis functions,

$$e^{i(2\pi/a)[1 \frac{1}{2} 0] \cdot \mathbf{r}}, e^{i(2\pi/a)[\bar{1} \frac{1}{2} 0] \cdot \mathbf{r}}, e^{i(2\pi/a)[0 \frac{\bar{1}}{2} \bar{1}] \cdot \mathbf{r}}, e^{i(2\pi/a)[0 \frac{\bar{1}}{2} 1] \cdot \mathbf{r}}, \quad (14.99)$$

corresponding to $\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3$, and $\mathbf{k}_4$ are *not* eigenfunctions. In our present approach, which does not make use of group theory, we find the eigenfunctions after determining the eigenvalues. We remedy this deficiency, beginning with the next section.

The four eigenvalues, corresponding to the four equivalent $\mathbf{k}$ values, $\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3$, and $\mathbf{k}_4$, are all plotted at the W point in the electron energy band diagram. These are the four degenerate lowest eigenvalues at W in the free electron band diagram of Figure 14.5. We now find a splitting of these lowest-lying degenerate energy levels because of the introduction of a periodic potential.

A key point One can easily lapse into carelessness and think of the $\mathbf{G}$ -vector denoted by, say, $[100]$ as representing a $\mathbf{G}$ -vector in the $\mathbf{k}_x$ direction, when it is actually indexed with respect to primitive reciprocal lattice vectors that are not directed along Cartesian coordinate axes, or vice versa. Similarly, one must know the coordinate system used for labeling $\mathbf{k}$ values. We have labeled a vector from the origin to the W point as $[1\frac{1}{2}0]$, indexed with respect to the Cartesian coordinate system of Figure 14.4, meaning $[HKL] = [1\frac{1}{2}0]$, but it is quite common to find $\mathbf{k}_W$ labeled as $[\frac{1}{2}\frac{1}{2}\frac{3}{4}]$, labeled with respect to the primitive $\mathbf{G}$ -vectors of (14.16), meaning $[hkl] = [\frac{1}{2}\frac{1}{2}\frac{3}{4}]$. One must be alert to the convention being followed.

In aluminum at the W point, all the higher bands are sufficiently far away that in the presence of a weak periodic potential (a pseudopotential to be justified later) we can make a reasonably accurate calculation of the splitting of the four lowest bands by ignoring all bands other than these four lowest bands, and treating their effect later as a second-order perturbation.

We obtain the following matrix eigenvalue equation involving $\mathbf{G}' = 0$ and $\mathbf{G}_{200}, \mathbf{G}_{111}$, and $\mathbf{G}_{1\bar{1}\bar{1}}$,

$$\begin{bmatrix} (\varepsilon_{1\frac{1}{2}0} - E) & V_{200} & V_{111} & V_{1\bar{1}\bar{1}} \\ V_{200} & (\varepsilon_{\bar{1}\frac{1}{2}0} - E) & V_{\bar{1}\bar{1}1} & V_{\bar{1}\bar{1}\bar{1}} \\ V_{\bar{1}\bar{1}\bar{1}} & V_{\bar{1}\bar{1}1} & (\varepsilon_{0\frac{1}{2}\bar{1}} - E) & V_{00\bar{2}} \\ V_{\bar{1}\bar{1}1} & V_{\bar{1}\bar{1}\bar{1}} & V_{00\bar{2}} & (\varepsilon_{0\frac{1}{2}1} - E) \end{bmatrix} \begin{bmatrix} C_{1\frac{1}{2}0} \\ C_{\bar{1}\frac{1}{2}0} \\ C_{0\frac{1}{2}\bar{1}} \\ C_{0\frac{1}{2}1} \end{bmatrix} = 0. \quad (14.100)$$

Note that each permutation of a subscript for V appears exactly once, and that the subscripts on V are antisymmetric about the matrix diagonal. This can be used as an error check on the matrix here and in other cases.

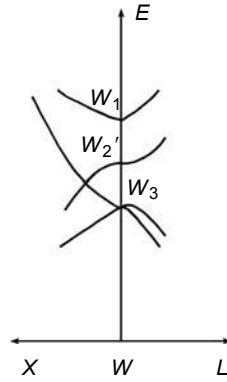
All the free electron energies in (14.100) are equal and thus we can replace each one by ε . Similarly, $V_{200} = V_{\bar{2}00} = V_{002} = V_{00\bar{2}}$, so we can replace these with just V_4 , where the subscript 4 is the sum of the squares of 2, 0, and 0. All the permutations of V_{111} can be replaced by a single V_3 , where the subscript 3 is the sum of the squares of 1, 1, and 1. This simplification is due to the fact that monatomic aluminum has the holohedral symmetry of the cubic lattice.

After a bit of tedious algebra, we find from (14.100) the four lowest energy solutions for E at the W point:

$$\begin{aligned} E &= \varepsilon + 2V_3 + V_4, \\ E &= \varepsilon - 2V_3 + V_4, \\ E &= \varepsilon - V_4 \quad (\text{doubly degenerate}). \end{aligned} \quad (14.101)$$

Table 14.2. *Eigenfunction coefficients (not normalized) for the W point of a face-centered cubic lattice.*

Energy	$C_{1\frac{1}{2}0}$	$C_{\bar{1}\frac{1}{2}0}$	$C_{0\frac{1}{2}\bar{1}}$	$C_{0\frac{1}{2}1}$
$E_1(\mathbf{k}_W) = \varepsilon + 2V_3 + V_4$	1	1	1	1
$E_2(\mathbf{k}_W) = \varepsilon - 2V_3 + V_4$	1	1	-1	-1
$E_3(\mathbf{k}_W) = \varepsilon - V_4$	2	-2	0	0
$E_4(\mathbf{k}_W) = \varepsilon - V_4$	0	0	-2	2

Fig. 14.8. The splitting at the W point in Al.

A schematic of the splitting is shown in Figure 14.8.

If we substitute the energy eigenvalues for the W point into (14.100), we can solve for the coefficients $C_{\mathbf{k}}(\mathbf{G})$ that determine the eigenfunctions

$$\Psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}. \quad (14.102)$$

The eigenfunctions for the W point are thus given by

$$\begin{aligned} \Psi_{\mathbf{k}_W,1}(\mathbf{r}) &= \frac{1}{\sqrt{4\Omega}} \left\{ e^{i(2\pi/a)[1\frac{1}{2}0]\cdot\mathbf{r}} + e^{i(2\pi/a)[\bar{1}\frac{1}{2}0]\cdot\mathbf{r}} \right. \\ &\quad \left. + e^{i(2\pi/a)[0\frac{1}{2}\bar{1}]\cdot\mathbf{r}} + e^{i(2\pi/a)[0\frac{1}{2}1]\cdot\mathbf{r}} \right\}, \\ \Psi_{\mathbf{k}_W,2}(\mathbf{r}) &= \frac{1}{\sqrt{4\Omega}} \left\{ e^{i(2\pi/a)[1\frac{1}{2}0]\cdot\mathbf{r}} + e^{i(2\pi/a)[\bar{1}\frac{1}{2}0]\cdot\mathbf{r}} \right. \\ &\quad \left. - e^{i(2\pi/a)[0\frac{1}{2}\bar{1}]\cdot\mathbf{r}} - e^{i(2\pi/a)[0\frac{1}{2}1]\cdot\mathbf{r}} \right\}, \end{aligned}$$

$$\begin{aligned}\Psi_{\mathbf{k}\mathbf{W},3}(\mathbf{r}) &= \frac{1}{\sqrt{2\Omega}} \left\{ e^{i(2\pi/a)[1\frac{1}{2}\mathbf{0}]\cdot\mathbf{r}} - e^{i(2\pi/a)[\bar{1}\frac{1}{2}\mathbf{0}]\cdot\mathbf{r}} \right\}, \\ \Psi_{\mathbf{k}\mathbf{W},4}(\mathbf{r}) &= \frac{1}{\sqrt{2\Omega}} \left\{ e^{i(2\pi/a)[0\frac{1}{2}\mathbf{1}]\cdot\mathbf{r}} - e^{i(\frac{2\pi}{a})[0\frac{1}{2}\bar{1}]\cdot\mathbf{r}} \right\},\end{aligned}$$

where the prefactor $1/\sqrt{4\Omega}$ or $1/\sqrt{2\Omega}$ normalizes the wavefunction over the volume, Ω , of the unit cell. The last two eigenfunctions belong to the doubly degenerate eigenvalue $\varepsilon - V_4$.

Finding the eigenvalues and eigenfunctions in the “brute force” way we have done is equivalent to diagonalizing the secular equation (14.100). It automatically leads to eigenfunctions that are either symmetrized basis functions or a linear combination of symmetrized basis functions, a topic to be taken up in the next section.

Let us be clear about what we have done by means of an illustration from a slightly different viewpoint. If we operate on the Schrödinger equation,

$$\hat{H}\Psi = E\Psi,$$

from the left, by Ψ^* , rearrange terms and integrate we have

$$\int \Psi^*(\mathbf{r})[\hat{H} - E]\Psi(\mathbf{r})d\mathbf{r} = 0. \quad (14.103)$$

If we have a set of four basis functions, $\Psi_1, \Psi_2, \Psi_3, \Psi_4$, a nontrivial solution exists only if the determinantal equation equals zero:

$$\begin{vmatrix} (H_{11} - E) & H_{12} & H_{13} & H_{14} \\ H_{21} & (H_{22} - E) & H_{23} & H_{24} \\ H_{31} & H_{32} & (H_{33} - E) & H_{34} \\ H_{41} & H_{42} & H_{43} & (H_{44} - E) \end{vmatrix} = 0. \quad (14.104)$$

If the basis functions are not symmetrized, as in our example above, we must diagonalize the entire matrix at once. On the other hand, if we had used symmetrized wave functions as basis functions, the matrix would be in block form, or even may be automatically diagonalized.

Let us consider a typical matrix element, say H_{23} , in (14.104). Using the now-known eigenfunctions, we find, for the contribution of the potential energy term to the matrix element, that

$$\begin{aligned}V_{23} &= \int d\mathbf{r} \Psi_{\mathbf{k}_2}^*(\mathbf{r}) \hat{V}(\mathbf{r}) \Psi_{\mathbf{k}_3}(\mathbf{r}) \\ &\sim \int d\mathbf{r} \left[e^{-i(2\pi/a)[1\frac{1}{2}\mathbf{0}]\cdot\mathbf{r}} + e^{-i(2\pi/a)[\bar{1}\frac{1}{2}\mathbf{0}]\cdot\mathbf{r}} - e^{-i(2\pi/a)[0\frac{1}{2}\bar{1}]\cdot\mathbf{r}} \right. \\ &\quad \left. - e^{-i(2\pi/a)[0\frac{1}{2}\mathbf{1}]\cdot\mathbf{r}} \right] V(\mathbf{r}) \left[e^{i(2\pi/a)[1\frac{1}{2}\mathbf{0}]\cdot\mathbf{r}} - e^{i(2\pi/a)[\bar{1}\frac{1}{2}\mathbf{0}]\cdot\mathbf{r}} \right] = 0,\end{aligned} \quad (14.105)$$

where use has been made of the orthonormality of the basis functions over the unit cell and the symmetry $V(\mathbf{r}) = V(-\mathbf{r})$.

We find in this case that *all* the off-diagonal terms are zero and that the determinantal equation is fully diagonalized

$$\begin{vmatrix} [\varepsilon + 2V_3 + V_4] - E & 0 & 0 & 0 \\ 0 & [\varepsilon - 2V_3 + V_4] - E & 0 & 0 \\ 0 & 0 & [\varepsilon - V_4] - E & 0 \\ 0 & 0 & 0 & [\varepsilon - V_4] - E \end{vmatrix} = 0. \quad (14.106)$$

Note that any momentary confusion between terms like V_3 in (14.106) and V_{23} in (14.105) is easily resolved by their context. We mention this in anticipation of a term V_{11} in which the subscript will represent the sum of the squares of 3, 1, and 1 rather than denoting a matrix element.

Construction of symmetry-adapted plane-wave functions and matrix block-diagonalization

When we apply the projection operator $^{(\mathbf{k})}\mathcal{P}$ to a plane-wave $\exp[i\mathbf{k}' \cdot \mathbf{r}]$, we obtain

$$\begin{aligned} ^{(\mathbf{k})}\mathcal{P} e^{i\mathbf{k}' \cdot \mathbf{r}} &= \frac{1}{N} \sum_{\mathbf{t}} ^{(\mathbf{k})}\Delta^*(\mathbf{t}) (E|\mathbf{t}) e^{i\mathbf{k}' \cdot \mathbf{r}} \\ &= \frac{1}{N} \sum_{\mathbf{t}} e^{i\mathbf{k} \cdot \mathbf{t}} e^{i\mathbf{k}' \cdot (\mathbf{r} - \mathbf{t})} = e^{i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}} \delta_{\mathbf{k}', \mathbf{k} + \mathbf{G}}, \end{aligned} \quad (14.107)$$

which allows us to sort these plane-wave functions, for a given wavevector $\mathbf{k}$ in the irreducible zone, according to $|\mathbf{k} + \mathbf{G}| \Rightarrow |\mathbf{k}| < |\mathbf{k} + \mathbf{G}_1| < |\mathbf{k} + \mathbf{G}_2|$, etc.

Next, we operate on the plane-wave $\exp[i(\mathbf{k} + \mathbf{G}_\ell) \cdot \mathbf{r}]$ by the projection operator of the μ th Irrep of the little-group of the first kind $\mathbb{Q}_{\mathbf{k}}$ of dimension d_μ , and obtain a symmetry-adapted wavefunction of the form

$$\begin{aligned} ^{(\mathbf{k}, \mu j)}\Psi_\ell &= ^{(\mathbf{k}, \mu)}\mathcal{P}_{jj}(\mathbb{Q}_{\mathbf{k}}) e^{i(\mathbf{k} + \mathbf{G}_\ell) \cdot \mathbf{r}} \\ &= \frac{d_\mu}{p_{\mathbf{k}}} \sum_{(R|\boldsymbol{\tau}) \in \mathbb{Q}_{\mathbf{k}}} ^{(\mathbf{k}, \mu)}\Lambda_{jj}^*(R|\boldsymbol{\tau}) e^{iR(\mathbf{k} + \mathbf{G}_\ell) \cdot (\mathbf{r} - \boldsymbol{\tau})}. \end{aligned} \quad (14.108)$$

For $\mathbf{k}$ inside the BZ, (14.108) reduces to

$$^{(\mathbf{k}, \mu j)}\Psi_\ell = \frac{d_\mu}{p_{\mathbf{k}}} \sum_{R \in \mathbb{P}_{\mathbf{k}}} ^{(\mu)}\tilde{\Lambda}_{jj}^*(R) e^{-iR\mathbf{G}_\ell \cdot \boldsymbol{\tau}} e^{i(\mathbf{k} + R\mathbf{G}_\ell) \cdot \mathbf{r}}, \quad (14.109)$$

where $^{(\mu)}\tilde{\Lambda}$ is the corresponding Irrep of $\mathbb{P}_{\mathbf{k}}$, the point-group isomorphic to $\mathbb{Q}_{\mathbf{k}}$; while, for $\mathbb{S}$ or $\mathbb{S}_{\mathbf{k}}$ symmorphic and $\mathbf{k}$ lying on the BZ boundary, we have

$$^{(\mathbf{k},\mu j)}\Psi_{\ell} = \frac{d_{\mu}}{p_{\mathbf{k}}} \sum_{R \in \mathbb{P}_{\mathbf{k}}} ^{(\mu)}\tilde{\Lambda}_{jj}^*(R) e^{iR(\mathbf{k}+\mathbf{G}_{\ell})\cdot\mathbf{r}}. \quad (14.110)$$

Notice that symmetrized plane-wave functions belonging to different irreducible zones, i.e. different prongs of $^*\mathbf{k}$, are orthogonal.

Example 14.3

The square-mesh $\mathcal{C}_{4v}$

We discuss the symmetry aspects of the $\bar{\Gamma}$ -point, the $\bar{\Sigma}$ - and $\bar{\Delta}$ -lines, and the $\bar{X}$ - and $\bar{M}$ -points, and we consider only the $\mathbf{G}$ -vectors (00) , $(\ell 0)$, $(\ell \ell)$, and $(2\ell \ell)$.

- (i) **$\bar{\Gamma}$ -point ($\mathcal{C}_{4v}$)** The (00) wave belongs to Γ_1 . For the remaining plane-waves, each set forms a basis for a representation of $\mathcal{C}_{4v}$. For example, in the case of the $(\ell 0)$ set, namely $\begin{bmatrix} (\ell, 0) & (0, \ell) & (-\ell, 0) & (0, -\ell) \end{bmatrix}$, we have

$$\begin{aligned} E &= \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, & C_4 &= \begin{pmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \end{pmatrix}, & C_4^{-1} &= \begin{pmatrix} 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}, \\ \sigma_x &= \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, & \sigma_y &= \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}, & C_2 &= \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}, \\ \sigma_d^1 &= \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}, & \sigma_d^2 &= \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}. \end{aligned}$$

Table 14.3. *Compatibilities.*

Γ_1	Γ_2	Γ_3	Γ_4	Γ_5	$\bar{X}_1$	$\bar{X}_2$	$\bar{X}_3$	$\bar{X}_4$	$\bar{M}_1$	$\bar{M}_2$	$\bar{M}_3$	$\bar{M}_4$	$\bar{M}_5$
$\bar{\Delta}$	$\bar{\Delta}_1$	$\bar{\Delta}_2$	$\bar{\Delta}_1$	$\bar{\Delta}_2$	$\bar{\Delta}_1, \bar{\Delta}_2$	$\bar{\Delta}_1$	$\bar{\Delta}_2$	$\bar{\Delta}_1$	$\bar{\Delta}_2$				
$\bar{\Sigma}$	$\bar{\Sigma}_1$	$\bar{\Sigma}_2$	$\bar{\Sigma}_2$	$\bar{\Sigma}_1$	$\bar{\Sigma}_1, \bar{\Sigma}_2$				$\bar{\Sigma}_1$	$\bar{\Sigma}_2$	$\bar{\Sigma}_2$	$\bar{\Sigma}_1$	$\bar{\Sigma}_1, \bar{\Sigma}_2$
$\bar{Y}$						$\bar{Y}_1$	$\bar{Y}_2$	$\bar{Y}_2$	$\bar{Y}_1$	$\bar{Y}_2$	$\bar{Y}_1$	$\bar{Y}_2$	$\bar{Y}_1, \bar{Y}_2$

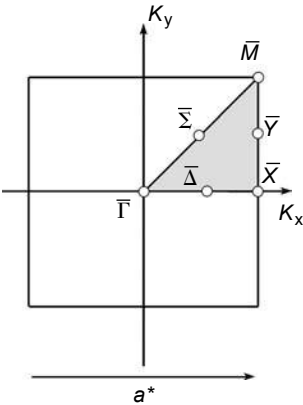


Fig. 14.9. Brillouin zone of a square net (a^* is a basis reciprocal lattice vector).

These Reps have the following characters:

Plane-wave	$\chi(E)$	$\chi(C_4)$	$\chi(C_2)$	$\chi(\sigma)$	$\chi(\sigma_a)$
$(\ell 0)$	4	0	0	1	0
$(\ell \ell)$	4	0	0	0	1
$(2\ell \ell)$	8	0	0	0	0

which yield the following Clebsch–Gordan series

$$\begin{aligned}\Gamma(\ell 0) &= \Gamma_1 + \Gamma_3 + \Gamma_5, \\ \Gamma(\ell \ell) &= \Gamma_1 + \Gamma_4 + \Gamma_5, \\ \Gamma(2\ell \ell) &= \Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4 + 2\Gamma_5.\end{aligned}$$

We then use (14.110) to obtain the following symmetrization coefficients:

Irrep	Row	$(\ell 0)$	$(\bar{\ell} 0)$	(0ℓ)	$(0 \bar{\ell})$	$(\ell \ell)$	$(\bar{\ell} \bar{\ell})$	$(\bar{\ell} \ell)$	$(\ell \bar{\ell})$
Γ_1	1	1	1	1	1	1	1	1	1
Ψ_1		$\cos(2\pi\ell x) + \cos(2\pi\ell y)$				$\cos(2\pi\ell(x+y)) + \cos(2\pi\ell(x-y))$			
Γ_3	1	1	1	-1	-1				
Ψ_3		$\cos(2\pi\ell x) - \cos(2\pi\ell y)$							
Γ_4						1	1	-1	-1
						$\cos(2\pi\ell(x+y)) + \cos(2\pi\ell(x-y))$			
Γ_5	1	1	-1	0	0	1	-1	0	0
Ψ_5^1		$\sin(2\pi\ell x)$				$\sin(2\pi\ell(x+y))$			
	2	0	0	1	-1	0	0	1	-1
Ψ_5^2				$\sin(2\pi\ell y)$				$\sin(2\pi\ell(x-y))$	

As for the plane-wave set $(2\ell\ell)$, we have

Irrep	Row	$(2\ell\ell)$	$(\bar{2}\ell\bar{\ell})$	$(\bar{2}\ell\ell)$	$(2\ell\bar{\ell})$	$(\ell 2\ell)$	$(\bar{\ell}\bar{2}\ell)$	$(\bar{\ell}2\ell)$	$(\ell\bar{2}\ell)$
Γ_1	1	1	1	1	1	1	1	1	1
Γ_2	1	1	1	1	1	-1	-1	-1	-1
Γ_3	1	1	1	1	1	-1	-1	-1	-1
Γ_4	1	1	1	-1	-1	1	1	-1	-1
Γ_5	1	1	-1	0	0	0	0	0	0
	2	0	0	0	0	0	0	1	-1
	1	0	0	1	-1	0	0	0	0
	2	0	0	0	0	1	-1	0	0

- (ii) **The $\bar{\Delta}$ -direction**, $\mathcal{G}_{\Delta} = \{E, \sigma_y\}$, **and the $\bar{\Sigma}$ -direction**, $\mathcal{G}_{\Sigma} = \{E, \sigma_{xy}\}$
 Compatibilities:

$$\bar{\Gamma}_1 \Rightarrow \bar{\Delta}_1 : (k0)$$

$$\bar{\Gamma}_1, \bar{\Gamma}_3, \bar{\Gamma}_5^1 \Rightarrow \bar{\Delta}_1 : \begin{cases} (k \pm \ell, 0) \\ (k\ell) + (k\bar{\ell}) \\ (k \pm \ell, \ell) + (k \pm \ell, \bar{\ell}) \end{cases}$$

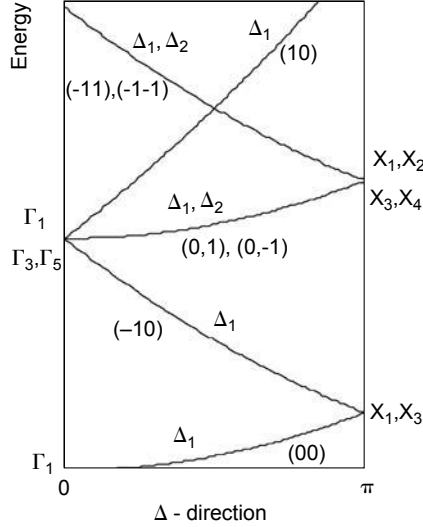


Fig. 14.10. Two-dimensional bands.

$$\bar{\Gamma}_4, \bar{\Gamma}_5^2 \Rightarrow \bar{\Delta}_2 : \begin{cases} (k\ell) - (k\bar{\ell}) \\ (k \pm \ell, \pm \ell) - (k \pm \ell, \mp \ell) \end{cases}$$

(iii) **The $\bar{X}$ -point** $(\pi, 0)$, $\mathcal{G}_X = C_{2v}$ In these cases we first determine the plane-wave set $R(\mathbf{k} + \mathbf{G}_\ell)$; we get

$$\begin{aligned} (00) &\rightarrow \left(0, \frac{1}{2}\right) & (\ell 0) &\rightarrow \begin{cases} \left(\pm\ell + \frac{1}{2}\right) \\ \pm \left(\frac{\ell}{2}\right) \end{cases} \\ (\ell\ell) &\rightarrow \left(\left(\pm\ell + \frac{1}{2}\right) \pm \ell\right) \end{aligned}$$

For the cases $\ell = 1$, $0 \leq k \leq 1$, we have:

$$\begin{aligned} \bar{\Delta}_1 \left[\begin{array}{c} k\pi, 0 \\ (k-2)\pi, 0 \end{array} \right] &\Rightarrow \begin{cases} \bar{X}_1 : \cos(\pi x) \\ \bar{X}_3 : \sin(\pi x) \end{cases} \\ \bar{\Delta}_1, \bar{\Delta}_2 \left[\begin{array}{c} (k\pi, \pm 2\pi) \\ (k-2)\pi, \pm 2\pi \end{array} \right] &\Rightarrow \begin{cases} \bar{X}_1 : \cos(\pi(x+2y)) + \cos(\pi(x-2y)) \\ \bar{X}_2 : \cos(\pi(x+2y)) - \cos(\pi(x-2y)) \\ \bar{X}_3 : \sin(\pi(x+2y)) + \sin(\pi(x-2y)) \\ \bar{X}_4 : \sin(\pi(x+2y)) - \sin(\pi(x-2y)) \end{cases} \end{aligned}$$

Projection of symmetry-adapted plane-waves

In all band-computation methods employing a plane-wave (PW) basis, the projection of symmetry-adapted PWs is desirable. Example 14.3 provides a clear illustration of the projection process. Here, we outline a generalized procedure for the construction of the corresponding projection operators [7].

We first determine the group of the wavevector $G_{\mathbf{k}}$. Next, we select a set of representative $\mathbf{G}$ -vectors with norms less than a prescribed value, say $G_{\max}$, and form the PWs

$$\exp [i(\mathbf{k} + \mathbf{G}_n) \cdot \mathbf{r}], \quad n = 1, \dots, r.$$

By operating on the PWs $(\mathbf{k} + \mathbf{G}_n)$ with all $R_i \in G_{\mathbf{k}}$, we generate an expanded s -component basis set,

$$R_i(\mathbf{k} + \mathbf{G}_n) = (\mathbf{k} + \mathbf{G}_n^m).$$

We relabel this set from $k1$ to ks , namely,

$$\Psi_{\mathbf{k}} = \{ \phi_{k1}, \dots, \phi_{ks} \},$$

such that

$$\begin{aligned} (R_i|\tau_i) \phi_{kn} &= (R_i|\tau_i) \exp [i(\mathbf{k} + \mathbf{G}_n) \cdot \mathbf{r}] = \exp [i(\mathbf{k} + \mathbf{G}_n) \cdot (R_i^{-1}|\tau_i) \mathbf{r}] \\ &= \exp [i(\mathbf{k} + \mathbf{G}_n^\ell) \cdot \tau] \exp [i(\mathbf{k} + \mathbf{G}_n^\ell) \cdot \mathbf{r}] \\ &= \exp [-i(\mathbf{k} + \mathbf{G}_n^\ell) \cdot \tau] \phi_{km}, \end{aligned}$$

thus engendering a tensor field $\text{Rep}^{(\mathbf{k})} \Gamma$

$$(R_i|\tau_i) \Psi_{\mathbf{k}} = \Psi_{\mathbf{k}}^{(\mathbf{k})} \Gamma [(R_i|\tau_i)], \quad (14.111)$$

where

$$^{(\mathbf{k})} \Gamma [(R_i|\tau_i)]_{mn} = \begin{cases} \exp [-i(\mathbf{k} + \mathbf{G}_m) \cdot \tau_i] & R_i(\mathbf{k} + \mathbf{G}_n) = \mathbf{k} + \mathbf{G}_m, \\ 0 & \text{otherwise.} \end{cases} \quad (14.112)$$

We now construct the projection operator for the i th row of allowable Irrep μ of $G_{\mathbf{k}}$ as

$$^{(\mathbf{k}, \mu)} \mathcal{P}_{ii} = \frac{d_\mu}{g_{\mathbf{k}}} \sum_{R_i \in G_{\mathbf{k}}} \Delta_{ii}^{(\mathbf{k}, \mu)} ((R_i|\tau_i))^{(\mathbf{k})} \Gamma [(R_i|\tau_i)]. \quad (14.113)$$

Symmetry-projected matrix elements By simply writing the electron system Hamiltonian as

$$\mathcal{H} = -\frac{\hbar^2}{2m} \nabla^2 + U(\mathbf{r}),$$

we obtain the symmetrized matrix element as

$$\begin{aligned}
 \mathcal{H}_{\ell\ell'}(\mathbf{k}, \mu j) &= \left\langle {}^{(\mathbf{k}, \mu j)}\psi_{\ell} \left| \mathcal{H} \right| {}^{(\mathbf{k}, \mu j)}\psi_{\ell'} \right\rangle \\
 &= \left\langle e^{i(\mathbf{k}+\mathbf{G}_{\ell})\cdot\mathbf{r}} \left| {}^{(\mathbf{k}, \mu)}\mathcal{P}_{jj} \mathcal{H} {}^{(\mathbf{k}, \mu)}\mathcal{P}_{jj} \right| e^{i(\mathbf{k}+\mathbf{G}_{\ell'})\cdot\mathbf{r}} \right\rangle \\
 &= -\frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}_{\ell}|^2 \delta_{\ell, \ell'} + \left\langle e^{i(\mathbf{k}+\mathbf{G}_{\ell})\cdot\mathbf{r}} \left| U^{(\mu)}\mathcal{P}_{jj}(\mathbb{P}_{\mathbf{k}}) \right| e^{i(\mathbf{k}+\mathbf{G}_{\ell'})\cdot\mathbf{r}} \right\rangle \\
 &= -\frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}_{\ell}|^2 \delta_{\ell, \ell'} + \sum_{R \in \mathbb{P}_{\mathbf{k}}} {}^{(\mu)}\Gamma_{jj}^*(R) U(\mathbf{K}_R), \tag{14.114}
 \end{aligned}$$

where

$$\mathbf{K}_R = R\mathbf{G}_{\ell'} - \mathbf{G}_{\ell},$$

and we used the Hermitian and idempotent properties of ${}^{(\mu)}\mathcal{P}_{jj}$. This symmetrized secular equation constitutes a matrix of infinite order, which is usually truncated by treating large $|\mathbf{k} + \mathbf{G}|$ s in a second-order perturbation series. However, because the crystal potential comprises a superposition of atomic potentials, a very large number of symmetrized plane-wave functions has to be employed in order to accurately represent the rapid oscillations of the wavefunction at atomic sites. This has the serious drawback of very low convergence of the calculations.

Program for constructing symmetry-adapted plane-waves

We present here program **SYMPW** that generates symmetry projection operators for constructing symmetry-adapted plane-wave functions and for block-diagonalizing the Hamiltonian matrix elements. We use the diamond structure as our example.

Program SYMPW

Required input data and *Mathematica* packages

Example: *Diamond structure*

```
<< C:file-path/Oh.m
```

```
<< C:file-path/DIAMOND.m
```

```
<< C:file-path/SPGR.nb
```

```
⇒ Files Oh and DIAMOND contains all the required
information about the diamond structure and its symmetry.
```

```
While Program SPGR generates all the symmetry and
structural information required. <=
```

```
<< DiscreteMath`Combinatorica`
<< NumberTheory`NumberTheoryFunctions`
```

Program SPGR was presented in Section 10.5.5; it generates space-group elements in Cartesian matrix form, `Rot[i]`, and gives the primitive and reciprocal lattice vectors, `RL` and `G`, respectively. The `G`-vectors are used to define the Brillouin zone, while the wavevectors along high-symmetry directions are defined in file `DIAMOND` as the `Array`:

$$\mathbf{Q} = \left\{ \Gamma : \{0, 0, 0\}, \Gamma_{\Delta X} : \{0, 0, 1\}, \right. \\ \left. \Gamma_{\Sigma K} : \{3/4, 3/4, 0\}, \Gamma_{\Lambda L} : \{1/2, 1/2, 1/2\} \right\},$$

with the number of wavevectors along these directions defined in `Array NQ`,

$$\mathbf{NQ} = \{1, 5, 4, 4\}.$$

Other quantities provided by SPGR and its input data files are not relevant here.

Rotation matrices in lattice coordinates

```
Do[
  RotG[i] = Transpose[RL].Rot[i].G, {i, 1, g}
];



---


GENERATE SHORTEST G-SETS

GM = 10;  ⇒  G2 of longest G-vector;
GX = {}; ng = 0; GN = {};
Do[ GY = Simplify[(1-1)*G[[1]] + (m-1)*G[[2]] + (n-1)*G[[3]]];
  Switch[And[G[[1]] ≥ 0, G[[2]] ≥ 0, G[[3]] ≥ 0, GY.GY ≤ GM],
    True, PM = Permutations[G];
    XT = 0;
  Do[
    Switch[FreeQ[GX, PM[[ij]]],
      False, XT = 1
    ], {ij, 1, Length[PM]}
  ];
];
```

```

Switch[XT == 0,
      True, AppendTo[GX, GY];
      AppendTo[GN, GY-GY]; ng + +
]
], {1, 1, 5}, {m, 1, 5}, {n, 1, 5}
];
Print["The number of generating Gs for Wavevector = ", K,
      " is ", ng];
GNN = Ordering[GN];

STORE THE G-REPRESENTATIVES IN INCREASING ORDER
GZ = {};
Do[
  ll = GNN[[j]];
  AppendTo[GZ, GX[[ll]]], {j, 1, ng}
];
Print[" G-sets are : ", MatrixForm[GZ]];

```

SYMMETRY-ADAPTED PLANE-WAVES

```

Do[
  K = Transpose[RL].Q[[i]];

  1. Determine the group of the wavevector, GK, of order ngk.

  GK = {1}; ngk = 1;
  Do[
    KK = RoG[jj].K;
    Switch[KK == Mod[K, 1],
      True, AppendTo[GK, jj]; ngk + +
    ], {jj, 2, g}
]; Print["GK = ", GK];

```

2. Generate sets of symmetry-adapted plane-waves $K + G$

```

GL = {};
Do[

```

```

Switch[(Q[[i]] + GZ[[ji]])· (Q[[i]] + GZ[[ji]]) < GM,
  True,
  KG = Q[[i]] + GZ[[ji]]; Print["K + G = ", KG];
  GGL = {KG}; nbasis = 1;
  Do[
    RK = GK[[lk]]; RG = Rot[RK].KG;
    Switch[FreeQ[GGL, RG],
      True, AppendTo[GGL, RG]; nbasis + +
    ], {lk, 1, ngk}
  ];
  Print["number of symmetry-adapted planewaves of
    type ", GZ[[ji]], " = ", nbasis];
  Print["GGL = ", MatrixForm[GGL]];

```

3. Construct the Rep engendered by the basis-set K + G

```

IDP = IdentityMatrix[nbasis]; PERM = IDP; ZRO = 0*IDP;
Do[
  Rog = ZRO;
  Do[
    RK = GK[[lk]]; RV = Rot[RK].GGL[[jm]];
    Do[
      Switch[RV == GGL[[km]],
        True, RGR = 2π * (GGL[[km]].Tau1[[RK]]);
        RGG = Simplify[Exp[-I RGR]];
        Rog[[jm, km]] = RGG
      ], {km, 1, nbasis}
    ], {jm, 1, nbasis}
  ]; AppendTo[PERM, Rog], {lk, 2, ngk}
];
Proj = Sum[PERM[[lm]],lm,ngk];
Proj = Simplify[Proj/ngk];
Print["Proj = ",MatrixForm[Proj]];
Sympro = {}; EGV = Eigenvalues[Proj];
Print["Eigenvalues[" , mu, "] = ", EGV];

```

```

EV = Eigenvectors[Proj];
Do[
  Switch[EGV[[ig]] == 1,
    True,
    AppendTo[Sympro, EV[[ig]]]
  ], {ig, 1, nbasis}
];
Write["C:/path/diamondout.txt",
  "Symmetry-adapted eigenvectors:", MatrixForm[Sympro]]
Print["Symmetry-adapted eigenvectors:", MatrixForm[Sympro]]
], {ji, 2, 4}
], {i, 1, 1} ];

```

Example 14.4

The diamond structure, $\mathcal{O}_h^7$

We consider the Γ -point, and include plane-waves with $\mathbf{G} = (0,0,0)$ (1), $2\pi(\ell, \ell, \ell)$ (8), and $2\pi(\ell, 0, 0)$ (6). It is obvious that the $\mathbf{G} = (0,0,0)$ vector belongs to $^{(1)}\Gamma^+$. The Rep characters of the remaining two bases are:

		E	$6(C_4 \boldsymbol{\tau})$	$3C_2$	$6(C'_2 \boldsymbol{\tau})$	$8C_3$	$(I \boldsymbol{\tau})$	$6IC_4$	$8(IC_3 \boldsymbol{\tau})$	$6\sigma_d$	$3(\sigma \boldsymbol{\tau})$
$(\ell\ell\ell)$	χ	8	0	0	0	2	0	0	0	4	0
$(\ell 00)$	χ	6	-2	2	0	0	0	0	0	2	-4

where $\boldsymbol{\tau} = (111)/4$ corresponds to a basis at (000) and $(111)/4$. This leads to the Clebsch-Gordan series

$$\Gamma(\ell\ell\ell) = {}^{(1)}\Gamma^+(\Gamma_1) + {}^{(2)}\Gamma^-(\Gamma'_2) + {}^{(4)}\Gamma^-(\Gamma_{15}) + {}^{(5)}\Gamma^+(\Gamma'_{25}),$$

$$\Gamma(\ell 00) = {}^{(2)}\Gamma^-(\Gamma'_2) + {}^{(3)}\Gamma^-(\Gamma'_{12}) + {}^{(5)}\Gamma^+(\Gamma'_{25}).$$

The symmetrization coefficients, referred to the *standard origin*,

$$\mathbf{a} = (111)/8$$

are listed in the two tables below. For the standard origin, the nonprimitive translations become

$$(R|\boldsymbol{\tau}') = (E|\mathbf{a})^{-1}(R|\boldsymbol{\tau})(E|\mathbf{a}) = (R|(E + R)\boldsymbol{\tau}/2).$$

The point-groups of the plane-wave sets are

$$\begin{aligned}\mathbb{P}_{\ell\ell\ell} &= \mathcal{C}_{3v} = \{E, C_3^{xyz}, C_3^{\bar{x}\bar{y}\bar{z}}, \sigma_d^{xy}, \sigma_d^{yz}, \sigma_d^{z\bar{x}}\}, \\ \mathbb{P}_{\ell 00} &= \mathcal{C}_{4v} = \{E, C_4^x, C_4^{\bar{x}}, C_2^x, \sigma_y, \sigma_z, \sigma_{yz}, \sigma_{y\bar{z}}\},\end{aligned}$$

with coset expansions

$$\begin{aligned}\mathcal{O}_h &= \{E + C_{2x} + C_{2y} + C_{2z} + I + IC_{2x} + IC_{2y} + IC_{2z}\} \mathbb{P}_{\ell\ell\ell} \\ &= \{E + C_3^{xyz} + C_3^{\bar{x}\bar{y}\bar{z}} + I + IC_3^{xyz} + IC_3^{\bar{x}\bar{y}\bar{z}}\} \mathbb{P}_{\ell 00}.\end{aligned}$$

Plane-wave type	Row	$(\ell\ell\ell)$ E	$(\bar{\ell}\bar{\ell}\bar{\ell})$ I	$(\ell\ell\bar{\ell})$ IC_{2z}	$(\bar{\ell}\bar{\ell}\ell)$ C_{2z}	$(\ell\bar{\ell}\bar{\ell})$ C_{2x}	$(\bar{\ell}\ell\ell)$ IC_{2x}	$(\bar{\ell}\bar{\ell}\bar{\ell})$ C_{2y}	$(\ell\bar{\ell}\ell)$ IC_{2y}
$(1)\Gamma^+$	1	1	1	-1	-1	-1	-1	-1	-1
$(2)\Gamma^-$	1	1	-1	1	-1	1	-1	1	-1
$(4)\Gamma^-$	1	1	-1	-1	1	-1	1	1	-1
	2	1	-1	-1	1	1	-1	-1	1
	3	1	-1	1	-1	1	-1	1	-1
$(5)\Gamma^+$	1	1	1	1	1	-1	-1	1	1
	2	1	1	1	1	1	1	-1	-1
	3	1	1	-1	-1	1	1	1	1

Plane-wave type	Row	$(\ell 00)$ E	$(\bar{\ell} 00)$ I	$(0\ell 0)$ C_3^{xyz}	$(0\bar{\ell} 0)$ $IC_3^{\bar{x}\bar{y}\bar{z}}$	(00ℓ) $C_3^{\bar{x}\bar{y}\bar{z}}$	$(00\bar{\ell})$ IC_3^{xyz}
$(2)\Gamma^-$	1	1	1	1	1	1	1
$(3)\Gamma^-$	1	1	1	1	1	1	1
	2	1	1	1	1	1	1
$(5)\Gamma^+$	1	1	1	1	1	1	1
	2	1	1	1	1	1	1
	3	1	1	1	1	1	1

Orthogonalized plane-wave (OPW) method

This method, proposed by Herring in 1940, circumvents the convergence problem through orthogonalizing the plane-wave functions to the ionic-core states, which carry the rapid oscillations that occur in the core region. The core states, $|(\mathbf{k}, \mu j, c)\rangle$, where indexed by c , are expected to remain largely unchanged in the condensed matter system environment. The orthogonalization can be simply effected with the aid of the projection operator $\sum_c |\mathbf{k}, \mu j, c\rangle \langle \mathbf{k}, \mu j, c|$; we write

$$|\mathbf{k}, \mu j, \ell; \text{opw}\rangle = |\mathbf{k}, \mu j, \ell\rangle - \sum_c |\mathbf{k}, \mu j, c\rangle \langle \mathbf{k}, \mu j, c | (\mathbf{k}, \mu j, \ell) \quad (14.115)$$

with

$$\langle \mathbf{k}, \mu j, \ell; c | \mathbf{k}, \mu j, \ell'; \text{opw}\rangle = 0, \quad (14.116)$$

$$\langle \mathbf{k}, \mu j, \ell; \text{opw} | \mathbf{k}, \mu j, \ell'; \text{opw}\rangle = \delta_{\ell\ell'} - \sum_c \langle \mathbf{k}, \mu j, \ell | \mathbf{k}, \mu j, c\rangle \langle \mathbf{k}, \mu j, c | \mathbf{k}, \mu j, \ell'\rangle, \quad (14.117)$$

The valence wavefunction is then constructed through varying the linear combination of the OPWs

$$\Psi(\mathbf{k}, \mathbf{r}) = \sum_{\ell} \alpha_{\mathbf{k}-\mathbf{G}_{\ell}} |\mathbf{k}, \mu j, \ell; \text{opw}\rangle \quad (14.118)$$

with respect to its coefficients $\alpha_{\mathbf{k}-\mathbf{G}_{\ell}}$. Unfortunately, a variational calculation for the coefficients α runs into the further complication presented by (14.117), namely, that these basis functions are not orthogonal. This difficulty can, however, be taken care of by standard algebraic procedures: the result is that the matrix for the coefficients $\alpha_{\mathbf{k}-\mathbf{G}}$, whose secular determinant must vanish at the energy eigenvalue $\mathcal{E}$, contains matrix elements of the form

$$\begin{aligned} & \langle \mathbf{k}, \mu j, \ell; \text{opw} | \mathcal{H}_{\ell\ell'} - E | \mathbf{k}, \mu j, \ell'; \text{opw}\rangle \\ &= - \left(\frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}_{\ell}|^2 - E \right) \delta_{\ell\ell'} + \sum_{R \in \mathbb{P}_{\mathbf{k}}} {}^{(\mu)}\Gamma_{jj}^*(R) U(\mathbf{K}_R) \\ &+ \sum_c (E - E_c) \langle \mathbf{k}, \mu j, \ell | \mathbf{k}, \mu j, c\rangle \langle \mathbf{k}, \mu j, c | \mathbf{k}, \mu j, \ell'\rangle. \end{aligned} \quad (14.119)$$

The real value of the OPW method, however, has been in elucidating the conceptual development of the method of *pseudopotentials* which has been one of the more successful techniques in electronic structure calculations [186, 187].

The method of pseudopotentials

The concept of the pseudopotential can be arrived at from the perspective of the orthogonality between the valence and the core states. Its most precise, but least instructive form, can be obtained simply from the secular determinant defined in (14.47) by combining the last two summations and forming the expression for the *crystal pseudopotential*:

$$V_{\text{PS}} = \left\langle \mathbf{k}, \mu j, \ell; \text{opw} \left| \left[U + \sum_c |\mathbf{k}, c\rangle (E - E_c) \langle \mathbf{k}, c| \right] \right| \mathbf{k}, \mu j, \ell'; \text{opw} \right\rangle, \quad (14.120)$$

where the second term in the square brackets is called the *core-orthogonality term*, and is always *positive*. In fact, it can go a long way toward *canceling the negative Fourier coefficients of the attractive potential* V , so that V_{PS} is, indeed, *weak enough to be treated as a perturbation on the free electron states*. The real mental revolution is to regard this as merely a *plane-wave representation* of

$$V_{\text{PS}} = U + V_{\text{R}}, \quad (14.121)$$

whose repulsive part is the operator

$$V_{\text{R}} = \sum_c |\mathbf{k}, c\rangle (E - E_c) \langle \mathbf{k}, c|. \quad (14.122)$$

The Schrödinger equation,

$$(-\nabla^2 + U) \Psi = E \Psi, \quad (14.123)$$

for the true Bloch function Ψ is thereby transformed symbolically into the equation

$$(-\nabla^2 + V_{\text{PS}}) \Phi = E \Phi, \quad (14.124)$$

for the pseudo-wavefunction Φ . Thus having determined, in principle, the coefficients α_ℓ in the conventional OPW procedure, we find Φ to be just the plane-wave part of Ψ , i.e.

$$\Phi(\mathbf{k}, \mathbf{r}) = \sum_{\mathbf{G}} \alpha_\ell |\mathbf{k}, \mu j, \ell\rangle,$$

and we notice that equations (14.123) and (14.124) are *isospectral*, i.e. they have identical sets of eigenvalues.

Atomic pseudopotentials By writing the lattice potential U as a superposition of atomic or *muffin-tin* potentials centered on the lattice sites ($j \equiv (l\kappa)$), namely,

$$U(\mathbf{r}) = \sum_j v_a(\mathbf{r} - \mathbf{R}_j),$$

we can express V_{PS} , in a similar way, as

$$\begin{aligned} V_{\text{PS}} &= \sum_j \left[v_a(\mathbf{r} - \mathbf{R}_j) + \sum_c \phi_c^*(\mathbf{r} - \mathbf{R}_j) (E - E_c) \phi_c(\mathbf{r}' - \mathbf{R}_j) \right] \\ &= \sum_j w_j, \end{aligned} \quad (14.125)$$

where w_j is an *atomic* pseudopotential centered on the site R_j , and takes the form

$$w_j = v_a(\mathbf{r} - \mathbf{R}_j) + \sum_c |c(j)\rangle (E - E_c) \langle c(j)|, \quad (14.126)$$

with $|c(j)\rangle \equiv \phi^c(\mathbf{r}-\mathbf{R}_j)$. The worst feature of this form is that the atomic pseudopotential is not *local*. This can be seen if we go back to the basic conventions of the Dirac notation:

$$\begin{aligned} w \phi(\mathbf{r}) &= v_a(r) \phi(\mathbf{r}) + \sum_c (E - E_c) \int d\mathbf{r}' \psi_c^*(\mathbf{r}') \phi(\mathbf{r}') \psi_c(\mathbf{r}) \\ &= v_a(r) \phi(\mathbf{r}) + \int d\mathbf{r}' v(\mathbf{r}, \mathbf{r}') \phi(\mathbf{r}'). \end{aligned} \quad (14.127)$$

As an elementary algebraic consequence of this *nonlocality*, a matrix element of the pseudopotential between two plane-waves is not just a function of the difference of the two wavevectors. In general

$$w_{\mathbf{G}\mathbf{G}'} \equiv \langle \mathbf{k} - \mathbf{G} | w | \mathbf{k} - \mathbf{G}' \rangle \neq w_a(\mathbf{G} - \mathbf{G}'),$$

for all different values of G and G' , so that an *atomic form factor* cannot be defined uniquely. On the other hand, it is worth noting that the pseudopotential (14.125), is diagonal in the angular momentum quantum numbers of the core states $|c(j)\rangle$. One may, therefore, separate w into a sum of terms

$$w = w_s + w_p + w_d + \cdots,$$

where w_s acts only on the part of the wavefunction transforming with s -like symmetry, etc. This is of course a consequence of the assumption of spherical symmetry of the atom or muffin-tin.

From these considerations and from the obvious dependence of V_{PS} on the energy E of the state under study, we conclude that:

the real value of the pseudopotential, as defined above, lies in the semiquantitative justification it provides for nearly free electron interpolation schemes with adjustable parameters.

An even more serious blow against this pseudoatom representation is that the pseudopotential is not unique. This follows essentially from the overcompleteness of the OPWs. For a detailed discussion of this issue the reader should consult Heine [186, 187].

The scattering approach to pseudopotentials

A correct pseudopotential was defined as one that gave the same energy levels as the real potential, at least for a range of states of interest, with the emphasis on transforming the Shrödinger equation from (14.123) to (14.124). In this section the final end will be the same, but the approach will lie in scattering theory [188]. Consider a single-atom scattering center, where the potential $v(\mathbf{r})$ is taken as zero beyond some finite radius R_c . The radial wavefunction $\mathcal{R}_l(r, \mathcal{E})$, corresponding to an orbital angular momentum l , is a solution of the radial equation,

$$-\frac{1}{2r^2} \frac{d}{dr} \left[r^2 \frac{d\mathcal{R}_l}{dr} \right] + \left[\frac{l(l+1)}{2r^2} + v(\mathbf{r}) \right] \mathcal{R}_l = \mathcal{E} \mathcal{R}_l, \quad (14.128)$$

inside the muffin-tin radius R_c and is matched at R_c onto the solution for $r > R_c$,

$$C_l \left[j_l(\kappa r) - \tan \eta_l n_l(\kappa r) \right], \quad (14.129)$$

where $\mathcal{E} = \frac{1}{2}\kappa^2$. $j_l(r)$ and $n_l(r)$ are the spherical Bessel and Neuman functions, respectively. The condition is

$$L_l \equiv \frac{\mathcal{R}_l'(R_c, \mathcal{E})}{\mathcal{R}_l(R_c, \mathcal{E})} = \frac{\kappa j_l'(\kappa R_c) - \kappa \tan \eta_l n_l'(\kappa R_c)}{j_l(\kappa R_c) - \tan \eta_l n_l(\kappa R_c)}, \quad (14.130)$$

i.e.

$$\tan \eta_l(\mathcal{E}) = \frac{j_l(\kappa R_c)L_l - \kappa j_l(\kappa R_c)}{n_l(\kappa R_c)L_l(\mathcal{E}) - \kappa n_l(\kappa R_c)}, \quad (14.131)$$

so as to ensure that both function and first derivative are continuous. The phase shifts η_l suffice to determine the scattering amplitude

$$f(\theta) = (2i\kappa)^{-1} \sum_l (2l+1) [\exp(2i\eta_l) - 1] P_l(\cos \theta), \quad (14.132)$$

for an incident plane-wave of energy $\mathcal{E}$ being scattered through an angle θ . They may be written in the form

$$\eta_l = m_l\pi + \delta_l, \quad (14.133)$$

where m_l is an integer chosen so that the reduced phase shift δ_l lies in the range

$$|\delta_l| \leq \frac{\pi}{2}, \text{ or } 0 \leq \delta < \pi.$$

The integer m_l counts the number of radial nodes in the core wiggles of $\mathcal{R}_l(r)$: if we gradually increase the potential inside the muffin-tin from zero to $v(r)$, the attractive potential pulls in more and more of the wave function so that the inner core oscillations may be considered in this sense to have been pulled in by phase shifting the free wave outside. It follows that m_l is also equal to the number of core states of angular momentum l .

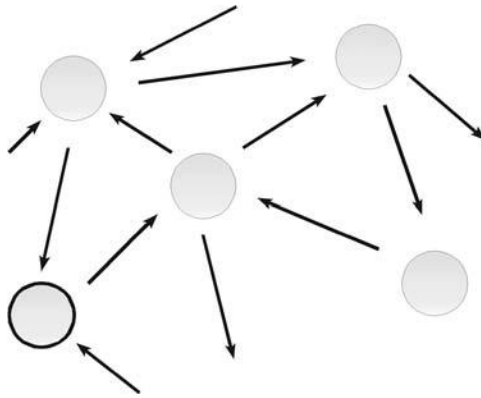


Fig. 14.11. Electrons propagate in the relatively weak potential between atomic cores approximately as plane-waves, being scattered by the strong potential inside the cores. The latter may be depicted as black boxes with given scattering properties, sufficing to determine the electronic motion.

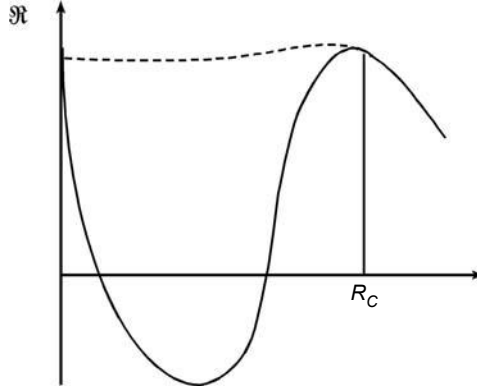


Fig. 14.12. Radial wavefunctions for the real potential (full curve) and the pseudopotential (broken curve). Note the same logarithmic derivative at radius R_c .

We now define a pseudopotential as one *whose complete phase shifts are equal to $\delta_l(\mathcal{E})$ without the $m_l\pi$, so that it has no core states*. Equation (14.132) shows that it gives the same amplitude $f(\theta)$ as the original potential since a factor $\exp(2im_l\pi) = 1$ has no effect.

The pseudo-wavefunction has no radial nodes, i.e. no rapid oscillations, so that we expect a rapidly convergent series of plane-waves to give a good representation of it. It is important to know that the *pseudo radial wavefunction* derived from the pseudopotential has the same *logarithmic derivative* $L_l(\mathcal{E})$ as the real wavefunction, the integer multiples of π again having no effect.

The scattering properties of the potential depend purely on *the logarithmic derivative at the radius R_c and not on any specific details of the potential or the wavefunction inside*. Consequently, the pseudopotential may be chosen to have any convenient shape, e.g. a square well, provided it has some parameters adjusted to give the correct scattering. Since the adjustment has to be made separately, a convenient form often is

$$v_{\text{ps}} = \sum_l f_l(r) \mathcal{P}_l, \quad (14.134)$$

where $f_l(\mathbf{r})$ is a spherically symmetric potential and $\mathcal{P}_l$ a projection operator which picks out the l th angular momentum component of the wavefunction so that $f_l(\mathbf{r})$ acts only on that.

Our first application of these ideas is to derive the so-called KKRZ pseudopotential of Ziman [188], in which v_{ps} for each atom is taken as zero everywhere except for a delta function of strength B_l at radius R :

$$v_{\text{ps}}^{\text{KKRZ}} = \sum_l B_l \delta(r - R_c) \mathcal{P}_l. \quad (14.135)$$

This leads to a set of radial equations of the form

$$-\frac{1}{2r^2} \frac{d}{dr} \left[r^2 \frac{d\mathcal{R}_l}{dr} \right] + v_{\text{ps}}^{\text{KKRZ}} \mathcal{R}_l = \mathcal{E} \mathcal{R}_l. \quad (14.136)$$

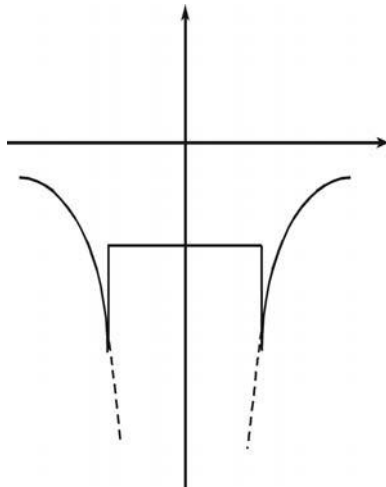


Fig. 14.13. The model pseudopotential of Heine and Abarenkov for a bare ion.

Inside the sphere the radial pseudo-wavefunction satisfies the radial equation

$$-\frac{1}{2r^2} \frac{d}{dr} \left[r^2 \frac{d\mathcal{R}_{\text{in}}}{dr} \right] = \mathcal{E} \mathcal{R}_{\text{in}}, \quad (14.137)$$

so that $\mathcal{R}_{\text{in}}$ is just $j_l(\kappa r)$, and the effect of the delta function is to give it a kink of the right amount to make the derivative outside equal to $L_l j_l(\kappa r)$ as required, where L_l is specified by the original potential. To determine B_l , we integrate (14.137) from $r = R_c - \epsilon$ to $r = R_c + \epsilon$ and obtain

$$\mathcal{R}'_{\text{out}} - \mathcal{R}'_{\text{in}} = 2B_l \mathcal{R}, \quad (14.138)$$

i.e.

$$L_l(\mathcal{E}) - \kappa \frac{j'_l(\kappa R_c)}{j_l(\kappa R_c)} = 2B_l. \quad (14.139)$$

Our second application is the pseudopotential of Heine and Abarenkov [188], $v_{\text{ps}}^{\text{HA}}$, usually termed the “model potential” for historical reasons. The aim is to calculate a pseudopotential for a single bare closed-shell ion such as Al^{+3} , which has the configuration $1s^2 2s^2 2p^4$. The model radius R_M is chosen at some convenient value greater than that of the core radius R_c , and outside R_M the pseudopotential is

$$v_{\text{ps}}^{\text{HA}} = -z/r, \quad r > R_M, \quad (14.140)$$

the bare Coulomb potential of the ion (ionic charge z). Inside R_M it is taken as a constant

$$v_{\text{ps}}^{\text{HA}} = - \sum_l A_l(\mathcal{E}) \mathcal{P}_l, \quad r < R_M, \quad (14.141)$$

adjusted to give the observed energy levels $\mathcal{E}_{3s}$, $\mathcal{E}_{3p}$, $\mathcal{E}_{4s}$, etc. of an extra electron in the field of the ion. The latter are taken from spectroscopic measurements on free ions, and

the procedure ensures that the pseudopotential gives the right logarithmic derivative, at least at these energies. In practice, for a given l , the values of $A_l(\mathcal{E})$ obtained from different energies, e.g. $\mathcal{E}_{3s}$, $\mathcal{E}_{4s}$, $\mathcal{E}_{5s}$, differ slightly so that $A_l(\mathcal{E})$ has to be considered as a weak function of energy. In accordance with the principle of pseudizing, the smallest possible value is always chosen of course.

Several other model-potential schemes are to be found in the literature. For example, Ashcroft has suggested that the atomic form factor of a bare ion may be adequately represented by the Fourier transform of an effective “empty-core” potential

$$v^{\text{ion}}(\mathbf{r}) = \begin{cases} 0 & r < R_c, \\ -\frac{z}{r} & r > R_c, \end{cases} \quad (14.142)$$

where R_c is an adjustable parameter that has approximately the radius of the physical atomic core.

Screening

Once the pseudopotential of the bare ion is obtained, the bare ions can be planted into an electron gas which then screens them to give the total pseudopotential of the whole solid. The point is that the screening by the electron gas can be treated by perturbation theory, the plane-waves of the free electron gas being the unperturbed pseudo-wavefunctions. While pseudizing is the formal justification for attempting perturbation theory at all, how good is it in practice?

We start by considering the pseudopotential of the bare ion, e.g. Al^{+3} , with only tightly bound closed-shell core electrons. We plant the ions at sites $\mathbf{r}_j$ in a uniform electron gas of density appropriate to the number of the outer electrons, assuming the electron density to remain constrained as uniform for the moment. The potential in the system is then

$$(\text{const}) + \sum_j [v^{\text{ion}}(q)S(\mathbf{q})] \exp(i\mathbf{q} \cdot \mathbf{r}), \quad (14.143)$$

In reality the electron gas relaxes to screen the ionic pseudopotential. To lowest order in perturbation theory the screening is linearly proportional to the bare potential, so that the final potential is

$$V(\mathbf{r}) = \sum \frac{v^{\text{ion}}(q)S(\mathbf{q})}{\epsilon(q)} \exp(i\mathbf{q} \cdot \mathbf{r}), \quad (14.144)$$

where

$$\begin{aligned} \epsilon(q) &= 1 - \left(\frac{8\pi e^2}{\Omega q^2} \right) \left[1 - \frac{q^2}{2(q^2 + k_F^2 + k_s^2)} \right] \chi(q), \\ \chi(q) &= -\frac{z}{2} \frac{3}{2E_{F0}} \left(\frac{1}{2} + \frac{4k_F^2 - q^2}{8qk_F} \right) \ln \left| \frac{2k_F + q}{2k_F - q} \right| \end{aligned} \quad (14.145)$$

is the Lindhart function, with z the number of valence electrons per atom, and $E_{F0} = \frac{1}{2}k_F^2$. The factor in square brackets in (14.145) comes from screened exchange, and k_s is the screening parameter $(2k_F/\pi)^{1/2}$ in atomic units.

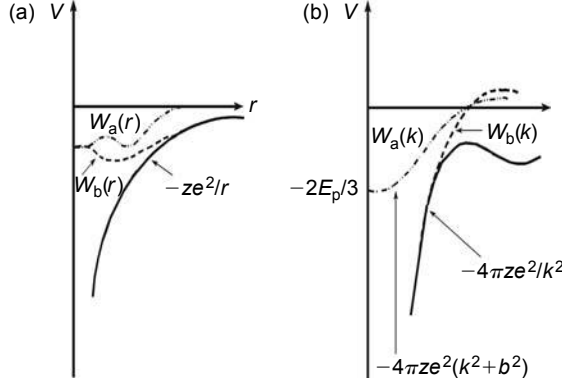


Fig. 14.14. Schematic representation, (a) in real space, (b) in reciprocal space, of transformation of bare atomic potential v_b into bare pseudopotential w_b , followed by screening to make “pseudoatom” potential w_a .

In the limit as $q \rightarrow 0$, the Fourier transform of an ionic potential is always dominated by the Coulombic part outside the pseudizing radius R_c . We therefore obtain

$$\begin{aligned} v^{\text{ion}}(q \rightarrow 0) &= -\frac{4\pi z}{\Omega q^2}, \\ v(q \rightarrow 0) &= -\frac{3}{2} E_{F0} + O(q^2). \end{aligned} \quad (14.146)$$

Using the *empty core* model for the bare pseudopotential we get

$$v(q) = -\frac{4\pi z}{q^2 \epsilon(q) \Omega} \cos(qR_c),$$

and $\epsilon(q)$ has the form derived in Section 14.2.1. Notice that the limit of $q \rightarrow 0$

$$v(q \rightarrow 0) = -\frac{2}{3} E_{F0} + O(q^2).$$

14.3.4 The tight-binding method

Our physical intuition that a crystal is merely an assembly of atoms, brought close together and allowed to interact, is expressed mathematically by trying to represent the Bloch functions as *linear combinations of atomic orbitals* (LCAO). It is convenient to replace the pair of angular momentum quantum numbers (l, m) by a single symbol L , together with a principal quantum number n , and to choose these in such a way that when $\kappa^2 = \mathcal{E}_{nL}$ the radial function $\mathcal{R}_l(r) \rightarrow 0$ as $r \rightarrow \infty$. We thus assume that our basis functions are restricted to bound states of the free atom potential $v_a(r)$, symbolized by $\phi_{nL}(\mathbf{r})$.

The most general Bloch function that can be constructed out of these functions is of the form

$$\Psi_{\mathbf{k}}^{\text{LCAO}} = \sum_{\mathbf{R}} \exp(i\mathbf{k} \cdot \mathbf{R}) \sum_{nL} \alpha_{nL} \phi_{nL}(\mathbf{r} - \mathbf{R}). \quad (14.147)$$

With (14.147) as a trial function, in minimizing the expectation value of the Hamiltonian of the crystal, we find

$$\sum_{n'L'} \{(\mathcal{E}_{nL} - \mathcal{E}) D_{nL,n'L'}(\mathbf{k}) + V_{nL,n'L'}(\mathbf{k})\} \alpha_{n'L'} = 0, \quad (14.148)$$

for all values of n and L included in the sum (14.147).

The functions D and V in (14.148) are a bit elaborate, but because of the translational symmetry they are easily expressed as lattice Fourier transforms, i.e.

$$V_{nL,n'L'}(\mathbf{k}) = \sum_{\mathbf{R}} \exp(i\mathbf{k} \cdot \mathbf{R}) V_{nL,n'L'}(\mathbf{R}), \quad (14.149)$$

$$D_{nL,n'L'}(\mathbf{k}) = \sum_{\mathbf{R}} \exp(i\mathbf{k} \cdot \mathbf{R}) D_{nL,n'L'}(\mathbf{R}), \quad (14.150)$$

whose direct lattice components are independent of $\mathcal{E}$ and $\bar{k}$:

$$V_{nL,n'L'}(\mathbf{R}) = \sum_{\mathbf{R} \neq 0} \int \phi_{nL}(\mathbf{r}) v_a(\mathbf{r} + \mathbf{R}) \phi_{n'L'}(\mathbf{r} + \mathbf{R}) d^3r, \quad (14.151)$$

known as the hopping integrals, and

$$D_{nL,n'L'}(\mathbf{R}) = \int \phi(\mathbf{r}) \phi_{n'L'}(\mathbf{r} + \mathbf{R}) d^3r, \quad (14.152)$$

the overlap integrals.

These integrals involving the overlap of functions centered on two or three neighboring sites are obviously rather nasty, and can only be evaluated with great labor. Nevertheless, the above formulation seems quite explicit, and was for long regarded as capable of giving a solution to the band structure problem to any required degree of accuracy.

This is the algebraic justification of one of the standard elementary principles of solid state physics – that as the atoms come together, each of their bound states becomes broadened into a band of Bloch functions of appropriate symmetry (Figure 14.15). The

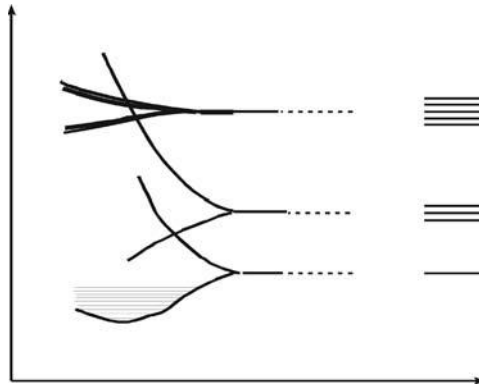


Fig. 14.15. Bands formed by combining atomic orbitals as atoms are brought together.

broadening occurs quite sharply, because bound-state functions decay exponentially outside the atomic sphere, so the overlap integrals are very small until the atoms come close together. Then, as the bands arising from distinct levels begin to overlap one another in energy, they *hybridize* into the linear combination that would be obtained by solving the above equations for α_{nL} . We thus refer to the “s-p band”, the “3d band”, etc. identifying the bands by the atomic levels from which they are ultimately derived.

This confidence in the LCAO or tight-binding method is, to a certain degree, misplaced. The overlap of wavefunctions eventually leads to an overlap of potentials, destroying the bound states (except for resonances) and liberating the electrons into “nearly free” bands in which the quantum numbers of the atomic levels are almost irrelevant (Figure 14.16). Even when there is no overlap of neighboring potentials, the representation (14.147) is functionally incomplete: the set of bound states of the atomic potential $v_a(\mathbf{r})$ does not contain the continuum of “scattered free electron” eigenfunctions of the Schrödinger equation at positive energies. It is impossible, therefore, to describe states in a metal or semiconductor in and above the valence and conduction bands, since they resemble free electron waves in the interstitial space. On the other hand, this is a legitimate description of the *bound bands* below $\mathcal{E}_{\text{MTZ}}$, the muffin-tin zero. As is well known, the deeper bound-state functions $\phi_{nL}(\mathbf{r})$ decay rapidly to zero outside the atomic core, so that the overlap integrals (14.149) and (14.150) become very small as we go down in energy, and the solutions of (14.147) are very narrow bands centered about each atomic level $\mathcal{E}_{nL}$. Unfortunately, it may be quite misleading to use a conventional determinant of Bloch functions to describe the *many-electron* states in such circumstances.

Having abandoned the notion of calculating band structures from first principles by the tight-binding method, we can still learn something from the general form of equation (14.148). These are made clumsy by the nonorthogonality of the basis functions (14.147), as a consequence of the nonorthogonality, in integrals such as (14.152), of atomic orbitals centered on different sites. But this is not an essential complication, for the simplifying assumption,

$$D_{nL,n'L'}(\mathbf{k}) = \delta_{nL,n'L'}, \quad (14.153)$$

may be justified in principle by supposing that the atomic orbitals in (14.147) have already been combined by a suitable unitary transformation so as to make (14.152) vanish for $\mathbf{r} \neq 0$. This is a standard property of *Wannier functions*, but can be achieved in many other ways.

Looking at the coefficients (14.151), we can apply group theory to obtain powerful selection rules governing the choice of L, L' , and $\mathbf{r}$ in various types of lattices. It is also reasonable to assume that these coefficients become negligibly small when they refer to lattice sites at any great distance apart. Thus there need only be a few distinct coefficients of importance: we have arrived at one of the standard *interpolation schemes* or *parametric representations* of band structure theory. The energy $\mathcal{E}(\mathbf{k})$ is supposed to be a root of the secular equation

$$\det \left| \{ \mathcal{E}_{nL} - \mathcal{E}(\mathbf{k}) \} \delta_{nL,n'L'} + V_{nL,n'L'}(\mathbf{k}) \right| = 0, \quad (14.154)$$

where $V_{nL,n'L'}(\mathbf{k})$ is given by a Fourier series and then treated as parameters to be adjusted empirically to bring $\mathcal{E}(\mathbf{k})$ into agreement with experiment. It must be emphasized,

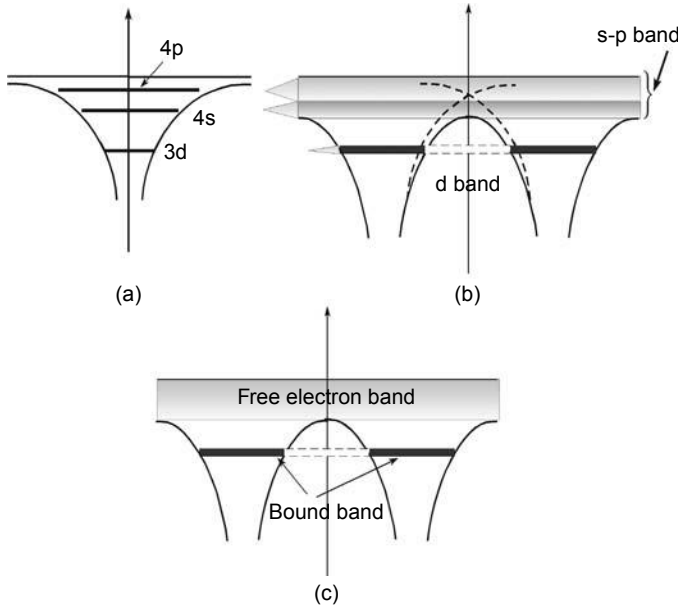


Fig. 14.16. (a) Atomic valence states. (b) Conventional description of formation of metallic conduction band. (c) Nearly free electron description.

however, that the actual values of the parameters arrived at in this way cannot be interpreted physically as overlap integrals of atomic orbitals. To a large extent, this type of representation is imposed upon the band structure by the symmetry of the crystal.

To illustrate this, suppose, as in the case of many monovalent metals, that there is only a single nearly free electron conduction band to be fitted to the shape of the Fermi surface. The function $\mathcal{E}(\mathbf{k})$ must necessarily be periodic in the reciprocal lattice; it must have Fourier representation in the direct lattice:

$$\mathcal{E}(\mathbf{k}) = \mathcal{E}_0 + \sum_{\mathbf{r} \neq 0} \exp(i\mathbf{k} \cdot \mathbf{r}) \mathcal{E}(\mathbf{r}), \quad (14.155)$$

But the Brillouin zone has the point-group symmetries of the crystal, so that many of the coefficients $\mathcal{E}(\mathbf{r})$ must be equal to one another, or zero. It is obvious, for instance, that $\mathcal{E}(\mathbf{r})$ must have the same value for all nearest neighbors in the f.c.c. lattice, so the leading terms of (14.154) would take the form

$$\begin{aligned} \mathcal{E}(\mathbf{k}) = \mathcal{E}_0 + 4\mathcal{E}\left(\frac{1}{2}, \frac{1}{2}, 0\right) \{ \cos(k_y a/2) \cos(k_z a/2) + \cos(k_z a/2) \cos(k_x a/2) \\ + \cos(k_x a/2) \cos(k_y a/2) \}. \end{aligned} \quad (14.156)$$

If we give to $\mathcal{E}(1/2, 1/2, 0)$ the value $(-\hbar^2/4ma^2)$, this function will behave like a simple free electron energy-momentum relation over a wide range of energy. Indeed, by the

addition of further terms in $\mathcal{E}(211)$, etc., the distorted and multiply connected Fermi surfaces of noble metals can be fitted exactly in this way.

Site-orbital basis and its transformation under the point-group operators

We consider a site-orbital basis, $\Phi_L = (\phi_1, \phi_2, \dots, \phi_L)$, comprising of Wannier-like functions and characterized by spherical-harmonic labels L [55, 91, 92]. It engenders a Rep $^{(L)}\Gamma$ under the action of the point-group $\mathcal{G}$ of the space-group, namely,

$$R\Phi_L = \Phi_L {}^{(L)}\Gamma(R), \quad R \in \mathcal{G}. \quad (14.157)$$

The Irreps engendered by the action of proper point-group rotations on a spherical-harmonic basis $\{lm\}$ can be written as

$$R(\alpha, \beta, \gamma) Y_l^m(\theta, \phi) = \sum_{m'=-l}^l Y_l^{m'}(\theta, \phi) {}^{(l)}\mathcal{D}_{m'm} (R(\alpha, \beta, \gamma)), \quad (14.158)$$

where (α, β, γ) are Euler angles (a list of these angles for point-group generators is given in Table 14.4), and

$${}^{(l)}\mathcal{D}_{m'm} (R(\alpha, \beta, \gamma)) = (i^{|m'|+m'}) (i^{-|m|-m}) e^{-im'\gamma} d_{m'm}^l(\beta) e^{-im\alpha}. \quad (14.159)$$

In (14.159)

$$\begin{aligned} d_{m'm}^l(\beta) &= \sum_{n=\text{Max}(0, m'-m)}^{\text{Min}(l+m', l-m)} (-1)^{n-m+m'} \frac{\sqrt{(l+m')!(l+m)!(l-m')!(l-m)!}}{(l-m'-n)!(l-m-n)!(n-m+m')!} \\ &\times \cos^{2l-2n+m-m'} \left(\frac{\beta}{2} \right) \sin^{2n-m+m'} \left(\frac{\beta}{2} \right). \end{aligned} \quad (14.160)$$

$d_{m'm}^l$ satisfies the symmetry relation

$$d_{m'm}^l(\beta) = d_{-m, -m'}^l(\beta) = (-1)^{m+m'} d_{mm'}^l(\beta), \quad (14.161)$$

hence,

$$d_{-m'm}^l(\beta) = (-1)^{m+m'} d_{m', -m}^l(\beta)$$

Table 14.4. Euler angles for crystallographic point-group generators.

Angle	α	β	γ	Angle	α	β	γ
E	0	0	0	C_2	π	0	0
U_x	π	π	0	U_y	0	π	0
C_4	$\pi/2$	0	0	C_3^d	$\pi/2$	$\pi/2$	0
C_6	$\pi/3$	0	0	C_3	$2\pi/3$	0	0
U_{cubic}^d	$\pi/2$	π	0	U'_{hex}	0	π	0

and we only need to determine its values for $-l \leq m \leq l$, $|m| \leq m' \leq l$. Moreover, starting from the element

$$d_{lm}^l(\beta) = (-1)^{l-m} \sqrt{\frac{(2l)!}{(l+m)!(l-m)!}} \cos^{l+m} \left(\frac{\beta}{2} \right) \sin^{l-m} \left(\frac{\beta}{2} \right) \quad (14.162)$$

we use the recurrence relation

$$\begin{aligned} & \sqrt{(l+m')(l-m'+1)} d_{m'-1,m}^l(\beta) \\ &= (m-m') \cot(\beta/2) d_{m'm}^l(\beta) - \sqrt{(l+m)(l-m+1)} d_{m'm-1}^l(\beta) \end{aligned} \quad (14.163)$$

to generate the remaining elements. We should note that (14.163) is valid for l, m, m' integers, only.

Some special cases should be considered here:

(i) When $\beta = 0$, we have a rotation of $\alpha + \gamma$ about the z -axis, namely

$${}^{(l)}\mathcal{D}_{m'm} (R(\alpha, 0, \gamma)) = e^{-im'\gamma} e^{-im\alpha} \delta_{mm'}.$$

(ii) When $\beta = \pi$, it can be shown that

$${}^{(l)}\mathcal{D}_{m'm} (R(\alpha, \pi, \gamma)) = (-1)^l e^{im'\gamma} e^{-im\alpha} \delta_{m',-m}.$$

(iii) When $\beta = \pi/2$, $\cos(\beta/2) = \sin(\beta/2) = 1/\sqrt{2}$, an extra symmetry of $d_{m'm}^l(\beta)$ appears, namely

$$d_{m',-m}^l(\beta) = (-1)^{l+m'} d_{m'm}^l(\beta).$$

(iv) For the inversion operation, we have

$$I Y_m^l(\theta, \phi) = (-1)^l Y_m^l(\theta, \phi). \quad (14.164)$$

Thus, the elements of ${}^{(L)}\Gamma$ for proper generating rotation operations are

$${}^{(L)}\Gamma(R) = {}^{(l)}\mathcal{D} (R(\alpha, \beta, \gamma)),$$

and for improper generating rotation operations $IR(\alpha, \beta, \gamma)$ are

$${}^{(L)}\Gamma(IR) = (-1)^l {}^{(l)}\mathcal{D} (R(\alpha, \beta, \gamma)).$$

Program for generating the spherical-harmonic basis Rep

The following program constructs the matrix Reps of the crystallographic point-group generators engendered by their action on the spherical-harmonic basis Y_m^l .

PROGRAM YLM

```
<< LinearAlgebra`MatrixManipulation`
```

```
L = 2; L1 = 2L + 1; NG = 9; L  $\equiv \ell$ , NG = # of generators.
```

```
Euler angles for generating rotations
```

```
Eul = {{ $\pi/2$ , 0, 0}, { $\pi$ ,  $\pi$ , 0}, {0,  $\pi$ , 0}, {0,  $\pi$ , 0},  
        { $\pi$ , 0, 0}, { $\pi/3$ , 0, 0}, {2 *  $\pi/3$ , 0, 0},  
        { $\pi/2$ ,  $\pi/2$ , 0}, { $\pi/2$ ,  $\pi$ , 0}};
```

```
Symbols of generating rotations
```

```
Opr = {C4, UX, UY, U', C2, C6, C3, C3d, Udc};
```

```
lx = L1*L1;
```

```
DLM = {}; DV = {}; Do[AppendTo[DV, 0], {i, 1, lx}];
```

```
DV = Partition[DV, L1];
```

```
Do[
```

```
DL = DV;
```

```
Switch[Eul[[i, 2]] == 0, True,
```

```
    Do[
```

```
        An = Eul[[i, 1]] + Eul[[i, 3]];

```

```
        DL[[j, j]] = Exp[I (j-L-1) * An], {j, 1, L1}

```

```
    ],
```

```
    False,
```

```
    Switch[Eul[[i, 2]] ==  $\pi$ , True,
```

```
        An = Eul[[i, 3]] - Eul[[i, 1]];

```

```
        Do[
```

```
            DL[[j, L1-j + 1]] =  $(-1)^L$  * Exp[I (L-j + 1)*An],

```

```
            {j, 1, 2 L + 1}

```

```
        Do[
```

```
            DL[[j, L1-j + 1]] =  $(-1)^L$  * Exp[I (L-j + 1)*An],

```

```
            {j, 1, 2 L + 1}

```

```
        ],
```

```
        False,
```

```
        Switch[Eul[[i, 2]] ==  $\pi/2$ , True,
```

```
            t1 =  $2^L$ ; t1 = 1/t1;

```

```
            Do[
```

```

DL[[L1, kk]] =  $\sqrt{\frac{(2L)!}{(kk-1)! * (L1-kk)!}}$  * t1;
DL[[L1, kk]] =  $(-1)^{(L1-kk)}$  * DL[[L1, kk]],
      {kk, 1, L1}
    ],
  False,
  Do[
DL[[L1, j]] =  $\left(\cos\left[\frac{\text{Eul}[[i, 2]]}{2}\right]\right)^{(j-1)}$ ;
DL[[L1, j]] = DL[[L1, j]] *  $\left(\sin\left[\frac{\text{Eul}[[i, 2]]}{2}\right]\right)^{(L1-j)}$ ;
DL[[L1, j]] =  $\sqrt{\frac{(2L)!}{(j-1)! * (2L-j+1)!}}$  * DL[[L1, j]];
DL[[L1, j]] =  $(-1)^{(2L-j+1)}$  * DL[[L1, j]],
      {j, 1, L1}
    ];
  ]
Do[
  DL[[kk, L1]] =  $(-1)^{(kk-1)}$  * DL[[L1, kk]];
  DL[[2L + 2 - kk, 1]] = DL[[L1, kk]];
  DL[[1, kk]] =  $(-1)^{(kk-1)}$  * DL[[L1, L1-kk + 1]],
    {kk, 2, L1}
  ];
Do[
  m = L1-k; mm = k + 1;
  Do[
    n = L1-j; mn = j + 1;
    Switch[Eul[[i, 2]] ==  $\pi/2$ , True,
      DL[[m, n]] =  $(k-j-1)$  * DL[[m + 1, n]];
      False,
      DL[[m, n]] =  $(k-j-1)$  *  $\cot\left[\frac{\text{Eul}[[i, 2]]}{2}\right]$  * DL[[m + 1, j]];
    ];
    DL[[m, n]] = Simplify[DL[[m, n]] -  $\sqrt{(j+1)(2L-j)}$  * DL[[m, n-1]]];
    DL[[m, n]] =  $N\left[\frac{\text{DL}[[m, n]]}{\sqrt{(L-k)k}}\right]$ ,

```

```

DL[[mn, mm]] = DL[[m, n]];
DL[[n, m]] = (-1)(2L-j-k) * DL[[m, n]];
DL[[m, mn]] = (-1)(L1-k) * DL[[m, n]];
DL[[mm, n]] = DL[[m, mn]], {j, 1, L}
                    ], {k, 1, L}
                    ]
                    ]
]; AppendTo[DLM, DL], {i, 1, NG}
];
Do[Print["D[" , Opr[[i]], " ] = " , MatrixForm[DLM[[i]]]],
  {i, 1, NG}]

```

Projection of symmetry-adapted space-orbitals

For the sake of simplicity, we consider crystals containing only one type of atomic species, and belonging to a space-group $\mathbb{S}$ with point-group $\mathcal{G}$ [7].

- (a) **Lattice atomic basis and its transformation under $\mathcal{G}$** We denote the atomic-basis sites by vectors $\mathbf{P} = \boldsymbol{\rho}_1, \boldsymbol{\rho}_2, \dots, \boldsymbol{\rho}_s$. We first show the action of $S = (R|\boldsymbol{\tau}) \in \mathbb{S}$ on orbital functions $\phi(\mathbf{r} - \boldsymbol{\rho}_i)$ centered at site $\boldsymbol{\rho}_i$, namely

$$\begin{aligned}
 (R|\boldsymbol{\tau}) \phi(\mathbf{r} - \boldsymbol{\rho}_i) &= \phi \left((R|\boldsymbol{\tau})^{-1}(\mathbf{r} - \boldsymbol{\rho}_i) \right) \\
 &= \phi \left((R^{-1}\mathbf{r} - R^{-1}(\boldsymbol{\rho}_i + \boldsymbol{\tau})) \right) \\
 &= \phi \left((R^{-1}\mathbf{r} - \boldsymbol{\rho}_j - \mathbf{t}_{ij}(S)) \right) \\
 &= (E|\mathbf{t}_{ij}(S))^{-1} \phi \left(R^{-1}\mathbf{r} - \boldsymbol{\rho}_j \right), \tag{14.165}
 \end{aligned}$$

where

$$\mathbf{t}_{ij}(S) = R^{-1}(\boldsymbol{\rho}_i + \boldsymbol{\tau}) - \boldsymbol{\rho}_j,$$

is uniquely determined by S and i . Thus, under the action of S , site i is transformed into site j ; and, more generally, $\mathbb{S}$ engenders a $\text{Rep}^{(P)}\Gamma$ of permutations among the $\boldsymbol{\rho}_i$ s, such that

$$S^{-1}\mathbf{P} = \mathbf{P}^{(P)}\Gamma(S). \tag{14.166}$$

- (b) We construct a Bloch basis set

$$\Psi(\mathbf{k}, \boldsymbol{\rho}_i) = {}^{(\mathbf{k})} \mathcal{P} \Phi_L(\mathbf{r} - \boldsymbol{\rho}_i) = \frac{1}{N} \sum_{\mathbf{t}} e^{i\mathbf{k} \cdot \mathbf{t}} \Phi_L(\mathbf{r} - \boldsymbol{\rho}_i - \mathbf{t}), \tag{14.167}$$

where we took the order of $\mathbb{T} \subset \mathbb{S}$ to be N . Operating with $(R|\boldsymbol{\tau} + \mathbf{s}) \in \mathbb{S}$ on it, we obtain

$$\begin{aligned}
 (R|\boldsymbol{\tau} + \mathbf{s}) \Psi(\mathbf{k}, \boldsymbol{\rho}_i) &= (E|\mathbf{s})(R|\boldsymbol{\tau}) \Psi(\mathbf{k}, \boldsymbol{\rho}_i) \\
 &= \frac{1}{N} \sum_{\mathbf{t}} e^{i\mathbf{k} \cdot \mathbf{t}} (E|\mathbf{s})(R|\boldsymbol{\tau}) \Phi_L(\mathbf{r} - \boldsymbol{\rho}_i - \mathbf{t}) \\
 &= \frac{1}{N} \sum_{\mathbf{t}} e^{i\mathbf{k} \cdot \mathbf{t}} (E|\mathbf{s}) \Phi_L \left((R|\boldsymbol{\tau})^{-1} (\mathbf{r} - \boldsymbol{\rho}_i - \mathbf{t}) \right) \\
 &= \frac{1}{N} \sum_{\mathbf{t}} e^{i\mathbf{k} \cdot \mathbf{t}} (E|\mathbf{s}) \Phi_L \left(R^{-1}\mathbf{r} - R^{-1}(\boldsymbol{\rho}_i + \boldsymbol{\tau} + \mathbf{t}) \right) \\
 &= \frac{1}{N} \sum_{\mathbf{t}} e^{i\mathbf{k} \cdot \mathbf{t}} \Phi_L(\boldsymbol{\rho}_j + \mathbf{t}')^{(L)} \Gamma(R), \tag{14.168}
 \end{aligned}$$

where

$$\mathbf{t}' = \mathbf{s} - R^{-1}\mathbf{t} + \mathbf{t}_{ij}(S).$$

We note that

$$\begin{aligned}
 \Phi_L \left(R^{-1}\mathbf{r} - \boldsymbol{\rho}_j - \mathbf{t}' \right) &= (E|\boldsymbol{\rho}_j + \mathbf{t}')^{-1} \Phi_L(R^{-1}\mathbf{r}) \\
 &= (E|\boldsymbol{\rho}_j + \mathbf{t}')^{-1} \Phi_L(\mathbf{r})^{(L)} \Gamma(R) \\
 &= \Phi_L(\boldsymbol{\rho}_j + \mathbf{t}')^{(L)} \Gamma(R).
 \end{aligned}$$

Now, if $S \in \mathbb{S}_{\mathbf{k}}$, then $R\mathbf{k} = \mathbf{k} + \mathbf{G}$ or $R^{-1}\mathbf{k} = \mathbf{k} + \mathbf{G}'$; and with

$$\mathbf{t} = R(\mathbf{s} + \mathbf{t}_{ij}(S) - \mathbf{t}')$$

we obtain

$$\exp[i\mathbf{k} \cdot \mathbf{t}] = \exp[i\mathbf{k} \cdot R(\mathbf{s} + \mathbf{t}_{ij}(S) - \mathbf{t}')], \tag{14.169}$$

and we write

$$\begin{aligned}
 (R|\boldsymbol{\tau} + \mathbf{s}) \Psi(\mathbf{k}, \boldsymbol{\rho}_i) &= \exp[i\mathbf{k} \cdot R(\mathbf{s} + \mathbf{t}_{ij}(S))] \\
 &\quad \times \frac{1}{N} \sum_{\mathbf{t}'} e^{i\mathbf{k} \cdot \mathbf{t}'} \Phi_L(\boldsymbol{\rho}_j - \mathbf{t}')^{(L)} \Gamma(R) \\
 &= \exp[i\mathbf{k} \cdot (\mathbf{s} + \mathbf{t}_{ij}(S))] \Psi(\mathbf{k}, \boldsymbol{\rho}_j - \mathbf{t}')^{(L)} \Gamma(R). \tag{14.170}
 \end{aligned}$$

- (c) We construct the projection operator $^{(\mathbf{k}, \mu)}\mathcal{P}$, where $(\mathbf{k}, \mu)$ is an allowable Irrep of $\mathcal{S}_{\mathbf{k}}$, as

$$\begin{aligned}
 ^{(\mathbf{k}, \mu)}\mathcal{P}_{\ell\ell} \Big|_{ij} &= \frac{d_{\mu}}{s_{\mathbf{k}}} \sum_{S_{\mathbf{k}} \in \mathbb{S}_{\mathbf{k}}} ^{(\mathbf{k}, \mu)} \Lambda_{\ell\ell}^*(S_{\mathbf{k}}) e^{i\mathbf{k} \cdot (\mathbf{s} + \mathbf{t}_{ij}(S))} ^{(L)} \Gamma(R) \\
 &= \frac{d_{\mu}}{g_{\mathbf{k}}} \sum_{(R|\boldsymbol{\tau}) \in \mathcal{G}_{\mathbf{k}}(i, j)} ^{(\mu)} \Lambda_{\ell\ell}^*(R) e^{i\mathbf{k} \cdot \mathbf{t}_{ij}(R)} ^{(L)} \Gamma(R), \tag{14.171}
 \end{aligned}$$

where $\mathcal{G}_{\mathbf{k}}(i, j)$ are the elements of $\mathcal{G}_{\mathbf{k}}$ that carry site i into site j , and we used the relations

$$s_{\mathbf{k}} = N g_{\mathbf{k}},$$

$$({\mathbf{k}}, \mu) \Lambda_{\ell\ell}^*(S_{\mathbf{k}}) = e^{-i\mathbf{k} \cdot \mathbf{s}^{(\mu)}} \Lambda_{\ell\ell}^*(R),$$

so that the N terms that have $(R|\boldsymbol{\tau})$ are identical.

Program for constructing symmetry-adapted space-orbitals

This program performs the following steps:

- (i) It converts all vectors and point-group matrices in terms of the lattice basis vectors (a-holohedry). This is very convenient when determining equivalent atomic positions. The resulting atomic-basis vectors are stored in **RATL**, and rotation matrices in **RotG**.
- (ii) The site-symmetry subgroups $\mathcal{G}_i$ are stored in **Atomsym**. The equivalent Wyckoff positions are identified with the aid of coset representatives of $\mathcal{G}_i$ in the crystallographic point-group $\mathcal{G}$.
- (iii) The site-permutation matrices are generated and stored in **PERMA**.

INPUT ATOMIC POSITIONS

1. Express all vectors and matrices in lattice vector basis

```
Switch[LAT == 1, True, RATL = RR;
  Print["Atomic Positions in Terms of Primitive Lattice
        Vectors = ", MatrixForm[RATL]]
  RATC = {};
  Do[B = RATL[[i, j]]·RL; AppendTo[RATC, B],
    {i, 1, NCEL}, {j, 1, NSP[[i]]}
  ],
False, RATC = RR;
RATL = {};
Do[B = Transpose[RATC[[i, j]]]·RL; AppendTo[RATL, B],
  {i, 1, NCEL}, {j, 1, NSP[[i]]}
]
Print["Atomic positions in Lattice Coordinates :
      ", MatrixForm[RATL]]
];
```


- Rotation matrices in lattice coordinates

```
Do[
RotG[i] = Transpose[RL].Rot[i].G, {i, 1, g}
];
```

2. Determine the symmetry of atomic positions

```
Print["Atomic positions in Cartesian Coordinates
      and Their Symmetries : "];

Do[
Atomsym = {}; PRT = 0;
RRK = RATL[[ik, jk]]; LK = {}; Ltmp = {};
Cosrep = {}; gr = 0;
Switch[RRK == {0, 0, 0},

      True,
      gr = g; AppendTo[Atomsym, Range[g]]; PRT = 1;
      Print["[" , ELMNT[[ik]], " , " , jk, "]" Position at = " ,
            RATC[[ik, jk]], " , its group is the Full
            Point Group, "],

      False,
      Do[
        RK1 = RotG[Inv[[i]]].(RRK + Tau[[i]]);
        RK1 = RK1 - RRK;
        Switch[And[Mod[RK1[[1]],1] == 0,
                  Mod[RK1[[2]],1] == 0,
                  Mod[RK1[[3]],1] == 0, FreeQ[LK, i]],
              True, gr ++ ; AppendTo[LK, i]
            ], {i, 1, g}
      ]; AppendTo[Atomsym, LK];
];

indeks = g/gr; Icoset = 1;
Acosrep = {1}; jj = 1; Ltmp = LK;
```

3. Generate coset Reps of site-symmetry subgroups

```

While[And[Icoset < indeks, jj < g], jj + + ;
  Switch[FreeQ[Ltmp, jj], True,
    Icoset + + ; AppendTo[Acosrep, jj];
    Do[cst = LK[[ij]];
      AppendTo[Ltmp, m[[1, jj, cst]]],
      {ij, 1, Length[LK]}
    ]
  ]
];
Switch[PRT == 0, True,
  Print["[", ELMNT[[ik]], ", ", jk, "] Position at = ",
    RATC[[ik, jk]], ", its group of Order ",
    gr, ", is ", LK, ", and its Coset Reps
    are ", Acosrep];
  Print["it has ", indeks, " equivalent
    Wyckoff positions."];
  ], {ik, 1, NCEL}, {jk, 1, NSP[[ik]]}
];

```

4. Generate site permutations by rotations

```

NSP2 = {}; Do[AppendTo[NSP2, NSP[[ii]]2, {ii, 1, NCEL}];
nrr = Apply[plus, NSP2];
PERMA = {Range[NAT]}; NPER = {}; tr = {};
Do[AppendTo[tr, {0, 0, 0}], {i, 1, nrr}];
Do[
  NP = 0;
  Do[RP = RotG[Inv[[kk]]]·(RATL[[ik, jk]] + Tau[[kk]]);
    kx = 0; park = 0;
    While[And[kx < NSP[[ik]], park == 0], kx + + ;
      RDF = RP - RATL[[ik, kx]];
      Switch[And[Mod[RDF[[1]], 1] == 0.,
        Mod[RDF[[2]], 1] == 0.,
        Mod[RDF[[3]], 1] == 0.],
        True,

```

```

AppendTo[tr,RDF];
Switch[Or[VectorNorm[RDF] == 0.,
        RDF[[1]]2 + RDF[[2]]2 +
        RDF[[3]]2 > 2],
      True,
      lx = NP + kx;
      AppendTo[NPER, lx]; park = 1
    ]
  ]
], {jk, 1, NSP[[ik]]}
]; NP += NSP[[ik]], {ik, 1, NCEL}
]; AppendTo[PERMA, NPER]; NPER = {}, {kk, 2, g}
];
Print[MatrixForm[Partition[PERMA, 8]]];
5. Construct the Irrep projection operators
ZRO = 0*IdentityMatrix[L]; Sympro = {};

L is the size of the electronic orbital set
Do[dmu[imu] = 0, {imu, 1, NC}];
  Initialize the tensor Rep in Pro
  • Tensor is initially an (L*NAT) × (L*NAT) zero matrix

Tensor = {}; LT = L*NAT; NT = NAT*NAT;
Do[
  AppendTo[Tensor, ZRO], {i, 1, NT}
];
Tensor = Partition[Tensor, NAT]

• Construct projection operator P(mu, i) in Tensor
Do[
  Do[
    ic = PERMA[[kk, ir]];
    Switch[dmu[[mu]] == 1,
      True,
      Tensor[[ir, ic]] += ch[mu, kk]*DLM[kk],
      False,

```

```

Tensor[[ ir, ic]] += IRREP[[mu,kk,nu,nu]]*DLM[kk]
                    ], {kk, 1, g}
                ], {ir, 1, NAT}
            ];
Do[
  Do[
    Do[
      im = L*(ir - 1) + i;
      Do[
        jm = L*(ic - 1) + j;
        Proj[im, jm] = dmu[[mu]]*Tensor[[ ir, ic, i, j]]/g,
          {j, 1, 3}
        ], {ic, 1, NAT}
      ], {i, 1, L}
    ], {ir, 1, NAT}
  ];
Project = Array[Proj, {LT, LT}];
EGV = Eigenvalues[Project];
Print["Eigenvalues[" , mu, "]" = " , EGV];
EV = Eigenvectors[Project];
Do[
  Switch[EGV[[ig]] = 1,
    True, dmux[mu] ++ ; AppendTo[Sympro, EV[[ig]]]
    ], {ig, 1, LT}
  ], {nu, 1, dmu[[mu]]}
]
]

```

Chemical bonds, bond-orbits, and their local site-symmetry

Sometimes it is convenient to deal with chemical bonds rather than atomic orbitals, as for example in the case of the tetrahedrally bonded systems C, Si, and Ge. This approach is also useful in determining the matrix elements between atomic orbitals.

To construct the interaction matrix element between two orbitals $|u\rangle$ and $|v\rangle$, we define orbit quantization with respect to the axis joining the centers of the two interacting orbits.

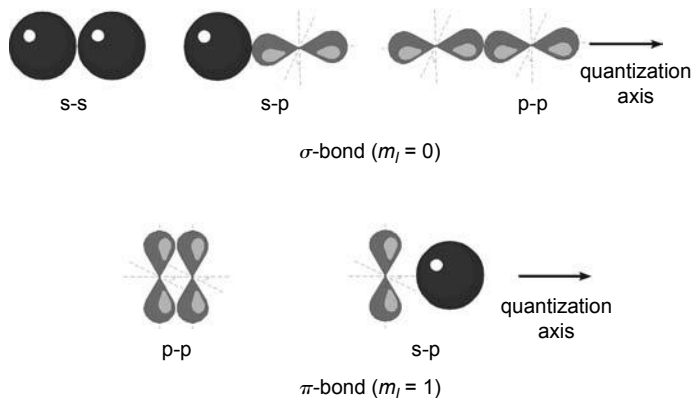


Fig. 14.17. Quantization of m_ℓ along the interatomic axis uses the designation $\sigma \Rightarrow m_\ell = 0$, and $\pi \Rightarrow m_\ell = 1$.

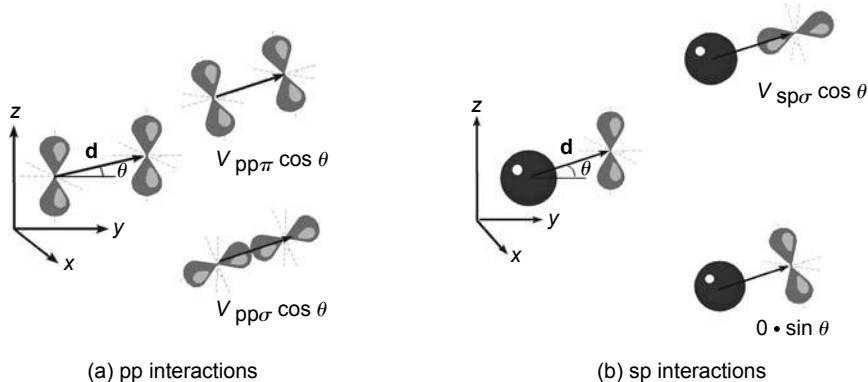


Fig. 14.18. (a) pp interactions are decomposed into $pp\sigma$ ($m_\ell = 0$) and $pp\pi$ ($m_\ell = 1$) types; (b) $sp\sigma$ corresponds to $m_\ell = 0$, while $sp\pi$ vanishes since it involves interaction between orbits of different m .

As we show in Figure 14.17, when the orbits have common angular momenta $m_\ell = 0, 1$, we refer to the geometry as σ and π , respectively. The case where one orbit has $L = 0$ and the other $L = 1$ involves two orthogonal orbits and the interaction is nulled.

In the general case, shown in Figure 14.18, the geometry of interaction is defined with respect to a fixed Cartesian coordinate system. We choose the direction of the vector, $\mathbf{d}$, joining their atomic centers as the axis of quantization. Taking the functional form of the spherical harmonics in Cartesian coordinates, namely,

$$p_x = x/r, \quad p_y = y/r, \quad p_z = z/r, \quad (14.172)$$

we obtain the geometric decompositions shown in Figure 14.18 in terms of the matrix elements V_{ss} , $V_{sp\sigma}$, $V_{pp\sigma}$, and $V_{pp\pi}$.

A similar argument can be given for interactions involving d-orbitals. Since these orbitals may have $m_\ell = 2$, we introduce a new interaction δ that involves d-orbitals with $m_\ell = 2$ along the quantization axis. Using the d-orbital forms

$$d_1 = 3\frac{z^2}{r^2} - 1, \quad d_2 = \frac{x^2}{r^2} - \frac{y^2}{r^2}, \quad d_3 = \frac{xy}{r^2}, \quad d_4 = \frac{xz}{r^2}, \quad d_5 = \frac{yz}{r^2}. \quad (14.173)$$

The results are shown in Figure 14.19.

sp₂ and sp₃ hybridization Tight-binding calculations involving crystals with local $\mathcal{D}_3$ (graphite and BN) or tetrahedral site-symmetry (diamond, zinc blende, and wurtzite) can be simplified by the construction of symmetry-adapted orbitals, called hybrids, out of s and p orbitals. Under planar symmetry in the xy -plane, we construct out of s, p_x , p_y , using $\mathcal{D}_3$ projection operators, three orthonormal hybrid orbitals, called sp_2 , of the form

$$|h_1\rangle = \frac{1}{\sqrt{3}} (|s\rangle + |p_x\rangle + |p_y\rangle), \quad |h_{2,3}\rangle = \frac{1}{\sqrt{3}} (|s\rangle \pm |p_x\rangle \mp |p_y\rangle).$$

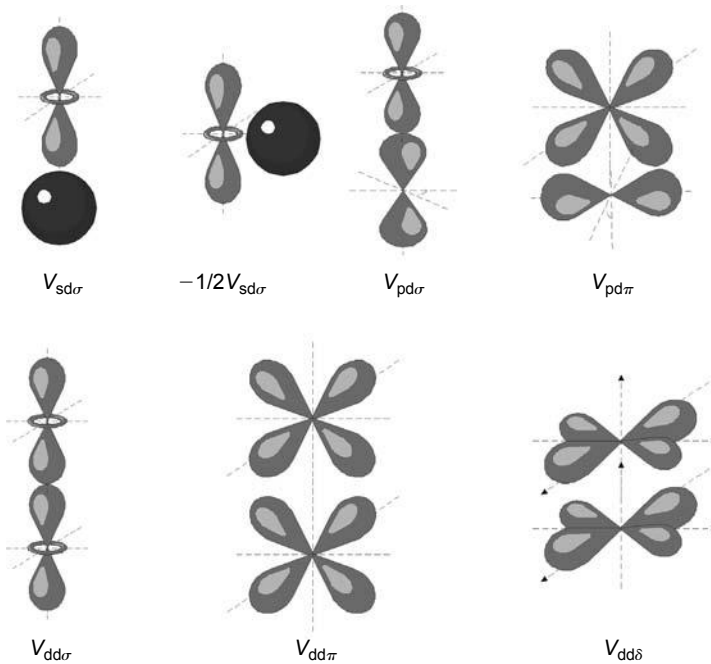


Fig. 14.19. sd, pd, and dd interactions.

Similarly, for tetrahedral site-symmetry we obtain the sp_3 orthonormal orbitals

$$\begin{aligned} |h_1\rangle &= \frac{1}{2}(|s\rangle + |p_x\rangle + |p_y\rangle + |p_z\rangle), & |h_2\rangle &= \frac{1}{2}(|s\rangle + |p_x\rangle - |p_y\rangle - |p_z\rangle), \\ |h_3\rangle &= \frac{1}{2}(|s\rangle - |p_x\rangle + |p_y\rangle - |p_z\rangle), & |h_4\rangle &= \frac{1}{2}(|s\rangle - |p_x\rangle - |p_y\rangle + |p_z\rangle). \end{aligned}$$

14.3.5 d-Bands and resonances

We have been looking so far at an over-simplified picture of the electronic structure – narrow tight-bound bands below the muffin-tin zero, with nearly free electron bands above. In the transition metals these categories become confused: a narrow band arising from the d-levels of the atoms lies within a broad band of s-electrons. Even without the additional complications of magnetic polarization, this situation requires careful analysis.

But this whole interpretation seems to be forbidden by our previous arguments. It was maintained that all atomic bound states would disappear above the muffin-tin zero, leaving only nearly free Bloch states. What did we overlook?

The answer is that the atomic levels of high angular momentum are not completely destroyed by the overlap of potentials, but become *virtual* or *resonance* levels. This

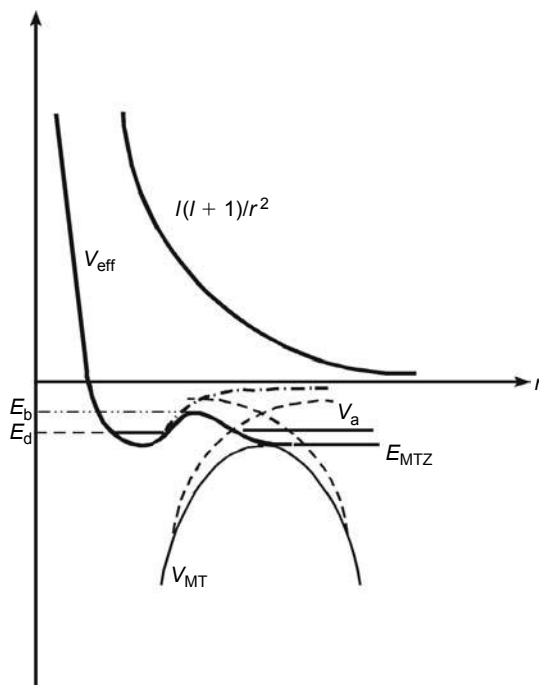


Fig. 14.20. The addition of the centrifugal energy $l(l+1)/r^2$ to an atomic potential v_a gives rise to an effective potential with a bound state at $\mathcal{E}_b$. Overlapping to produce muffin-tin potentials v_{MT} turns this into a resonance.

phenomenon, which is quite familiar in atomic and nuclear physics, arises as follows: The radial Schrödinger equation contains the term $l(l+1)/r^2$, which behaves like the potential of a centrifugal force repelling the electron from the region of the nucleus. In a bound state of high angular momentum ($l \leq 2$), the electron becomes confined to the annular space between this barrier and the ordinary external Coulomb potential of the atom. When atoms are brought together, this outer barrier may not be completely lost, but may still interpose a hill through which the electron in the original atomic level must tunnel if it is to escape. Thus, although we may now be above the muffin-tin zero, we find a strong tendency for the wavefunction to concentrate within the atom as we pass through the energy $\mathcal{E}_d$. This effect cannot be perfectly sharp (as it would be for a true bound state) but must spread over a width W , which would depend in detail on the characteristics of the centrifugal barrier and of the self-consistent potential of the atom.

The simplest description is to treat the “d-electrons” and the “s-electrons” as distinct entities, whose occasional interaction or interchange (s-d scattering) gives rise to special phenomena such as electrical resistivity. The s-electrons are then assumed to be quite free, with energy k^2 , while the five degenerate d-states, $b_m(\bar{r})$, of each atom are combined into a typical tight-bound band of the type discussed above.

In practice, we cannot calculate the width and other properties of this d-band with any accuracy, so we fall back upon the empirical LCAO representation. The d-states of the atom have the same energy, $\mathcal{E}_d$, but different magnetic, quantum numbers, $m = -2, \dots, 2$, so that we have to find the eigenvalues of a 5×5 matrix:

$$\mathcal{H}_{mm'} = \mathcal{E}_d \delta_{mm'} + V_{mm'}(\mathbf{k}). \quad (14.174)$$

Can we now incorporate the s-electrons in the same description? In principle, we could extend our set of atomic orbitals to include the s- and p- states of the free atom, and by adding a further four rows and columns to the matrix (14.174) we should presumably have enough parameters to give a fair account of the band structure.

But the LCAO representation is quite unsatisfactory for free electron bands and we should naturally employ the nearly free electron (NFE) representation. This tells us to find the eigenvalues of the matrix

$$\mathcal{H}_{\mathbf{G}\mathbf{G}'} = |\mathbf{k} - \mathbf{G}|^2 \delta_{\mathbf{G}\mathbf{G}'} + \Gamma_{\mathbf{G}\mathbf{G}'}; \quad (14.175)$$

here again the pseudopotential matrix elements $\Gamma_{\mathbf{G}\mathbf{G}'}$ are often treated as empirically adjustable parameters.

To gain the advantage of both representations, let us combine them. In other words, let us suppose that our true Bloch functions are a linear combination of d atomic orbitals and plane-waves, i.e.

$$\Psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{r}} \sum_m \alpha_m b_m(\mathbf{r} - \mathbf{R}) + \sum_{\mathbf{G}} \alpha_{\mathbf{k}-\mathbf{G}} \phi_{\mathbf{k}-\mathbf{G}}. \quad (14.176)$$

We would then be called upon to find the eigenvalues of the matrix

$$\begin{pmatrix} \mathcal{H}_{\mathbf{G}\mathbf{G}'} & \gamma_{m\mathbf{G}'} \\ \gamma_{\mathbf{G}'m} & \mathcal{H}_{mm'} \end{pmatrix}.$$

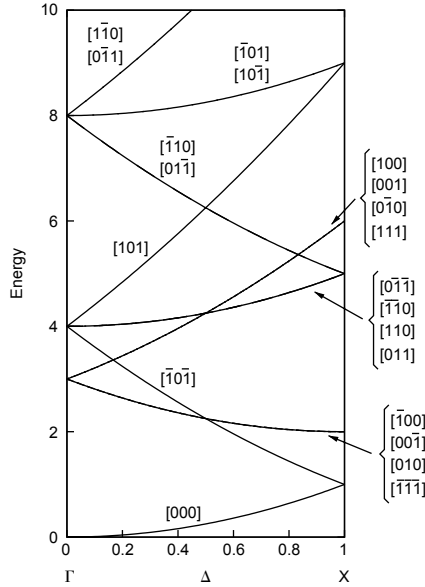


Fig. 14.21. Band structure of Cu in the $[111]$ -direction, showing splitting and hybridization of the NFE sp-band and one of the five d-bands.

This expression is called the *model Hamiltonian*. The $\gamma_{m\bar{G}'}$ are called hybridization coefficients. If they are zero, we are back to the simple model of noninteracting s- and d-bands; otherwise, these have the effect of distorting the simple bands a little, and splitting them apart at points in $\mathbf{k}$ -space where they cross.

A wavefunction of the form (14.176) – something like a bound state with a free electron part outside – is therefore a reasonable trial function for the Bloch function. But the computational disadvantages of such a hybrid representation can be avoided by an extension of the general NFE procedure: Each muffin-tin can be treated as a “black box,” whose only known properties are its partial wave phase shifts $\delta(\mathcal{E})$.

In any standard text on quantum theory, it is shown that the phase shift near a resonance should behave like

$$\delta(\mathcal{E}) = \tan^{-1}[12W/(\mathcal{E}_r - \mathcal{E})], \quad (14.177)$$

showing that it passes rapidly but continuously through the value $\pi/2$ at $\mathcal{E} = \mathcal{E}_r$.

14.4 Electronic structure of magnetically ordered systems

In Chapter 12, we established that the symmetry of a paramagnetic system belongs to one of the type II Shubnikov space-groups. Here, we consider the consequences of the symmetry changes that ensue when the system undergoes a transition from the paramagnetic phase (para-phase) to a magnetically ordered one. The ordered system is no longer invariant under the pure operation of time-reversal. Yet, almost certainly, it is still invariant

under some compound antiunitary operations in the magnetic phase. Consequently, the symmetry of the emerging magnetically ordered system will be based on one of the type III or IV Shubnikov space-groups [13, 58, 60, 73, 93]. This dichromatic space-group is a subgroup of the gray group characterizing the parent paramagnetic phase. This emerging symmetry of the dichromatic space-group will define the labeling and classification of the quasi-particle eigenstates in a magnetic crystal according to the corresponding CoIrreps at the various points of the Brillouin zone. To be more precise, the quasi-particle eigenstates of a magnetic crystal are labeled according to the CoIrreps of $\mathcal{M}_{\mathbf{k}}$, the magnetic little-group, or group of $\mathbf{k}$ [60].

Here, we consider magnons, the electronic spin-wave excitations, as part of the electronic properties of a magnetic crystal, and we discuss their symmetry manifestations below.

We write the dichromatic space-group, $\mathbb{M}$, of a magnetically ordered system as

$$\mathbb{M} = \mathbb{H} + \mathcal{A}\mathbb{H},$$

where $\mathbb{H}$ is a unitary space-group and $\mathcal{A}$ is an antiunitary Seitz operator. The magnetic little-group $\mathcal{M}_{\mathbf{k}}$ of $\mathbf{k}$ then consists of [60]:

- (i) the subgroup $\mathbb{G}_{\mathbf{k}}$ consisting of all the unitary elements of the space-group $\mathbb{H}$ that send $\mathbf{k}$ into an equivalent $\mathbf{k}$,
- (ii) the coset $\mathbb{G}_{\mathbf{k}}^I$ containing all the antiunitary elements of $\mathcal{A}\mathbb{H}$ that send $\mathbf{k}$ into a wavevector equivalent to $-\mathbf{k}$.

We therefore write

$$\mathcal{M}_{\mathbf{k}} = \mathbb{G}_{\mathbf{k}} + \Theta \mathbb{G}_{\mathbf{k}}^I.$$

Since $\mathbb{G}_{\mathbf{k}} \subset \mathbb{H}$, its Irreps may be determined in the usual way for classical space-groups. Two possible scenarios now emerge:

- (i) $\Theta \mathbb{G}_{\mathbf{k}}^I$ contains no elements at all, and $\mathcal{M}_{\mathbf{k}} = \mathbb{G}_{\mathbf{k}}$;
- (ii) $\Theta \mathbb{G}_{\mathbf{k}}^I$ contains exactly the same number of elements as $\mathbb{G}_{\mathbf{k}}$, so that $\mathcal{M}_{\mathbf{k}}$ is a nonunitary group whose CoIrreps can then be constructed from the Irreps $^{(\mu)}\Gamma$ of $\mathbb{G}_{\mathbf{k}}$. The implementation of the DW sum test will reveal whether the CoIrrep is of type (a), (b), or (c).

Type (a) the CoIrrep $\theta^{(\mu)}\Gamma$ of $\mathcal{M}_{\mathbf{k}}$, derived from the Irrep $^{(\mu)}\Gamma$, has no extra degeneracy due to the presence of the antiunitary elements.

Type (b) $\theta^{(\mu)}\Gamma$ has dimension equal to twice that of $^{(\mu)}\Gamma$; in which case two energy levels belonging to the same Irrep $^{(\mu)}\Gamma$ stick together because of the antiunitary elements.

Type (c) $\theta^{(\mu)}\Gamma$ has dimension equal to twice that of $^{(\mu)}\Gamma$; and two energy levels belonging to two inequivalent Irreps $^{(\mu)}\Gamma$ and $^{(\nu)}\Gamma$ of $\mathcal{G}_{\mathbf{k}}$ stick together.

We consider in this section the symmetry properties of two aspects of the electronic structure: the electron energy-band dispersion of ferromagnetic metals and the spin-wave dispersion curves.

14.4.1 The space-group and Brillouin zone of a magnetic metal

The common metallic structures are based on simple f.c.c., b.c.c. and h.c.p. lattices. Thus, in the para-phase their symmetries are described by the gray Shubnikov space-groups $Fm\bar{3}m\bar{1}$, $Im\bar{3}m\bar{1}$ and $P6_3/mmc\bar{1}$, respectively [94, 95].

The space-group of the ferromagnetic phase

A ferromagnetic metal usually comprises many domains, each characterized by a well-defined direction of its spontaneous magnetization $\mathbf{M}$, which is an axial vector that may be specified relative to the crystallographic axes. We consider here a single magnetic domain. The point-group of the symmetry of the domain will be the *intersection* of the gray point-group of the para-phase with the dichromatic point-group $\infty/m\bar{m}$ which leaves the magnetic moment $\mathbf{M}$ invariant. $\infty/m\bar{m}$ comprises:

- (i) all rotations about the axis of $\mathbf{M}$,
- (ii) all combinations of Θ with two-fold rotations about any axis normal to $\mathbf{M}$,
- (iii) product of I with each of the preceding operations.

The elements contained in the intersection of gray point-group and $\infty/m\bar{m}$ will depend on the orientation of $\mathbf{M}$ with respect to the crystallographic axes in the metal. The corresponding space-group will be some subgroup of the gray space-groups ($Fm\bar{3}m\bar{1}$, $Im\bar{3}m\bar{1}$ or $P6_3/mmc\bar{1}$) of the metal in its para-phase, and will generally be one of the dichromatic space-groups containing both unitary and antiunitary elements.

The Brillouin zone of the ferromagnetic phase

Because all the ordered electronic spins in the metal are parallel to each other, and assuming that no displacements of the atoms occur, the space-group/subgroup relation is of the lattice-equal type.

The Brillouin zone (BZ) for the magnetically ordered crystal, neglecting possible magnetostriction distortions, is therefore identical with that of the para-phase. However, the reduction in symmetry due to $\mathbf{M}$ means that the irreducible part of the BZ is larger than 1/48 of the cubic BZ volume, and 1/24 of the h.c.p. BZ volume.

Example 14.5

Face-centered cubic structure

The symmetry point-group will be the intersection of $m\bar{3}m\bar{1}$ with $\infty/m\bar{m}$, which, in turn, will depend on the orientation of $\mathbf{M}$ with respect to the crystallographic axes in the metal.

The magnetic point-groups, their elements, and other pertinent information are given in Table 14.5 for $\mathbf{M}$ parallel to the [001], [111], and [110] directions. The corresponding magnetic space-groups will then be the subgroups of $Fm\bar{3}m\bar{1}$. The elements of the magnetic little-group, $\mathcal{M}_{\mathbf{k}}$, of the wave vector $\mathbf{k}$ are identified in Table 14.6 for a ferromagnetic face-centered cubic metal magnetized parallel to [001].

Table 14.5. *Symmetries of a ferromagnetic cubic metal [96].*

Direction of $\mathbf{M}$	Magnetic point-group	$\mathcal{G}$	$\mathcal{M} - \mathcal{G}$	Space- group	System
[001]	$4/m\bar{m}\bar{m}$	$4/m$ $E, C_4^+, C_4^-, C_2,$ $I, \sigma_h, S_4^-, S_4^+$	U_x, U_y, U_1^d, U_2^d $\sigma_x, \sigma_y, \sigma_1^d, \sigma_2^d$	$I 4/m\bar{m}\bar{m}$	Tetragonal
[111]	$\bar{3}m$	$\bar{3}$ $E, C_3^+, C_3^-,$ I, S_6^-, S_6^+	U_1^d, U_2^d, U_3^d $\sigma_1^d, \sigma_2^d, \sigma_3^d$	$R \bar{3}m$	Trigonal
[110]	$\bar{m}m\bar{m}$	$2/m$ E, U_1^d, I, σ_1^d	$U_2^d, C_2, \sigma_2^d, \sigma_h$	$I \bar{m}m\bar{m}$	Orthorhombic

Table 14.6. *Magnetic little-group $\mathcal{M}_{\mathbf{k}}$ for a ferromagnetic f.c.c. metal with $\mathbf{M} \parallel [001]$ [96].*

Symmetry point/line	$\mathbf{k}$		$\mathcal{G}$	$\mathcal{M} - \mathcal{G}$	Space subgroup
Γ	0,0,0	$\left. \vphantom{\begin{matrix} \Gamma \\ X_2 \end{matrix}} \right\} 4/m \left\{ \begin{matrix} E, C_4^+, C_4^-, C_2, \\ I, \sigma_h, S_4^-, S_4^+ \end{matrix} \right.$	$E, C_4^+, C_4^-, C_2,$	U_x, U_y, U_1^d, U_2^d	$4/m\bar{m}\bar{m}$
X_2	0,0,1		$I, \sigma_h, S_4^-, S_4^+$	$\sigma_x, \sigma_y, \sigma_1^d, \sigma_2^d$	
X_1	0,1,0	$2/m$	E, C_2, I, σ_h	$U_x, U_y, \sigma_x, \sigma_y$	$\bar{m}m\bar{m}$
L	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	$\bar{1}$	E, I	U_2^d, σ_2^d	$\underline{2}/m$
W_2	$0, 1, \frac{1}{2}$	$\bar{4}$	E, S_4^+, S_4^-, C_2	$U_x, U_y, \sigma_1^d, \sigma_2^d$	$\bar{4} \underline{2}m$
W_3	$0, \frac{1}{2}, 1$	m	E, σ_h	U_x, σ_y	$\underline{2}m m$
W_1	$\frac{1}{2}, 1, 0$	m	E, σ_h	U_y, σ_x	$\underline{2}m m$
Δ_2	0,0, κ	4	E, C_4^+, C_4^-, C_2	U_x, U_y, U_1^d, U_2^d	$4 \underline{2} \underline{2}$
Δ_1	0, κ ,0	m	E, σ_h	U_x, σ_y	$\underline{2}m m$
Σ_1	$\kappa, \kappa, 0$	m	E, σ_h	U_2^d, σ_1^d	$\underline{2}m m$
Σ_2	0, κ , κ	1	$E,$	—	—
Λ	κ, κ, κ	1	E	U_2^d	$\underline{2}$

The irreducible zone is now 1/16 instead of 1/48 of the BZ. Consequently, we find that many of the high-symmetry points/directions, which were equivalent in the para-phase, such as the X-point, may now occur in several different nonequivalent positions.

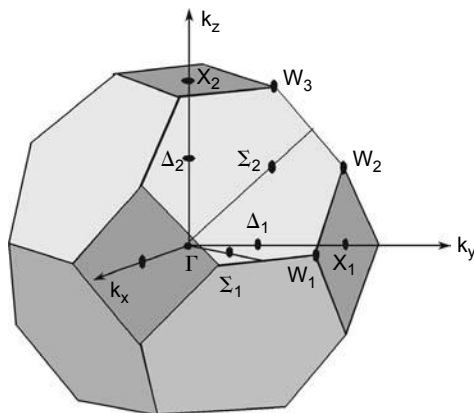


Fig. 14.22. Brillouin zone of a ferromagnetic f.c.c. metal, $\mathbf{M} \parallel [001]$ -direction.

Because $Fm\bar{3}m$ is a symmorphic space-group, the unitary elements for each wavevector $\mathbf{k}$ in Table 14.6 correspond to one of the classical crystallographic point-groups. Each of the magnetic little-groups $\mathcal{M}_{\mathbf{k}}$ is then also isomorphic with one or other of the 58 dichromatic point-groups. The presence of the antiunitary elements should lead to an extra degeneracy, at $\mathbf{k}$, in the electronic band structure for any bands that belong to a double-valued Irrep of $\mathcal{G}_{\mathbf{k}}$ which leads to a case (b) or case (c) corepresentation of $\mathcal{M}_{\mathbf{k}}$. However, we actually find that for each of the double-valued corepresentations of the magnetic point-groups in Table 14.6 only case (a) corepresentations actually occur.

14.4.2 Labeling of spin-wave dispersion curves

We show in this section how the CoIrreps of a compatible magnetic space-group can be applied in the labeling of the spin-wave (magnon) dispersion curves. This, in turn, allows us to predict the degeneracy of the magnon dispersion relations at the various points in the Brillouin zone in the case of both ferromagnetic and antiferromagnetic crystals. The assignment of CoIrreps to magnon dispersion curves can be established by studying the transformation properties of the corresponding magnon creation operators [97]. We illustrate this process by presenting a detailed analysis of the magnon bands of the antiferromagnetic crystals MnF_2 and NiF_2 . We first present a brief outline of spin-wave theory.

Spin-wave theory

The theory of spin-waves is based on small deviations from an otherwise fully ordered magnetic ground-state. Although the ground-state of an antiferromagnet (AF) is known to contain some degree of disorder, we neglect this disorder and adopt here the Néel state as the ground-state. It comprises two ordered spin sublattices, A and B , where each site of a given sublattice has maximal spin S oriented along a fixed axis of quantization, the z -axis; the two sublattices then maintain antiparallel orientations of their spins.

A spin-wave then corresponds to collective deviations of the spins from their maximal spin S . Thus, in the assumed ground (or Néel) state $|0\rangle$ we have

$$\hat{\mathbf{S}}_a^+ |0\rangle = \hat{\mathbf{S}}_b^- |0\rangle = 0, \quad \Rightarrow \quad \hat{\mathbf{S}}^\pm = \frac{1}{2} (\hat{S}_x \pm i\hat{S}_y), \quad (14.178)$$

where subscripts a and b refer to sublattices A and B , respectively. All of the A spins are chosen to be “up”, and all of the B spins are “down”. The Hamiltonian for such a system, in the absence of an external magnetic field, can be written as

$$\begin{aligned} \mathcal{H}_{\text{AF}} &= 2J \sum_{\alpha\beta} \hat{\mathbf{S}}_\alpha \cdot \hat{\mathbf{S}}_\beta - g\mu_B B_{\text{an}} \left[\sum_{\alpha} \hat{S}_\alpha^z - \sum_{\beta} \hat{S}_\beta^z \right] \\ &= \sum_{\alpha} \left[\hat{S}_\alpha^z \hat{S}_\beta^z + \frac{1}{2} (\hat{S}_\alpha^+ \hat{S}_\beta^- + \hat{S}_\alpha^- \hat{S}_\beta^+) \right] - g\mu_B B_{\text{an}} \left[\sum_{\alpha} \hat{S}_\alpha^z - \sum_{\beta} \hat{S}_\beta^z \right], \end{aligned} \quad (14.179)$$

where α, β span sublattices A and B , respectively; B_{an} is a fictitious staggered mean-field anisotropy. The magnitude of the spin at each sublattice is the same, i.e. $S_a = S_b = S$. We now employ the spin-deviation operators, defined in Appendix 2, retaining only terms linear in these operators, namely,

$$\begin{aligned} \hat{S}_\alpha^+ &\approx (2S)^{1/2} \hat{\mathbf{a}}_\alpha, & \hat{S}_\alpha^- &\approx (2S)^{1/2} \hat{\mathbf{a}}_\alpha^\dagger, & S - \hat{S}_\alpha^z &= \hat{\mathbf{a}}_\alpha^\dagger \hat{\mathbf{a}}_\alpha, \\ \hat{S}_\beta^+ &\approx (2S)^{1/2} \hat{\mathbf{b}}_\beta^\dagger, & \hat{S}_\beta^- &\approx (2S)^{1/2} \hat{\mathbf{b}}_\beta, & S + \hat{S}_\beta^z &= \hat{\mathbf{b}}_\beta^\dagger \hat{\mathbf{b}}_\beta. \end{aligned} \quad (14.180)$$

We also introduce the spin-wave transformations:

Sublattice A	Sublattice B
$\hat{\mathbf{a}}_\alpha = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{-i\mathbf{k} \cdot \mathbf{R}_\alpha} \hat{\mathbf{a}}_{\mathbf{k}}$	$\hat{\mathbf{b}}_\beta = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{-i\mathbf{k} \cdot \mathbf{R}_\alpha} \hat{\mathbf{b}}_{\mathbf{k}}$
$\hat{\mathbf{a}}_\alpha^\dagger = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{R}_\alpha} \hat{\mathbf{a}}_{\mathbf{k}}^\dagger$	$\hat{\mathbf{b}}_\beta^\dagger = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{R}_\alpha} \hat{\mathbf{b}}_{\mathbf{k}}^\dagger$
$\hat{\mathbf{a}}_\alpha^\dagger \hat{\mathbf{a}}_\alpha = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}, \mathbf{k}'} e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{R}_\alpha} \hat{\mathbf{a}}_{\mathbf{k}}^\dagger \hat{\mathbf{a}}_{\mathbf{k}'}$	$\hat{\mathbf{b}}_\beta^\dagger \hat{\mathbf{b}}_\beta = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}, \mathbf{k}'} e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{R}_\alpha} \hat{\mathbf{b}}_{\mathbf{k}}^\dagger \hat{\mathbf{b}}_{\mathbf{k}'}$

Here $\hat{\mathbf{a}}_{\mathbf{k}}^\dagger$, $\hat{\mathbf{a}}_{\mathbf{k}}$ and $\hat{\mathbf{b}}_{\mathbf{k}}^\dagger$, $\hat{\mathbf{b}}_{\mathbf{k}}$ are the spin-deviation creation and annihilation operators for the two sublattices in question. The wavevector $\mathbf{k}$ spans the N points of the Brillouin zone, corresponding to N spins of each sublattice. The transformed Hamiltonian is

$$\begin{aligned} \mathcal{H}_{\text{AF}} &= \text{constant} + 2JS\mathcal{Z} \sum_{\mathbf{k}} \left[\hat{\mathbf{a}}_{\mathbf{k}}^\dagger \hat{\mathbf{a}}_{\mathbf{k}} + \hat{\mathbf{b}}_{\mathbf{k}}^\dagger \hat{\mathbf{b}}_{\mathbf{k}} + \mathcal{Y}_{\mathbf{k}} (\hat{\mathbf{a}}_{\mathbf{k}}^\dagger \hat{\mathbf{b}}_{\mathbf{k}}^\dagger + \hat{\mathbf{a}}_{\mathbf{k}} \hat{\mathbf{b}}_{\mathbf{k}}) \right] \\ &\quad + g\mu_B B_{\text{an}} \sum_{\mathbf{k}} \left[\hat{\mathbf{a}}_{\mathbf{k}}^\dagger \hat{\mathbf{a}}_{\mathbf{k}} + \hat{\mathbf{b}}_{\mathbf{k}}^\dagger \hat{\mathbf{b}}_{\mathbf{k}} \right], \end{aligned} \quad (14.181)$$

where $\mathcal{Z}$ is the coordination number, and

$$\mathcal{Y}_{\mathbf{k}} = \frac{1}{\mathcal{Z}} \sum_h \exp(i\mathbf{k} \cdot \mathbf{R}_h),$$

where h runs over nearest neighbors only. $\mathcal{H}_{\text{AF}}$ in (14.181) is not diagonal. To cast it in a diagonal form we make use of the Bogoliubov canonical transformation

$$\begin{aligned}\hat{\mathbf{a}}_{\mathbf{k}} &= \hat{\alpha}_{\mathbf{k}} \cosh \theta_{\mathbf{k}} + \hat{\beta}_{\mathbf{k}}^{\dagger} \sinh \theta_{\mathbf{k}} \\ \hat{\mathbf{b}}_{\mathbf{k}} &= \hat{\alpha}_{\mathbf{k}}^{\dagger} \sinh \theta_{\mathbf{k}} + \hat{\beta}_{\mathbf{k}} \cosh \theta_{\mathbf{k}} \\ \cosh^2 \theta_{\mathbf{k}} - \sinh^2 \theta_{\mathbf{k}} &= 1\end{aligned}\quad (14.182)$$

together with their Hermitian conjugates. The coefficients $\cosh \theta_{\mathbf{k}}$ and $\sinh \theta_{\mathbf{k}}$ were chosen in order to satisfy the commutation relations for the new operators. The Hamiltonian then becomes

$$\begin{aligned}\mathcal{H}_{\text{AF}} &= \text{constant} + \mathcal{E} \\ &+ \sum_{\mathbf{k}} \left\{ \left[(g\mu_{\text{B}} B_{\text{an}} - 2JSZ)u_{\mathbf{k}} - 2JSZ\mathcal{Y}_{\mathbf{k}}v_{\mathbf{k}} \right] \hat{\alpha}_{\mathbf{k}}^{\dagger} \hat{\alpha}_{\mathbf{k}} \right. \\ &+ \left[(g\mu_{\text{B}} B_{\text{an}} - 2JSZ)u_{\mathbf{k}} - 2JSZ\mathcal{Y}_{\mathbf{k}}v_{\mathbf{k}} \right] \hat{\beta}_{\mathbf{k}}^{\dagger} \hat{\beta}_{\mathbf{k}} \\ &\left. + \left[(g\mu_{\text{B}} B_{\text{an}} - 2JSZ)v_{\mathbf{k}} - 2JSZ\mathcal{Y}_{\mathbf{k}}u_{\mathbf{k}} \right] \left[\hat{\alpha}_{\mathbf{k}}^{\dagger} \hat{\beta}_{\mathbf{k}}^{\dagger} + \hat{\alpha}_{\mathbf{k}} \hat{\beta}_{\mathbf{k}} \right] \right\}, \quad (14.183) \\ u_{\mathbf{k}} &= \cosh^2 \theta_{\mathbf{k}} + \sinh^2 \theta_{\mathbf{k}}, \quad v_{\mathbf{k}} = 2 \cosh \theta_{\mathbf{k}} \sinh \theta_{\mathbf{k}}.\end{aligned}$$

In order to diagonalize the Hamiltonian, the coefficients must satisfy the relations

$$2 \cosh \theta_{\mathbf{k}} \sinh \theta_{\mathbf{k}} (g\mu_{\text{B}} B_{\text{an}} - 2JSZ) - (\cosh^2 \theta_{\mathbf{k}} + \sinh^2 \theta_{\mathbf{k}}) 2JSZ\mathcal{Y}_{\mathbf{k}} = 0$$

or

$$\tanh 2\theta_{\mathbf{k}} = \frac{\omega_{\text{ex}}\mathcal{Y}_{\mathbf{k}}}{\omega_{\text{an}} - \omega_{\text{ex}}},$$

where

$$\begin{aligned}\omega_{\text{ex}} &= 2ZSJ/\hbar, \\ \omega_{\text{an}} &= g\mu_{\text{B}} B_{\text{an}}/\hbar.\end{aligned}$$

Thus the Hamiltonian becomes

$$\mathcal{H}_{\text{AF}} = \sum_{\mathbf{k}} \left[\hbar\omega_{\mathbf{k}}^{(+)} \left(\hat{\alpha}_{\mathbf{k}}^{\dagger} \hat{\alpha}_{\mathbf{k}} + \frac{1}{2} \right) + \hbar\omega_{\mathbf{k}}^{(-)} \left(\hat{\beta}_{\mathbf{k}}^{\dagger} \hat{\beta}_{\mathbf{k}} + \frac{1}{2} \right) \right], \quad (14.184)$$

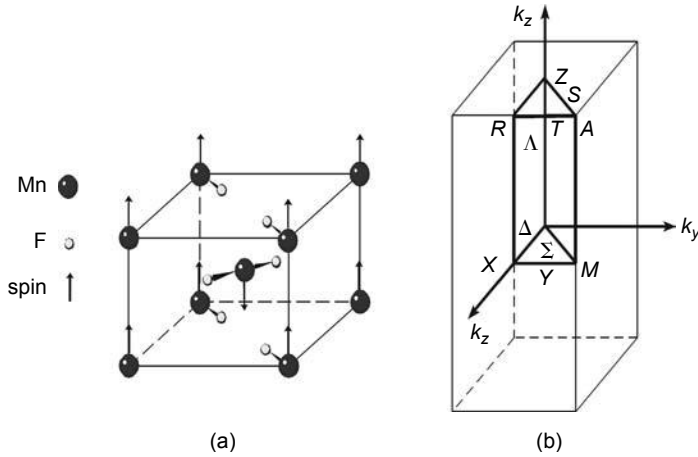
where

$$\omega_{\mathbf{k}}^{(\pm)} = \left[(\omega_{\text{ex}} + \omega_{\text{an}})^2 - \omega_{\text{ex}}^2 \mathcal{Y}_{\mathbf{k}}^2 \right]^{1/2}.$$

Let us now consider the dispersion relation. In the long-wavelength limit, and neglecting the anisotropy energy, the dispersion relation is considerably simplified. We obtain for cubic systems:

$$\hbar\omega_{\mathbf{k}}^{(\pm)} = 2(2Z)^{1/2}SJka. \quad (14.185)$$

In this respect, magnons in AF systems behave like phonons, in the absence of anisotropy.

Fig. 14.23. (a) Unit cell of MnF₂, (b) Brillouin zone.*Symmetry of magnons in the AF fluorides*

Using (14.180) and (14.182) we write

$$\begin{aligned}\alpha_{\mathbf{k}}^{\dagger} &= \frac{1}{\sqrt{2SN}} \left[\cosh \theta_{\mathbf{k}} \sum_{\alpha} e^{i\mathbf{k} \cdot \mathbf{R}_{\alpha}} \hat{S}_{\alpha}^{-} - \sinh \theta_{\mathbf{k}} \sum_{\beta} e^{-i\mathbf{k} \cdot \mathbf{R}_{\beta}} \hat{S}_{\beta}^{-} \right], \\ \beta_{\mathbf{k}}^{\dagger} &= \frac{1}{\sqrt{2SN}} \left[\cosh \theta_{\mathbf{k}} \sum_{\beta} e^{i\mathbf{k} \cdot \mathbf{R}_{\beta}} \hat{S}_{\beta}^{+} - \sinh \theta_{\mathbf{k}} \sum_{\alpha} e^{i\mathbf{k} \cdot \mathbf{R}_{\alpha}} \hat{S}_{\alpha}^{+} \right].\end{aligned}\quad (14.186)$$

Following Dimmock and Wheeler [71], we take the direction of sublattice magnetization to be the 3-axis, then a spin-wave propagating along $\mathbf{k}$ will transform under the operations of the little-group of $\mathbf{k}$ as $S_1 \pm iS_2$ where $\hat{\mathbf{e}}_1 \times \hat{\mathbf{e}}_2 = \hat{\mathbf{e}}_3$ form a right-handed system of axes, and S_1, S_2 transform as axial vectors.

We illustrate this method by applying it to MnF₂ crystals. These crystals have a rutile structure in their paramagnetic phase, with space-group $P4_2/mnm \underline{1}$. In the AF phase the spin-ordering, Figure 14.23, does not change the unit cell, with $\hat{\mathbf{e}}_3$ coinciding with the crystallographic four-fold axis.

The subgroup schematic is

	Nonunitary	Unitary
Nonmagnetic	$P4_2/mnm \underline{1}$	$P4_2/mnm$
	$\downarrow$	$\downarrow$
Magnetic	$P\bar{4}_2/mnm$	$Pnnm$

We start with the unitary double space-group $\mathfrak{D}Pnnm$ and consider here the Γ -point ($\mathbf{k} = (0,0,0)$). The corresponding character table is given in Table 14.7. We find that $S_1 - iS_2$ and $S_1 + iS_2$ transform as Γ_3^+ and Γ_4^+ , respectively, which, according to Table 14.7, form a (c) degenerate pair.

Compatibilities with other points and lines in the reduced BZ is given in Table 14.8. Figure 14.24 shows the magnon dispersion curves for MnF_2 along the $[001]$ and $[100]$ directions.

Model spin Hamiltonians and spin space-groups

Our definition of magnetic or dichromatic point-groups implied that its rotation/roto-reflection operators act on both space positions and spins simultaneously; the latter are

Table 14.7. Character table for the little-group of Γ -point for $Pnnm$.

	$(E \mathbf{0})$	$(\bar{E} \mathbf{0})$	$(C_2 \mathbf{0})$	$(U_x \boldsymbol{\tau})$ $(\bar{U}_x \boldsymbol{\tau})$	$(U_y \boldsymbol{\tau})$ $(\bar{U}_y \boldsymbol{\tau})$	$(I \mathbf{0})$	$(\bar{I} \mathbf{0})$	$(\sigma_h \mathbf{0})$	$(\sigma_x \boldsymbol{\tau})$ $(\bar{\sigma}_x \boldsymbol{\tau})$	$(\sigma_y \boldsymbol{\tau})$ $(\bar{\sigma}_y \boldsymbol{\tau})$	Θ
Γ_1^+	1	1	1	1	1	1	1	1	1	1	(a)
Γ_2^+	1	1	1	-1	-1	1	1	1	-1	-1	(a)
Γ_3^+	1	1	-1	1	-1	1	1	-1	1	-1	} (c)
Γ_4^+	1	1	-1	-1	1	1	1	-1	-1	1	
Γ_1^-	1	1	1	1	1	-1	-1	-1	-1	-1	(a)
Γ_2^-	1	1	1	-1	-1	-1	-1	-1	1	1	(a)
Γ_3^-	1	1	-1	1	-1	-1	-1	1	-1	1	} (c)
Γ_4^-	1	1	-1	-1	1	-1	-1	1	1	-1	
Γ_5^+	2	-2	0	0	0	2	-2	0	0	0	(a)
Γ_5^-	2	-2	0	0	0	-2	2	0	0	0	(a)

Table 14.8. Compatibility in the reduced zone.

$\Gamma_{3,4}$					
Δ_3, Δ_4		$2\Sigma_2$		$\Lambda_{3,4}$	
X_2		M_3^+, M_4^+		Z_2	
W_1	Y_3, Y_4	V_3, V_4	S_1, S_2	U_1	
R_1^+		A_2		R_1^+	

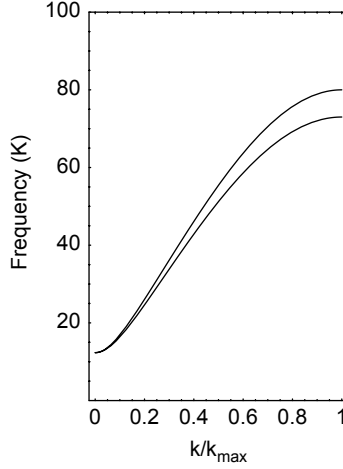


Fig. 14.24. Magnon dispersion curves in MnF_2 , along $[001]$ and $[100]$ directions. $J_1 = 0.32$ K, $J_2 = -1.76$ K and $D = 1.06$ K.

treated as pseudovectors. The action of this group, in conjunction with time-reversal, when applicable, leaves the system invariant.

However, in many cases, calculations of the properties of magnetic materials, e.g. spin-dispersion curves, are based on model spin Hamiltonians, which are the result of several simplifying assumptions. For example, the original Hamiltonian may contain various types of interactions among the spins or between the spins and the lattice, such as crystal fields. In many cases justifiable simplifications lead to the isotropic Heisenberg Hamiltonian with an effective anisotropy field to stabilize the ground-state spin orientation, namely

$$\mathcal{H}_H = - \sum_{ij} J_{ij} \mathbf{S}(\mathbf{R}_i) \cdot \mathbf{S}(\mathbf{R}_j) + \sum_i \mathbf{H}(\mathbf{R}_i) \cdot \mathbf{S}(\mathbf{R}_i),$$

where J_{ij} is the coupling between spin vectors $\mathbf{S}(\mathbf{R}_i)$ and $\mathbf{S}(\mathbf{R}_j)$ at sites $\mathbf{R}_i$ and $\mathbf{R}_j$, respectively. The second term represents interaction with an external magnetic field $\mathbf{H}$.

We notice that, in this model Hamiltonian, the spin vectors can be rotated independently of their coordinates. Thus, such model Hamiltonians may have more symmetry than the magnetic space-group $\mathcal{M}$ of the system they are supposed to represent. Consequently, the calculated spin-wave dispersion relations will exhibit more degeneracies than allowed by the magnetic space-group of the system.

The group of all spin and space rotations which commute with a model Hamiltonian $\mathcal{H}$ is called a *spin space-group*, denoted by $\mathbb{S}^s$ [98, 99, 100]. The extra symmetry manifest in, say, the calculated spin-wave dispersions, is simply described in terms of the Irreps of $\mathbb{S}^s$.

To determine $\mathbb{S}^s$ that is compatible with a model Hamiltonian, Brinkman and Elliott [98, 99] proposed the following method.

We start with the symmetry of an ideal paramagnetic crystal, where we assume that there is no spin-orbit interaction in the crystal. In the absence of spin the symmetry of a crystal is described by a Fedorov space-group $\mathbb{S}$. Since the symmetry of the spin system

is that of $\theta\mathcal{R}(3)$, the full group that describes the symmetry of a paramagnetic crystal is $\theta\mathcal{R}(3) \otimes \mathbb{S}$.

Thus, if $(R_i(\mathbf{r})|\boldsymbol{\tau}_i\mathbf{t}) \in \mathbb{S}$, we can write a corresponding element of the full group of the paramagnetic crystal as $(R_i(\mathbf{r}) R_j(\mathbf{s})|\mathbf{t}_i)$ where $R_j(\mathbf{s}) \in \theta\mathcal{R}(3)$ and $R_j(\mathbf{s})$ acts only on the spins. The complete group of the ideal paramagnetic crystal, with no interactions between the spins and the lattice, can be written as

$$\mathfrak{S} = \sum_i \sum_j (R_i(\mathbf{r}) R_j(\mathbf{s})|\boldsymbol{\tau}_i) \mathbb{T}, \quad (14.187)$$

where $(R_i(\mathbf{r})|\boldsymbol{\tau}_i)$ are the left coset representatives of $\mathbb{S}$ in $\mathbb{T}$, and $\mathbb{T}$ is the group of the translational operations of the paramagnetic Bravais lattice.

In contrast, a magnetic space-group $\mathcal{M}$, associated with the ordered magnetic system, has the coset expansion

$$\mathcal{M} = \sum_q (R_q(\mathbf{r}) R_q(\mathbf{s})|\boldsymbol{\tau}_i) \mathbb{T}_M, \quad (14.188)$$

where $\mathbb{T}_M$ is the group of the translation operations of the Bravais lattice of the magnetic crystal. $\mathcal{M}$ is a direct inner-product, with $i = j = q$, and is a subgroup of $\mathfrak{S}$. In $\mathcal{M}$, the point-group operations in $\mathbb{S}$ act simultaneously on the space coordinates and on the spins.

We first consider the symmetry of the magnetic structure in coordinate space. Ignoring nonmagnetic atoms, we partition the magnetic structure into sublattices according to their spin orientations, i.e. each sublattice will have a single, well-defined orientation of its spins. We construct a Fedorov space-group, denoted by $\mathbb{G}'$, that

- (a) consists of all operations which, acting on the atomic positions but not on the spin vectors, take each sublattice into itself;
- (b) its translation subgroup is $\mathbb{T}_M$ and not $\mathbb{T}$.

We also construct $\mathcal{S}$, the symmetry point-group of the spin system.

Example 14.6

$\mathcal{S}$ of the Heisenberg ferromagnet

Here, the ferromagnetic spins define a z -axis of cylindrical symmetry and we identify $\mathcal{S}$ as the dichromatic point-group $\infty_2 \subset \theta\mathcal{O}(3)$.

∞_2 contains all rotations about the spin z -axis and products of time-inversion Θ with a two-fold rotation about any axis normal to the z -axis.

The spin space-group $\mathbb{S}^s$ is then

$$\mathbb{S}^s = \mathbb{G}' \otimes \mathcal{S}.$$

Since $\mathbb{G}' \subseteq \mathbb{S}$, we conclude that $\mathcal{M} \subseteq \mathbb{S}^s \subseteq \mathbb{S}$. When some operations of $\mathcal{S}$ are of the form $(R_j(\mathbf{s})|\boldsymbol{\tau})$, $\boldsymbol{\tau} \neq \mathbf{0}$, as in the case of a simple two-sublattice antiferromagnet, $\mathcal{S} \not\subseteq \theta\mathcal{O}(3)$. In this case with $S_i \in \mathcal{S}$, we still can write $\mathbb{S}^s$ as

$$\mathbb{S}^s = \sum_{i=1}^n S_i \mathbb{G}'. \quad (14.189)$$

Irreps of $\mathbb{S}^s$

We now consider how to apply and modify space-group Irrep theory to obtain the appropriate Irreps of $\mathbb{S}^s$, and explore the compatibility relations between $\mathbb{S}^s$ and $\mathcal{M}$. Since some of the operations in $\mathcal{S}$ may be of the form $(R_j(\mathbf{s})|\boldsymbol{\tau})$, $\boldsymbol{\tau} \neq \mathbf{0}$, we express $\mathbb{S}^s$ as an expansion in terms of left coset representatives of $\mathbb{T}_M$ of the form

$$\mathbb{S}^s = \sum_i \sum_s (R_i(\mathbf{r})R_s(\mathbf{s})|\boldsymbol{\tau}_i + \boldsymbol{\tau}_s) \mathbb{T}_M, \quad (14.190)$$

subject to the multiplication rule

$$\begin{aligned} (R_2(\mathbf{r})R_u(\mathbf{s})|\boldsymbol{\tau}_2 + \boldsymbol{\tau}_u)(R_1(\mathbf{r})R_s(\mathbf{s})|\boldsymbol{\tau}_1 + \boldsymbol{\tau}_s) \\ = (R_2(\mathbf{r})R_1(\mathbf{r})R_u(\mathbf{s})R_s(\mathbf{s})|\boldsymbol{\tau}_2 + R_2\boldsymbol{\tau}_1 + \boldsymbol{\tau}_u + R_2\boldsymbol{\tau}_s). \end{aligned}$$

Notice that because $R_s(\mathbf{s})$ and $R_u(\mathbf{s})$ act only on the spin coordinates they do not act on any of the $\boldsymbol{\tau}$ s. This also applies to the elements of $\mathbb{T}_M$ which has Irreps characterized by $\mathbf{k}$ in the first Brillouin zone.

Selecting a $\mathbf{k}$ -vector, the problem reduces to finding the CoIrreps of the little-group of $\mathbf{k}$, $\mathbb{S}_{\mathbf{k}}^s$. Since spin rotations do not affect $\mathbf{k}$, this little-group will always contain the elements $(R_j(\mathbf{s})|\boldsymbol{\tau} + \mathbf{t})$.

For a general point in the Brillouin zone, the little-group $\mathbb{S}_{\mathbf{k}}^s$ can be written as

$$\mathbb{S}_{\mathbf{k}}^s = \sum_j (E(\mathbf{r})R_j(\mathbf{s})|\boldsymbol{\tau}_j) \mathbb{T}_M. \quad (14.191)$$

The relationship between the Reps of $(E(\mathbf{r})R_j(\mathbf{s})|\boldsymbol{\tau}_j + \mathbf{t})$ and $[R_j(\mathbf{s})]$ is

$$\begin{aligned} \Gamma[(E(\mathbf{r})R_j(\mathbf{s})|\boldsymbol{\tau}_j + \mathbf{t})] &= \exp[-i\mathbf{k} \cdot (\boldsymbol{\tau}_j + \mathbf{t})] \Gamma[(E(\mathbf{r})R_j(\mathbf{s})|\mathbf{0})] \\ &= \exp[-i\mathbf{k} \cdot (\boldsymbol{\tau}_j + \mathbf{t})] \Gamma[R_j(\mathbf{s})]. \end{aligned} \quad (14.192)$$

The problem of determining the space-group Irreps or CoIrreps of $\mathbb{S}^s$ at a general Brillouin zone point reduces to that of determining the CoIrreps of $\mathcal{S}$.

Example 14.7

Irreps of ∞_2

The unitary subgroup ∞ is an Abelian group with one-dimensional Irreps. If $\chi(\phi)$ is the Irrep character for an angular axial rotation ϕ , then it has to satisfy the condition

$$\chi(0) = \chi(2\pi) = 1 \quad \Rightarrow \quad \chi(\phi) = e^{im\phi}, \quad m \text{ integer.}$$

Applying the Dimmock/Wheeler test we get

$$\sum \chi(R^2) \Rightarrow \int_0^{2\pi} d\phi e^{2im\phi} = 0,$$

and we have case (c). Thus, the Irreps m and $-m$ are degenerate.

The Heisenberg ferromagnet $\mathcal{S} = \infty 2$ has a unitary subgroup ∞ whose Irreps are characterized by m_s , the eigenvalues of the spin-deviation operator! The CoIrreps of $\mathcal{S} = \infty 2$ have Kramers' degeneracy.

For lines of symmetry and planes of symmetry that are completely within the Brillouin zone the space-group Irreps of $\mathbb{S}^s$ can be found by identifying it with some Fedorov space-group.

Example 14.8

$\mathbb{S}^s$ for the simple two-sublattice antiferromagnet MnF_2 [99, 100]

In MnF_2 , the Mn ion has a $^6A_{1g}$ ground-state, derived from the ^6S of the free Mn^{2+} ion; it has no orbital angular momentum component. The higher states lie about 2 eV above. Consequently, the lowest excitations occur around this ground-state; they are purely spin-waves, i.e. normal magnons, involving no electronic transitions. Higher excitations, referred to as exciton-like states, are collective spin-wave excitations about higher excited electronic states.

The space-group of the paramagnetic structure $P4_2/mnm1$ may be written as

$$P4_2/mnm1 = (E, \Theta) \otimes P4_2/mnm.$$

$P4_2/mnm$ has generating elements $(C_4^+|\tau)$, $(U_x|\tau)$, and $(I|\mathbf{0})$, where $\tau = 1/2(a, a, c)$. We may write $P4_2/mnm$ as the coset expansion

$$P4_2/mnm = P \frac{2}{m} + P \frac{2}{m} \otimes (U_1^d|\mathbf{0}) + P \frac{2}{m} \otimes (C_4^+|\tau) + P \frac{2}{m} \otimes (U_x|\tau)$$

with

$$\begin{aligned} \frac{2}{m} &= (E|\mathbf{0}), (C_2|\mathbf{0}), (I|\mathbf{0}), (\sigma_h|\mathbf{0}) = A, \\ \frac{2}{m} \otimes (U_1^d|\mathbf{0}) &= (U_1^d|\mathbf{0}), (U_2^d|\mathbf{0}), (\sigma_1^d|\mathbf{0}), (\sigma_2^d|\mathbf{0}) = B, \\ \frac{2}{m} \otimes (C_4^+|\tau) &= (C_4^+|\tau), (C_4^-|\tau), (S_4^+|\tau), (S_4^-|\tau) = C, \\ \frac{2}{m} \otimes (U_x|\tau) &= (U_x|\tau), (U_y|\tau), (\sigma_x|\tau), (\sigma_y|\tau) = D. \end{aligned}$$

In $\mathbb{S}^s$ of MnF_2 these operations act only on the space coordinates. The sublattice space-group $\mathbb{G}'$ comprises

$$\mathbb{G}' = P \frac{2}{m} \otimes \left[(E|\mathbf{0}) + (U_1^d|\mathbf{0}) + (E|\tau)^{-1} \otimes ((C_4^+|\tau) + (U_x|\tau)) \right].$$

Notice that $\mathbb{T}_M = \mathbb{T}$, and

$$\mathcal{S} = (E|\mathbf{0}) \otimes \infty 2 + \Theta(E|\boldsymbol{\tau}) \otimes \infty 2,$$

where, in addition to $\infty 2$, it contains products of $\Theta(E|\boldsymbol{\tau})$ with all rotations about the spin axis, and products of $(E|\boldsymbol{\tau})$ with a two-fold rotation about any axis normal to the spin axis. $\mathbb{S}^s$ may therefore be written as

$$\mathbb{S}^s = \mathbb{G}' \otimes \mathcal{S} = \mathbb{G}' \otimes (E|\mathbf{0}) \otimes \infty 2 + \mathbb{G}' \otimes \Theta(E|\boldsymbol{\tau}) \otimes \infty 2. \quad (14.193)$$

The CoIrreps of the dichromatic space-group of the AFM structure, $P4_2/mnm$, have been left as exercise 12.10.

It is now possible to construct the group of $\mathbf{k}$, $\mathbb{S}_{\mathbf{k}}^s$, at the various points in the Brillouin zone, and to determine its Irreps or CoIrreps. At a general point in the Brillouin zone, there is a double degeneracy between m on one sublattice and $-m$ on the other sublattice.

At each of the points of symmetry, Γ, X, M, Z, L , and R , in the Brillouin zone of MnF_2 , the little-cogroup $\overline{\mathbb{G}}^{\mathbf{k}}$ is the same and comprises

$$\overline{\mathbb{G}}^{\mathbf{k}} = \frac{2}{m} [(E|\mathbf{0}) + (E|-\boldsymbol{\tau}) \otimes (C_4|\boldsymbol{\tau})]. \quad (14.194)$$

At each point of symmetry, $\overline{\mathbb{G}}^{\mathbf{k}}$ is either isomorphic with a point-group or with the direct product of $(E|\mathbf{t})$ and one of the ordinary point-groups, so that the character table of $\overline{\mathbb{G}}^{\mathbf{k}}$ is then immediately available. We can use (14.193) and (14.194) to write down the elements of $\overline{\mathbb{H}}_S^{\mathbf{k}}$, the unitary subgroup of $\overline{\mathbb{S}}_S^{\mathbf{k}}$,

$$\overline{\mathbb{H}}_S^{\mathbf{k}} = \infty \otimes \overline{\mathbb{G}}^{\mathbf{k}} + (U_y(\mathbf{s})|\boldsymbol{\tau}) \otimes \infty \otimes \overline{\mathbb{G}}^{\mathbf{k}}.$$

The Irreps of $\overline{\mathbb{H}}_S^{\mathbf{k}}$ can be found from the Irreps of $\overline{\mathbb{G}}^{\mathbf{k}}$ by the methods described in Chapter 11. We study the properties of the representations of $\overline{\mathbb{G}}^{\mathbf{k}}$ under conjugation with $(U_y(\mathbf{s})|\boldsymbol{\tau})$. If two representations $^{(\mu)}\Gamma$ and $^{(\nu)}\Gamma$ are conjugate, then they stick together to form one irreducible representation of $\overline{\mathbb{H}}_S^{\mathbf{k}}$, but if a representation $^{(\mu)}\Gamma$ of $\overline{\mathbb{G}}^{\mathbf{k}}$ is self-conjugate, it leads to two representations of $\overline{\mathbb{H}}_S^{\mathbf{k}}$ in which the character of $(U_y(\mathbf{s})|\boldsymbol{\tau})$ is either $+n$ or $-n$, where n is the dimension of $^{(\mu)}\Gamma$. At the point Γ at the center of the Brillouin zone, each representation of $\overline{\mathbb{G}}^{\mathbf{k}}$ is self-conjugate, so that each representation of $\overline{\mathbb{G}}^{\mathbf{k}}$ leads to two representations of $\overline{\mathbb{H}}_S^{\mathbf{k}}$. At other points, the situation is a little more complicated. For example, at X ($\mathbf{k} = \mathbf{b}_2/2$), $\overline{\mathbb{G}}^{\mathbf{k}}$ contains the elements

$$(E|\mathbf{0}), (C_2|\mathbf{0}), (U_x|\mathbf{0}), (U_y|\mathbf{0}), (I|\mathbf{0}), (\sigma_x|\mathbf{0}), (\sigma_y|\mathbf{0}), (\sigma_h|\mathbf{0}) \quad (14.195)$$

together with their products with $(E|\mathbf{a}_2)$. According to the Herring method, only Irreps for which $\chi(E|\mathbf{a}_2) = -1$ are to be considered at the X -point. The result of the conjugation of the elements in Equation (14.195) is to produce

$$(E|\mathbf{0}), (C_2|-\mathbf{a}_2), (U_x|\mathbf{0}), (U_y|-\mathbf{a}_2), (I|-\mathbf{a}_2), (\sigma_x|\mathbf{0}), (\sigma_y|-\mathbf{a}_2), (\sigma_h|\mathbf{0})$$

respectively, which means that the representations are conjugate in pairs:

$$\{X_1^+, X_3^-\}; \{X_2^-, X_4^-\}; \{X_3^+, X_1^-\}; \{X_4^+, X_2^-\}.$$

$\bar{\mathbb{S}}_S^{\mathbf{k}}$ is constructed by the addition of the antiunitary element $\Theta(U_y|-\mathbf{a}_2)$ to $\bar{\mathbb{H}}_S^{\mathbf{k}}$. The corepresentations of $\bar{\mathbb{S}}_S^{\mathbf{k}}$ can be determined from the representations of $\bar{\mathbb{H}}_S^{\mathbf{k}}$ by using (12.117)–(12.119) and the test given in (12.133). At X , all the representations of $\bar{\mathbb{H}}_S^{\mathbf{k}}$ lead to case (c) corepresentations of $\bar{\mathbb{S}}_S^{\mathbf{k}}$ which are two-fold degenerate. In this example, the spin space-group Gsk and the magnetic group $\mathcal{M}^{\mathbf{k}}$ [71] both lead to corepresentations at X which are two-fold degenerate. The argument that we have outlined for X can also be applied to the remaining special points in the Brillouin zone. As we mentioned before, we find that, in general, there may be some extra degeneracy in Gsh that was not present in $\mathcal{M}^{\mathbf{k}}$. It is then possible to construct compatibility tables between the representations of Gsk and the representations of $\mathcal{M}^{\mathbf{k}}$, and some examples of these are given by Brinkman and Elliott [97].

Strictly speaking, the symmetries of magnons below the transition temperature will be determined by the CoIrreps of $\mathcal{M}$, but, when simple model spin Hamiltonians are used, they may be determined by $\mathbb{S}^s$, in which case extra degeneracies will appear.

Above the transition temperature, the symmetries of paramagnons will be determined by the corepresentations of $\mathcal{G}_L$; the form of the interactions which are allowed in the Hamiltonian used in determining the frequencies of paramagnons can be determined from the condition that they must be invariant under $\mathcal{G}_L$.

Appendix 1 Derivation of the Hartree–Fock equations

Substituting (14.20) into (14.19), summing over spin, and using (14.18) we then find

$$\begin{aligned}
 \int d\mathbf{r}^N \delta\Psi^* \mathcal{H} \Psi = & \sum_i \int d\mathbf{r}_1 \left(\delta\psi_i^*(\mathbf{r}_1) \left[\mathcal{H}_1 + e^2 \sum_j' \int d\mathbf{r}_2 \frac{|\psi_j(\mathbf{r}_2)|^2}{r_{12}} \right. \right. \\
 & + \sum_j' \int d\mathbf{r}_2 \psi_j^*(\mathbf{r}_2) \mathcal{H}_2 \psi_j(\mathbf{r}_2) + \frac{1}{2} \sum_{j,k}'' e^2 \int d\mathbf{r}_2 d\mathbf{r}_3 \frac{|\psi_j(\mathbf{r}_2)|^2 |\psi_k(\mathbf{r}_3)|^2}{r_{23}} \\
 & \left. \left. - \frac{1}{2} \sum_{j,k;\uparrow\uparrow}'' e^2 \int d\mathbf{r}_2 d\mathbf{r}_3 \frac{\psi_j^*(\mathbf{r}_2) \psi_k^*(\mathbf{r}_3) \psi_j(\mathbf{r}_3) \psi_k(\mathbf{r}_2)}{r_{23}} + \eta_{ii} \right] \psi_i(\mathbf{r}_1) \right. \\
 & \left. - \left[\sum_{j;\uparrow\uparrow}' e^2 \int d\mathbf{r}_2 \frac{\psi_j^*(\mathbf{r}_2) \psi_i(\mathbf{r}_2)}{r_{12}} + \sum_j' \int d\mathbf{r}_2 \psi_j^*(\mathbf{r}_2) H_2 \psi_i(\mathbf{r}_2) + \eta_{ij} \right] \psi_j(\mathbf{r}_1) \right), \tag{14.196}
 \end{aligned}$$

where

$$\mathcal{H}_i = T_i + v(\mathbf{r}_i).$$

The Lagrange multipliers η_{ij} are conveniently redefined through

$$\lambda_{ii} = \eta_{ii} + \sum_j' \int d\mathbf{r}_2 \psi_j(\mathbf{r}_2) H_2 \psi_j(\mathbf{r}_2) + \frac{1}{2} \sum_{j,k}' e^2 \int d\mathbf{r}_2 d\mathbf{r}_3 \frac{|\psi_j(\mathbf{r}_2)|^2 |\psi_k(\mathbf{r}_3)|^2}{r_{23}} \\ - \frac{1}{2} \sum_{j,k;\uparrow\uparrow}'' e^2 \int d\mathbf{r}_2 d\mathbf{r}_3 \frac{\psi_j^*(\mathbf{r}_2) \psi_k^*(\mathbf{r}_3) \psi_j(\mathbf{r}_3) \psi_k(\mathbf{r}_2)}{r_{23}}, \quad (14.197)$$

$$\lambda_{ij} = \eta_{ij} + \sum_j' \int d\mathbf{r}_2 \psi_j^*(\mathbf{r}_2) H_2 \psi_i(\mathbf{r}_2). \quad (14.198)$$

At this point we equate the coefficient of $\delta\psi_i(\mathbf{r}_1)$ to zero, and then we find

$$\left[T_1 + v(\mathbf{r}_1) + \sum_j e^2 \int d\mathbf{r}_2 \frac{|\psi_j(\mathbf{r}_2)|^2}{r_{12}} + \lambda_{ii} \right] \psi_i(\mathbf{r}_1) \\ - \sum_{j;\uparrow\uparrow}' \left[e^2 \int d\mathbf{r}_2 \frac{\psi_i^*(\mathbf{r}_2) \psi_j(\mathbf{r}_2)}{r_{12}} + \lambda_{ij} \right] \psi_j(\mathbf{r}_1) = 0. \quad (14.199)$$

Appendix 2 Holstein–Primakoff (HP) operators

In 1940, Holstein and Primakoff showed how spin operators could be expressed in terms of true Bose fields. The HP representation is best understood as a special case of the Schwinger coupled-boson representation.

Coupled-boson representation

The general matrix structure of the angular momentum operators,

$$\begin{aligned} \langle j'm' | \mathbf{J}^\pm | jm \rangle &= \delta_{jj'} \delta_{m\pm 1, m'} \hbar \sqrt{(j \mp m)(j \pm m + 1)}, \\ \langle j'm' | \hat{J}^z | jm \rangle &= \delta_{jj'} \delta_{m, m'} \hbar m, \\ \langle j'm' | \hat{J}^2 | jm \rangle &= \delta_{jj'} \delta_{m, m'} \hbar^2 j(j+1), \end{aligned} \quad (14.200)$$

resembles in many respects the matrix structure of harmonic oscillator operators,

$$\hat{a}^\dagger = \frac{1}{\sqrt{2\hbar}} \left(\frac{\hbar}{i} \frac{\partial}{\partial x} + ix \right), \quad \hat{a} = \frac{1}{\sqrt{2\hbar}} \left(\frac{\hbar}{i} \frac{\partial}{\partial x} - ix \right) \quad (14.201)$$

with commutation relations

$$[\hat{a}_l, \hat{a}_m^\dagger] = \delta_{lm}, \quad [\hat{a}_l, \hat{a}_m] = [\hat{a}_l^\dagger, \hat{a}_m^\dagger] = 0$$

and

$$[\hat{n}_l, \hat{a}_m^\dagger] = \delta_{lm} \hat{a}_m^\dagger, \quad [\hat{n}_l, \hat{a}_m] = -\delta_{lm} \hat{a}_m.$$

The normalized two-particle states are $\hat{a}_1^\dagger \hat{a}_2^\dagger |0\rangle$ and $(\hat{a}_1^{\dagger 2}/\sqrt{2}) |0\rangle$. The general many-particle state is

$$\frac{(\hat{a}_1^\dagger)^{n_1} (\hat{a}_2^\dagger)^{n_2} \dots}{\sqrt{(n_1! n_2! \dots)}} |0\rangle$$

with $n_i > 0$, and the total occupation is given by $\sum_i n_i$.

Schwinger showed that with the aid of only two harmonic oscillators the entire matrix structure of a single angular momentum could be exactly reproduced. Labeling the two oscillators by 1 and 2, we introduce the *spinor operators*

$$\hat{\mathbf{a}}^\dagger = (\hat{a}_1^\dagger, \hat{a}_2^\dagger) \quad \text{and} \quad \hat{\mathbf{a}} = \begin{pmatrix} \hat{a}_1 \\ \hat{a}_2 \end{pmatrix}, \quad (14.202)$$

which are merely two-component vectors with operator components. Moreover, if we contract these operators with the Pauli spin matrices, we obtain the desired representation. That is, let

$$J^z = \frac{\hbar}{2} \hat{\mathbf{a}}^\dagger \cdot \hat{\sigma}_z \cdot \hat{\mathbf{a}} = \frac{\hbar}{2} \hat{a}^\dagger \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \hat{a} = \frac{\hbar}{2} (\hat{n}_1 - \hat{n}_2),$$

and similarly for the other components, with the following compact result:

$$\hat{\mathbf{J}} = \frac{\hbar}{2} \hat{\mathbf{a}}^\dagger \cdot \hat{\sigma} \cdot \hat{\mathbf{a}}. \quad (14.203)$$

We next define

$$\hat{\mathbf{J}} = \frac{1}{2} \hat{\mathbf{a}}^\dagger \cdot \hat{\mathbf{I}} \cdot \hat{\mathbf{a}} = \frac{1}{2} (\hat{n}_1 + \hat{n}_2) \quad (14.204)$$

so that we write the state $|jm\rangle$ as

$$|jm\rangle = \frac{(\hat{a}_1^\dagger)^{j+m} (\hat{a}_2^\dagger)^{j-m}}{\sqrt{(j+m)!(j-m)!}} |0\rangle.$$

It may be verified that the eigenvalues of $\hat{\mathbf{J}}$ are indeed $j = 0, 1/2, 1, 3/2, \dots$, where $\mathbf{J}^2$ has eigenvalue $\hbar^2 j(j+1)$. The coupled-boson operators have more flexibility than the original angular momentum operators. For example, we can make use of the extra degrees of freedom to construct the so-called hyperbolic operators which conserve m , but raise or lower j .

Holstein and Primakoff proposed an irreducible representation of the Schwinger coupled-boson in a subspace of fixed j according to the following argument: Since from (14.204) we have

$$\hat{\mathbf{J}} = \frac{1}{2} (\hat{a}_1^\dagger \hat{a}_1 + \hat{a}_2^\dagger \hat{a}_2),$$

we find that

$$\hat{a}_2^\dagger \hat{a}_2 = 2\hat{\mathbf{J}} - \hat{n}_1 = \sqrt{(2\hat{\mathbf{J}} - \hat{n}_1)} \sqrt{(2\hat{\mathbf{J}} - \hat{n}_1)}.$$

In a subspace of fixed j , this equation is solved by treating $\hat{a}_2$ and its conjugate as two diagonal operators:

$$\hat{a}_2 = \hat{a}_2^\dagger = (2j)^{1/2} \sqrt{1 - \frac{\hat{\mathbf{n}}}{2j}}, \quad (14.205)$$

and hence we find

$$\begin{aligned} \mathbf{J}^+ &= \hbar \hat{a}_1^\dagger \hat{a}_2 = \hbar (2j)^{1/2} \hat{\mathbf{a}}^\dagger \sqrt{1 - \frac{\hat{\mathbf{n}}}{2j}}, \\ \mathbf{J}^- &= \hbar \hat{a}_2^\dagger \hat{a}_1 = \hbar (2j)^{1/2} \sqrt{1 - \frac{\hat{\mathbf{n}}}{2j}} \hat{\mathbf{a}}, \\ \mathbf{J}^z &= \hbar(\hat{\mathbf{n}} - j). \end{aligned} \quad (14.206)$$

If $n > 2j$ the formalism is incorrect; however, within that range the commutation relations

$$\begin{aligned} \hat{\mathbf{J}} \times \hat{\mathbf{J}} &= i\hbar \hat{\mathbf{J}}, \\ [\hat{J}^z, \hat{J}^\pm] &= \pm \hbar \hat{J}^\pm, \\ [\hat{J}^+, \hat{J}^-] &= 2\hbar \hat{J}^z, \\ [\hat{J}^2, \hat{\mathbf{J}}] &= [\hat{J}^2, \hat{J}^\pm] = 0 \end{aligned} \quad (14.207)$$

are satisfied. Remembering that

$$\mathbf{J}^z |jm\rangle = \hbar m |jm\rangle = \hbar(n - j) |jm\rangle,$$

we find that $n = j - m$, and hence we obtain

$$\begin{aligned} \langle m | \hat{J}^+ | m - 1 \rangle &= \langle n | \hat{J}^+ | n + 1 \rangle = \sqrt{(j - m + 1)(j + m)} \\ &= \sqrt{(n + 1)(2j - n)}. \end{aligned} \quad (14.208)$$

We may then consider $\hat{\mathbf{n}}$ as a number operator associated with *angular-momentum deviation* from the state with maximal m , i.e. $m = j$.

Consequently, Holstein and Primakoff introduced the operator $\hat{\mathbf{n}}_l$ as the spin-deviation number operator from the ground-state value S at site l , namely,

$$\hat{\mathbf{n}}_l = \mathbf{a}_l^\dagger \mathbf{a}_l = S - \hat{\mathbf{S}}_l^z, \quad (14.209)$$

and thus were able to write the equations for $\hat{\mathbf{S}}_l^-$ and $\hat{\mathbf{S}}_l^+$ as

$$\begin{aligned} \hat{\mathbf{S}}_l^+ |n_l\rangle &= (2S)^{1/2} \left[1 - \frac{n_l - 1}{2S}\right]^{1/2} \sqrt{n_l} |n_l - 1\rangle, \\ \hat{\mathbf{S}}_l^- |n_l\rangle &= (2S)^{1/2} \sqrt{n_l + 1} \left[1 - \frac{n_l}{2S}\right]^{1/2} |n_l + 1\rangle, \end{aligned} \quad (14.210)$$

which can be recast in the form of (14.206) as

$$\begin{aligned}\hat{S}_l^- &= (2S)^{1/2} \hat{\mathbf{a}}_l^\dagger \sqrt{1 - \frac{\hat{\mathbf{a}}_l^\dagger \hat{\mathbf{a}}_l}{2S}}, \\ \hat{S}_l^+ &= (2S)^{1/2} \sqrt{1 - \frac{\hat{\mathbf{a}}_l^\dagger \hat{\mathbf{a}}_l}{2S}} \hat{\mathbf{a}}_l,\end{aligned}\quad (14.211)$$

where $\hat{\mathbf{a}}_l^\dagger$ and $\hat{\mathbf{a}}_l$ can be interpreted as spin-deviation creation and annihilation operators obeying Bose commutation relations. A few words about the HP radical, i.e.

$$\mathcal{T}_l = \sqrt{1 - \frac{\hat{\mathbf{a}}_l^\dagger \hat{\mathbf{a}}_l}{2S}}, \quad (14.212)$$

are in order. For any given value of S (integral or half-integral), it is always possible to construct a polynomial of order $2S$ which has the same structure as the HP radical in the physical domain, i.e. $0 \leq \hat{\mathbf{a}}_l^\dagger \hat{\mathbf{a}}_l \leq 2S$. Outside this physical domain, of course, the correspondence is lost. For large values of S , however, it is not easy to construct the above polynomial. On the other hand, for small values of $n_l/2S$ the Taylor expansion, namely

$$\mathcal{T}_l(S) = 1 - \frac{1}{2} \left(\frac{n_l}{2S} \right) + \frac{1}{8} \left(\frac{n_l}{2S} \right)^2 + \dots \quad (14.213)$$

becomes asymptotically exact for $n_l/2S \rightarrow 0$. Accordingly, for small fractional spin deviation ($n_l/2S \ll 1$), we can truncate the above expansion at an appropriate stage. This is evidently valid in the low-temperature regime. On substituting (14.211) into the third equation in (14.207) we obtain

$$[\hat{\mathbf{a}}_l, \hat{\mathbf{a}}_m^\dagger] = \delta_{lm}, \quad (14.214)$$

all other commutators being zero. These commutation relations are reminiscent of bosons.

Exercises

- 14.1 Derive an expression for the electron energy band dispersion of a monovalent b.c.c. metal, such as Na, using only first-neighbor terms in (14.154).
- 14.2 Describe the motion in real space of free electrons in each of the eight free electron states just referred to.
- 14.3 Verify that the free electron energy bands of Figure 14.5 are correct.
- 14.4 Show that the X point in Figure 14.4 occurs at $2\pi/a$ and not at π/a , as it does for a one-dimensional crystal. What is the reason for the difference?
- 14.5 Using the eigenvalues of (14.101) show that the eigenfunction coefficients, $C_{\mathbf{k}-\mathbf{G}}$, for wavefunctions at the W point of the Brillouin zone for the f.c.c. lattice are as given in Table 14.2.
- 14.7 Verify (14.105) and (14.106).
- 14.8 Estimate the form of the band structure of the 2s band of Li using a single OPW orthogonalized to the 1s core state $\phi_{1s}^c(\mathbf{r}) = (\alpha^3/\pi)^{1/2} \exp(-\alpha r)$, given that $E_{1s} = -1.883$ au, $V_0 = -0.5$ au, the volume of the unit cell = 153 au, the bottom of

the band energy $E(0) = 0.343$ au, and $\alpha = 2.7$ au. (For numerical evaluation it is convenient to use atomic units, $\hbar = m = e = 1$ atomic unit. Distances are measured in Bohr radii ($0.529 \text{ \AA}$), masses in units of the electron mass, and energies are in atomic units (1 atomic unit $= 2$ Rydbergs $= 27.2$ eV)).

14.9 Show that the matrix element of $v_{\text{ps}}^{\text{KKRZ}}$ between plane-waves is

$$V_{\text{ps}, G'G'}^{\text{KKRZ}} = V_{\mathbf{G}\mathbf{G}'} + \frac{4\pi R_c}{\Omega} \sum_l (2l+1) \left[L_l - \kappa \frac{j_l'(\kappa R_c)}{j_l(\kappa R_c)} \right] \\ \times j_l(|\mathbf{k} - \mathbf{G}| R_c) j_l(|\mathbf{k} - \mathbf{G}'| R_c) P_l(\cos \theta_{\mathbf{G}\mathbf{G}'}), \quad (14.215)$$

and that the term in square brackets in (14.215) can be written as

$$-(1/\kappa)[Rj_l(\kappa R)]^{-2} \tan \eta_l', \quad (14.216)$$

in terms of the modified phase shift η_l' defined by

$$\cot \eta_l' = \cot \eta_l - n_l(\kappa R_c)/j_l(\kappa R_c). \quad (14.217)$$

The proof follows readily from (14.131) by using the Wronskian identity $x^2(jn' - j'n) = 1$.

15

Dynamical properties of molecules, solids, and surfaces

15.1 Introduction

The problem of simplifying the computation of the normal modes of vibrations of molecules and solids has been presented, over the past century, as a classic application of symmetry. It has been extensively discussed in a plethora of books on applications of group theoretical techniques. The dynamical problem of surfaces has been a relative latecomer.

A major contribution of group theoretical techniques to the dynamics of condensed matter systems has been to simplify the secular problem for the determination of normal mode eigenfrequencies and eigenvectors in the harmonic approximation. The secular matrix is found to be reducible, i.e. “block-diagonalizable”, with respect to the Irreps of the symmetry group of the system’s Hamiltonian.

For the sake of pedagogy, and in order to prepare the way for tackling the dynamics of the more complex condensed matter systems, we consider first the simpler dynamics of molecules.

15.2 Dynamical properties of molecules

The application of group theoretical techniques to study the dynamical properties of molecules involves the determination of symmetrized normal modes prior to the computation of the eigenfrequencies and eigenvectors. A typical example of such an approach has been presented in Chapter 6, to motivate the concept of projection operators. In that example, we were able to obtain the symmetry-adapted translation, rotation, and vibrational vectors describing the dynamics of water molecules. Here, we expand on this approach and extend it to enable the computation of corresponding eigenfrequencies and eigenvectors.

15.2.1 *The adiabatic approximation*

A convenient starting point for investigating the classical dynamics of molecules is to glance at an outline of a typical procedure for determining the electronic structure of molecules. Typically, the nuclear positions $\{\mathbf{R}_i\}$ of the different constituent atoms are specified from the outset. Next, some variational method is employed, such as Hartree–Fock or density functional, to calculate the electronic structure and lowest total electronic

energy of the molecule $E_0(\{\mathbf{R}_i\})$ under the constraint of fixed atomic positions $\{\mathbf{R}_i\}$. This procedure is repeated for different sets of $\{\mathbf{R}_i\}$, until a minimum value $E_0(\{\mathbf{R}_i^0\})$ is obtained, and the set $\{\mathbf{R}_i^0\}$ constitutes the equilibrium configuration of the molecule. In the classical picture, it is assumed that there is a unique electronic configuration that corresponds to the total energy minimum for each set of atomic positions $\{\mathbf{R}_i\}$.

To proceed with the classical calculation of the dynamical normal modes of the molecule, we have to introduce the crucial assumption that the time scale of the electronic motion is much faster than that of the nuclear motions of the constituent atoms. This approximation is known as the *adiabatic approximation*, and it assumes that as the nuclei move, electrons instantaneously conform with the ground-state electronic configuration. Invoking this approximation allows us to identify the function $E(\{\mathbf{R}_i\})$ as the ground-state electronic energy of the molecule. The geometric depiction of $E(\{\mathbf{R}_i\})$, in the $3N$ -dimensional space of the position vectors $\mathbf{R}_i$ of the N constituent atoms, presents an energy surface which is called the *adiabatic potential energy surface* of the molecule's ground-state. This adiabatic energy is the starting point of our analysis here, as well as in the sections on dynamical properties of solids and surfaces that follow.

15.2.2 The equations of motion in the harmonic approximation

In our investigation of the normal vibrational modes of molecules, we are concerned mainly with small atomic displacements about their equilibrium positions. Thus, we write the instantaneous position of atom i as

$$\mathbf{R}_i = \mathbf{R}_i^0 + \mathbf{u}(i), \quad (15.1)$$

and expand the adiabatic potential energy as a power series in the displacements $\{\mathbf{u}(i)\}$, namely,

$$E_0(\{\mathbf{R}_i\}) = E_0(\{\mathbf{R}_i^0\}) + \frac{1}{2} \sum_{ij, \alpha\beta} u_\alpha(i) \Phi_{\alpha\beta}(ij) u_\beta(j) + \cdots, \quad (15.2)$$

where the dots indicate the presence of higher-degree terms in the expansion, and where

$$\Phi_{\alpha\beta}(ij) = \left. \frac{\partial^2 E_0}{\partial u_\alpha(i) \partial u_\beta(j)} \right|_{\mathbf{u}(i)=\mathbf{u}(j)=0} \quad (15.3)$$

are known as *force constants*.

It is immediately obvious that the matrix $\Phi_{\alpha\beta}(ij)$ is symmetric with respect to its indices, i.e.

$$\Phi_{\alpha\beta}(ij) = \Phi_{\beta\alpha}(ji). \quad (15.4)$$

We follow Lax [101] and introduce a “flipping” operator F that transposes all the force constant indices. This operation may be viewed as a reversal of the bond between sites i and j and will be quite useful later.

We also point out that the displacements $\mathbf{u}(i)$ are real

$$\mathbf{u}^*(i) = \mathbf{u}(i),$$

which, together with (15.4), implies that the matrix Φ is real.

The assumption of small displacements allows us to terminate the expansion after the second-degree term; this termination is called the *harmonic approximation*. The absence of the first-degree term is a consequence of the fact that the expansion is carried out around the equilibrium configuration, which ensures that

$$\frac{\partial E_0}{\partial u_\alpha(i)} = 0, \quad \forall i, \alpha.$$

The reader should be alerted to two points of caution at this time:

- (i) The validity of the adiabatic approximation depends on the absence of intersections between the ground-state potential-energy surface and higher-excited-state energy surfaces, which would induce concomitant electronic transitions.
- (ii) The validity of the harmonic approximation is sometimes dependent on the existence of a nondegenerate minimum in the potential energy surface. Degeneracy may lead to quantum tunneling, which cannot be treated classically. A typical example of such degeneracy is the ammonia molecule.

The kinetic energy of the molecule can be expressed in terms of $\{\partial u_\alpha(i)/\partial t = \dot{u}_\alpha(i)\}$, as

$$T = \frac{1}{2} \sum_{i\alpha} M_i \dot{u}_\alpha^2(i), \quad (15.5)$$

and the system Lagrangian is written as

$$\mathcal{L} = \frac{1}{2} \sum_{i\alpha} M_i \dot{u}_\alpha^2(i) - \frac{1}{2} \sum_{i\alpha} \sum_{j\beta} u_\alpha(i) \Phi_{\alpha\beta}(ij) u_\beta(j). \quad (15.6)$$

The corresponding equations of motion are obtained using

$$\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{u}_\alpha(i)} - \frac{\partial \mathcal{L}}{\partial u_\alpha(i)} = 0, \quad (15.7)$$

which yields the set of coupled equations of motion

$$M_i \ddot{u}_\alpha(i) + \sum_{j\beta} \Phi_{\alpha\beta}(ij) u_\beta(j) = 0. \quad (15.8)$$

At this point, we find it useful to introduce two simplifying substitutions, which can be effected simultaneously by writing

$$\sqrt{M_i} u_\alpha(i) = U_\alpha(i) e^{-i\omega t}, \quad (15.9)$$

and recast (15.8) as

$$\omega^2 U_\alpha(i) = \sum_{j\beta} \mathfrak{D}_{\alpha\beta}(ij) U_\beta(j), \quad (15.10)$$

where

$$\mathfrak{D}_{\alpha\beta}(ij) = \frac{1}{\sqrt{M_i M_j}} \Phi_{\alpha\beta}(ij) \quad (15.11)$$

is called the *dynamical matrix*.

General symmetries of the force constant matrix

In addition to the flip symmetry expressed in (15.4), the force constant matrices exhibit other general symmetries.

If we apply the same arbitrary displacement ϵ_β to all the atoms in a molecule, it is left undistorted, and no forces are experienced by any of the constituent atoms, hence $\ddot{u}_\alpha(i) = 0, \forall i, \alpha$. We then obtain from (15.8) the conditions

$$\sum_j \Phi_{\alpha\beta}(ij) = 0 \quad \Rightarrow \quad \sum_j \Phi(ij) = 0. \quad (15.12)$$

This allows us to define the self-force constant matrix as

$$\Phi(ii) = - \sum_j' \Phi(ij),$$

where the prime indicates omitting the term $j = i$ in the summation.

Next, we apply an infinitesimal rotation to the molecule, so that the corresponding atomic displacements are

$$\mathbf{u}(i) = \begin{bmatrix} 0 & -\epsilon_z & \epsilon_y \\ \epsilon_z & 0 & -\epsilon_x \\ -\epsilon_y & \epsilon_x & 0 \end{bmatrix} \begin{bmatrix} X_1 \\ X_2 \\ X_3 \end{bmatrix} = \boldsymbol{\epsilon} \wedge \mathbf{R}(i)$$

where $\boldsymbol{\epsilon} = \begin{bmatrix} \epsilon_x & \epsilon_y & \epsilon_z \end{bmatrix}$, so that

$$u_\alpha(i) = \left(\boldsymbol{\epsilon} \wedge \mathbf{R}(i) \right) \Big|_\alpha = \epsilon_\beta X_\gamma - \epsilon_\gamma X_\beta, \quad \alpha \neq \beta \neq \gamma = x, y, z. \quad (15.13)$$

Since the molecule suffers no distortion, then again $\ddot{u}_\alpha(i) = 0$ and we obtain

$$\begin{array}{c}
 \sum_{j,\beta\delta} \Phi_{\alpha\beta}(ij) X_{\delta}(j) \varepsilon_{\gamma\delta\beta} = 0, \\
 \text{or} \\
 \sum_j \Phi_{\alpha\beta}(ij) X_{\gamma}(j) = \sum_j \Phi_{\alpha\gamma}(ij) X_{\beta}(j).
 \end{array}
 \tag{15.14}$$

Example 15.1

We consider a rotation $\epsilon_3 \hat{\mathbf{z}}$ about the z -axis, with displacements:

$$u_x = -\epsilon_3 X_2, \quad u_y = \epsilon_3 X_1, \quad u_z = 0.$$

From (15.10) we obtain:

$$\begin{array}{l}
 \ddot{u}_x(i) = 0 = \epsilon_3 \sum_j (-\Phi_{11}(ij) X_2(j) + \Phi_{12}(ij) X_1(j)), \\
 \text{or} \quad \sum_j \Phi_{11}(ij) X_2(j) = \sum_j \Phi_{12}(ij) X_1(j); \\
 \ddot{u}_y(i) = 0 = \epsilon_3 \sum_j (-\Phi_{21}(ij) X_2(j) + \Phi_{22}(ij) X_1(j)), \\
 \text{or} \quad \sum_j \Phi_{21}(ij) X_2(j) = \sum_j \Phi_{22}(ij) X_1(j); \\
 \ddot{u}_z(i) = 0 = \epsilon_3 \sum_j (-\Phi_{31}(ij) X_2(j) + \Phi_{32}(ij) X_1(j)), \\
 \text{or} \quad \sum_j \Phi_{31}(ij) X_2(j) = \sum_j \Phi_{32}(ij) X_1(j).
 \end{array}$$

Particular symmetries of the force constant matrix

The operations of the symmetry group $\mathcal{G}$ of a molecule introduce further relations among the elements of the force constant matrices. We find that some group operations permute equivalent atomic positions and bonds (orbits), while others leave a particular position or bond invariant (stabilizers). This invariance establishes linear dependence among the components of the force constant matrix.

We start by examining the effect of symmetry operations on the potential energy in the harmonic approximation

$$V = \frac{1}{2} \sum_{ij} \mathbf{u}(i) \cdot \Phi(ij) \cdot \mathbf{u}(j). \tag{15.15}$$

We first rewrite the transposition or flip symmetry of (15.4) as

$$F \Phi(ij) = \tilde{\Phi}(ji) = \Phi(ij). \quad (15.16)$$

Next, we consider the action of a symmetry operation R , which leaves the molecule invariant, on the equilibrium and instantaneous atomic positions $\mathbf{R}^0(i)$ and $\mathbf{R}(i)$, respectively,

$$\begin{aligned} R \mathbf{R}^0(i) &= \mathbf{R}^0(i') \\ R \mathbf{R}(i) &= R(\mathbf{R}^0(i) + \mathbf{u}(i)) = \mathbf{R}(i') \\ &= \mathbf{R}^0(i') + \mathbf{u}(i'), \end{aligned} \quad (15.17)$$

or

$$\mathbf{u}(i') = R \mathbf{u}(i), \quad \text{and } R[i] = i'. \quad (15.18)$$

The Rep $\Delta(R)$ of R engendered by its action on the set $\mathbf{U} \equiv \{\mathbf{u}(i)\}$ is given by

$$R u_\alpha(i) = \sum_{j\beta} \delta(j, R[i])^{(\vee)} \Gamma_{\alpha\beta}(R) u_\beta(j) = \sum_{j\beta} \Delta_{\alpha\beta}^{ij} u_\beta(j), \quad (15.19)$$

where $\delta(j, R[i])$ is a component of a permutation matrix, and $^{(\vee)}\Gamma$ is the 3D vector Rep. It is obvious from this definition that $\Delta(R)$ is given by

$$\Delta = {}^{(\text{perm})} \Gamma \otimes {}^{(\vee)} \Gamma. \quad (15.20)$$

Since the potential energy remains invariant under such operation, i.e. $\mathcal{V}' = \mathcal{V}$,

$$\begin{aligned} \mathcal{V}' &= \frac{1}{2} \sum \mathbf{u}(i) \cdot \tilde{R} \cdot \Phi(R[i]R[j]) \cdot R \mathbf{u}(j) \\ &= \frac{1}{2} \sum_{ij} \mathbf{u}(i) \cdot \Phi'(ij) \cdot \mathbf{u}(j) \\ &= \frac{1}{2} \sum_{ij} \mathbf{u}(i) \cdot \Phi(ij) \cdot \mathbf{u}(j) \end{aligned} \quad (15.21)$$

and we obtain

$$\Phi(ij) = \tilde{R} \cdot \Phi(R[i]R[j]) \cdot R. \quad (15.22)$$

We also find, with the aid of (15.16), that

$$F \Phi(ij) = \Phi(ij) = R \cdot \tilde{\Phi}(R[j]R[i]) \cdot \tilde{R}. \quad (15.23)$$

Equations (15.22) and (15.23) provide symmetric and antisymmetric Reps for R , with the symmetrized and antisymmetrized elements of the force constant matrix as basis, namely:

$$\begin{aligned} R \Phi^\pm(ij) &= R \cdot \Phi(R[i]R[j]) \cdot \tilde{R} \pm \tilde{R} \cdot \tilde{\Phi}(R[j]R[i]) \cdot R \\ &= \sum_{i'j'} \Phi^\pm(i'j') \Delta^\pm(R), \end{aligned} \quad (15.24)$$

where

$$\Delta_{i \ j \ \alpha \ \beta}^{\pm, \alpha' \beta'}(R) = \frac{1}{2} \left(\Delta_{\alpha \alpha'}^{ii'}(R) \Delta_{\beta \beta'}^{jj'}(R) \pm \Delta_{\alpha \beta'}^{ij'}(R) \Delta_{\beta \alpha'}^{ji'}(R) \right).$$

Since the force constant matrices are symmetric, only Δ^+ is applicable, and its character is given by

$$\chi_{\phi}^+(R) = \frac{1}{2} \sum_{ij} [\delta(i, R[i]) \delta(j, R[j]) |\chi(R)|^2 + \delta(i, R[j]) \delta(j, R[i]) \chi(R^2)]. \quad (15.25)$$

Equations (15.22) and (15.23) present additional constraints on the force constant matrices.

Stabilizers and orbits

We designate the stabilizer of a given atomic position (i) or a given bond (ij) as the subgroups $\mathcal{H}_a$ (*atom subgroup*) and $\mathcal{H}_b$ (*bond subgroup*) of $\mathcal{G}$, respectively. The left, or right, cosets of these stabilizers generate the corresponding orbits as well as the associated conjugate subgroups, namely $\mathcal{H}_b(i'j')$ ($\mathcal{H}_a(i')$), which leave the equivalent bond $[i'j']$ (atom $[i']$) invariant.

We can then state that:

The force constants associated with each member of a set of equivalent bonds (atoms) can be expressed in terms of those of a prototype bond (atom).

The subgroup of the atom $\mathcal{H}_a(i)$ The elements $H_a \in \mathcal{H}_a(i)$, the subgroup that leaves atom i invariant, are defined according to (15.17) as

$$H_a \mathbf{R}_i^0 = \mathbf{R}_i^0, \quad (15.26)$$

and the characters of this subgroup induced by its self force constant matrix are given by

$$\chi_{\phi}^i(H_a) = \frac{1}{2} [|\chi(H_a)|^2 + \chi(H_a^2)].$$

We then obtain the number of independent force constant elements as

$$N = \frac{1}{h} \sum_{H_a} \chi_{\phi}^i(H_a). \quad (15.27)$$

The subgroup of the bond $\mathcal{H}_b(ij)$ The operators $H_b \in \mathcal{H}_b(ij)$ of the subgroup of the bond (ij) are defined, using (15.17) and (15.23), as

$$H_b (\mathbf{R}_j^0 - \mathbf{R}_i^0) = \pm (\mathbf{R}_j^0 - \mathbf{R}_i^0), \quad (15.28)$$

with the stipulation that

$$\begin{aligned} \tilde{H}_b \cdot \Phi(ij) \cdot H_b &= \Phi(ij) \\ \text{or} \end{aligned} \quad (15.29)$$

$$H_b \cdot \tilde{\Phi}(ij) \cdot \tilde{H}_b = \Phi(ji) = F \tilde{\Phi}(ij) = \Phi(ij).$$

Example 15.2

The H₂O molecule

The point-group of H₂O is C_{2v} . In Figure 15.1 we choose O at $(0, 0, 0)$, H₁ at $(0, a, h)$, and H₂ at $(0, -a, h)$. We identify two bond types, O–H and H–H. The group of the O–H bond is that of H, namely E, σ_x , and we require

$$\Delta(\sigma_x) \Phi(\text{O–H}) \Delta(\sigma_x) = \Phi(\text{O–H}).$$

The group of the H–H bond is C_{2v} itself, and we require

$$\begin{aligned} \Delta(\sigma_x) \Phi(\text{H–H}) \Delta(\sigma_x) &= \Delta(\sigma_y) \Phi(\text{H–H}) \Delta(\sigma_y) \\ &= \Delta(C_2) \Phi(\text{H–H}) \Delta(C_2) \\ &= \Phi(\text{H–H}). \end{aligned}$$

Because the molecule lies in the y - z plane, Example 15.1 implies that all its symmetry-adapted vibrational displacements lie in that plane. Labeling the atoms O $\rightarrow$ 0, H(1) $\rightarrow$ 1, H(2) $\rightarrow$ 2, and using (15.14), we get

$$\begin{aligned} (\Phi_{11}(01) + \Phi_{11}(02)) h + \Phi_{11}(00) \times 0 &= 0 \times (\Phi_{13}(01) + \Phi_{13}(02) + \Phi_{13}(00)), \\ (\Phi_{11}(01) - \Phi_{11}(02)) a + \Phi_{11}(00) \times 0 &= 0 \times (\Phi_{13}(01) + \Phi_{13}(02) + \Phi_{13}(00)), \end{aligned}$$

which gives $\Phi_{11}(01) = \Phi_{11}(02) = 0$. Similar arguments show that $\Phi_{12}(01) = \Phi_{21}(01) = \Phi_{31}(02) = \Phi_{13}(02) = 0$. This allows us to write the force constant matrices associated with both the O–H and H–H bonds in the form $\begin{bmatrix} \Phi_{22} & \Phi_{23} \\ \Phi_{32} & \Phi_{33} \end{bmatrix}$. Since the action of σ_x in the y - z plane is represented by the identity matrix $\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$, no further relations can be

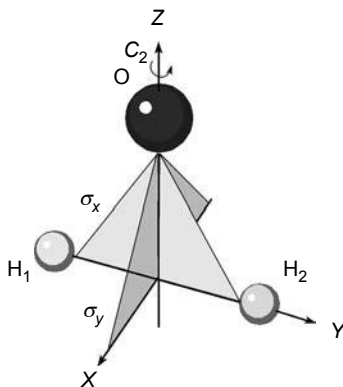


Fig. 15.1. The water molecule and its symmetry.

established among the force constants of the O–H bond, and we write its force constant matrix as

$$\Phi(\text{O–H}) = \begin{bmatrix} \alpha & \gamma \\ \delta & \beta \end{bmatrix}.$$

As for the H–H bond, both C_2 and σ_y reduce to $\begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix}$, and we obtain

$$\begin{aligned} \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} \Phi_{22} & \Phi_{23} \\ \Phi_{32} & \Phi_{33} \end{bmatrix} \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} &= \begin{bmatrix} \Phi_{22} & -\Phi_{23} \\ -\Phi_{32} & \Phi_{33} \end{bmatrix}, \\ &= \begin{bmatrix} \Phi_{22} & \Phi_{23} \\ \Phi_{32} & \Phi_{33} \end{bmatrix}, \end{aligned}$$

which yields $\Phi_{23} = \Phi_{32} = 0$, and

$$\Phi(\text{H(1)–H(2)}) = \begin{bmatrix} a & 0 \\ 0 & b \end{bmatrix}.$$

The translation constraints (15.11) give the self force constants $\Phi(ii)$.

We can thus write the force constant matrix for the H_2O molecule, in the y and z components only, as

$$\Phi = \begin{pmatrix} -(a + \alpha) & -\gamma & a & 0 & \alpha & \gamma \\ -\delta & -(b + \beta) & 0 & b & \delta & \beta \\ a & 0 & -(a + \alpha) & \gamma & \alpha & -\gamma \\ 0 & b & \delta & -(b + \beta) & -\delta & \beta \\ \alpha & \delta & \alpha & -\delta & -2\alpha & 0 \\ \gamma & \beta & -\gamma & \beta & 0 & -2\beta \end{pmatrix}.$$

Example 15.3

The ammonia molecule

Here, we find that the group of the N–H(i) bond is simply the group of the H(i) atom, namely E, σ_i ; while that of the H(i)–H(j) bond is E, σ_k , where i, j, k are taken to be cyclic.

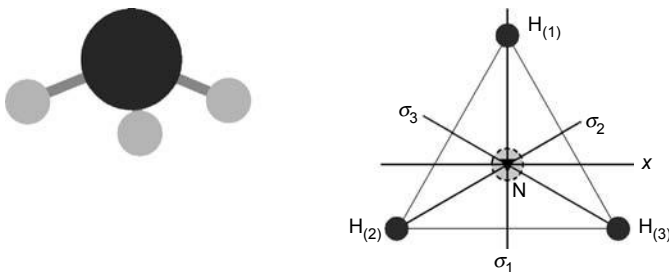


Fig. 15.2. The NH_3 molecule.

Thus, the bonds O–H(1) (y - z plane) and H(2)–H(3) (along the x -axis) have the same form of the force constant matrix, namely,

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \Phi_{11} & \Phi_{12} & \Phi_{13} \\ \Phi_{21} & \Phi_{22} & \Phi_{23} \\ \Phi_{31} & \Phi_{32} & \Phi_{33} \end{bmatrix} \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} \Phi_{11} & -\Phi_{12} & -\Phi_{13} \\ -\Phi_{21} & \Phi_{22} & \Phi_{23} \\ -\Phi_{31} & \Phi_{32} & \Phi_{33} \end{bmatrix},$$

which requires that $\Phi_{12} = \Phi_{13} = 0$, and we write

$$\Phi(\text{N–H(1)}) = \begin{bmatrix} \alpha & 0 & 0 \\ 0 & \beta & \delta \\ 0 & \epsilon & \gamma \end{bmatrix}, \quad \Phi(\text{H(2)–H(3)}) = \begin{bmatrix} a & 0 & 0 \\ 0 & b & d \\ 0 & e & c \end{bmatrix}.$$

Choosing C_3 and C_3^2 to take $1 \rightarrow 2$ and $1 \rightarrow 3$, respectively, we obtain

$$\begin{aligned} \Phi(\text{H(1)–H(3)}) &= C_3 \begin{bmatrix} a & 0 & 0 \\ 0 & b & d \\ 0 & e & c \end{bmatrix}, \quad C_3^2 = \frac{1}{4} \begin{bmatrix} a+3b & \sqrt{3}(b-a) & -2\sqrt{3}d \\ \sqrt{3}(b-a) & 3a+b & -2d \\ -2\sqrt{3}e & -2e & 4c \end{bmatrix}, \\ \Phi(\text{H(1)–H(2)}) &= C_3^2 \begin{bmatrix} a & 0 & 0 \\ 0 & b & d \\ 0 & e & c \end{bmatrix}, \quad C_3 = \frac{1}{4} \begin{bmatrix} a+3b & \sqrt{3}(a-b) & 2\sqrt{3}d \\ \sqrt{3}(a-b) & 3a+b & -2d \\ 2\sqrt{3}e & -2e & 4c \end{bmatrix}. \end{aligned}$$

15.2.3 Displacement tensor field and its tensor field Rep

We may view the displacements $\mathbf{u}(i)$ as a vector tensor field $\mathbf{u}(\mathbf{r})$ whose values are only defined at the atomic positions $\mathbf{R}^0(i) \equiv (X_1(i), X_2(i), X_3(i))$. We consider a molecule comprising N atoms. In the spirit of Section 13.2, we find that the vector $[\mathbf{u}(1)\mathbf{u}(2)\dots\mathbf{u}(N)]$ transforms under operations R of the point-group of the molecule $\mathcal{G}$ as

$$\begin{aligned} R \begin{bmatrix} \mathbf{u}(1) \\ \mathbf{u}(2) \\ \vdots \\ \mathbf{u}(N) \end{bmatrix} &= [\mathbf{u}(1)\mathbf{u}(2)\dots\mathbf{u}(N)]^{(\text{perm})} \Gamma(R) \otimes \Gamma^v(R) \\ &= [\mathbf{u}(1)\mathbf{u}(2)\dots\mathbf{u}(N)] \Gamma^{\text{TF}}(R), \end{aligned} \tag{15.30}$$

where ${}^{(v)}\Gamma$ is the vector Rep ${}^{(1)}\Gamma^-$, and ${}^{(\text{perm})}\Gamma$ the permutation Rep defined in Section 15.2.2. To generate ${}^{(\text{perm})}\Gamma$ of a molecule, we reduce the molecule to some basic submolecules, which we call *simple molecules*. Each simple molecule is an orbit under the action of $\mathcal{G}$, i.e. its constituents permute among themselves under the operations of $\mathcal{G}$. Thus, we need only know the position of one member of each simple molecule and its stabilizer $\mathcal{H} \subset \mathcal{G}$. As we showed in Section 13.2, ${}^{(\text{perm})}\Gamma(i)$ associated with the i th simple molecule is just the ground Rep of $\mathcal{H}$ in $\mathcal{G}$. If the molecule consists of r simple molecules,

then $^{(\text{perm})}\Gamma$ is given by

$$^{(\text{perm})}\Gamma = \sum_{i=1}^r \oplus ^{(\text{perm})}\Gamma(i). \quad (15.31)$$

Γ^{TF} can be subduced onto the Irreps of $\mathcal{G}$ as

$$\Gamma^{\text{TF}} = \sum_{\mu} \langle (\text{TF}) | (\mu) \rangle ^{(\mu)}\Gamma, \quad (15.32)$$

with basis set

$$|\mu, j, s\rangle, \quad j = 1, \dots, d_{\mu}, \quad s = 1, \dots, f_{\mu}, \quad (15.33)$$

where $f_{\mu} = \langle (\text{TF}) | (\mu) \rangle$. The set $\{|\mu, j, s\rangle\}$ is complete over the tensor field space of the molecule.

Another way to view this tensor field is by considering a continuous field ket $|\mathbf{u}(\mathbf{r})\rangle$, together with position kets $|\mathbf{R}^0(i)\rangle$, such that

$$\begin{aligned} |\mathbf{u}(\mathbf{r})\rangle &\equiv |U_1(i)\rangle, |U_2(i)\rangle, |U_3(i)\rangle, \\ |\mathbf{R}^0(i)\rangle &\equiv |X_1(i)\rangle, |X_2(i)\rangle, |X_3(i)\rangle, \\ U_{\alpha}(i) &= \langle X_{\alpha}(i) | \mathbf{u}(\mathbf{r}) \rangle. \end{aligned} \quad (15.34)$$

Since $\{|X_{\alpha}(i)\rangle\}$, which we will denote simply by $\{|i\alpha\rangle\}$, is complete over the vector space of the molecule, we can write

$$\begin{aligned} U_{\alpha}(i) &= \sum_{\mu j s} \langle i\alpha | \mu, j, s \rangle \langle \mu, j, s | \mathbf{u}(\mathbf{r}) \rangle \\ &= \sum_{\mu j s} \mathfrak{U}_{i\alpha, \mu j s}^{\dagger} {}^{(\mu)}Q_j^s, \end{aligned} \quad (15.35)$$

where

$$\begin{aligned} \mathfrak{U}_{i\alpha, \mu j s}^{\dagger} &= \langle i\alpha | \mu, j, s \rangle \text{ is a symmetry-adapted unitary transformation,} \\ {}^{(\mu)}Q_j^s &= \langle \mu, j, s | \mathbf{u}(\mathbf{r}) \rangle \text{ is the corresponding symmetry coordinate.} \end{aligned}$$

We can also express the symmetry kets $|\mu, j, s\rangle$ in the position representation as

$$|\mu, j, s\rangle = \sum_{i\alpha} |i\alpha\rangle \langle i\alpha | \mu, j, s \rangle. \quad (15.36)$$

In matrix notation we write

$$\langle i2 | = \begin{bmatrix} 1 & 2 & \dots & i & \dots & N \\ 0, 0, 0 & 0, 0, 0 & \dots & 0, 1, 0 & \dots & 0, 0, 0 \end{bmatrix}. \quad (15.37)$$

From (15.16–15.20), we arrive at the transformation

$$\mathfrak{U} = \begin{bmatrix} \langle (1), 1, 1 | i\alpha \rangle \\ \langle (1), 2, 1 | i\alpha \rangle \\ \vdots \\ \langle (1), d_1, 1 | i\alpha \rangle \\ \langle (1), 1, 2 | i\alpha \rangle \\ \vdots \\ \langle (1), d_1, f_1 | i\alpha \rangle \\ \vdots \\ \langle (\text{nc}), d_{\text{nc}}, f_{\text{nc}} | i\alpha \rangle \end{bmatrix} \quad (15.38)$$

where nc is the number of classes.

The center-of-mass translation modes, which transform like $^{(\text{v})}\Gamma$, can be expressed as a linear combination of the symmetry-adapted kets as

$$\begin{aligned} \langle (\text{v}), 1 | \mathbf{u}(\mathbf{r}) \rangle &= \frac{1}{\sqrt{N}} \begin{bmatrix} 1, 0, 0 & 1, 0, 0 & \dots & 1, 0, 0 \end{bmatrix} \\ &= \sum_{i\alpha}^{\oplus} \langle (\text{v}), 1 | i\alpha \rangle \langle i\alpha | \mathbf{u}(\mathbf{r}) \rangle \\ &= \sum_{i\alpha}^{\oplus} \frac{\delta_{\alpha 1}}{\sqrt{N}} \langle i1 | \mathbf{u}(\mathbf{r}) \rangle \\ &= \sum_{i\alpha, \mu, js} \frac{\delta_{\alpha 1}}{\sqrt{N}} \langle i1 | (\mu), j, s \rangle \langle (\mu), j, s | \mathbf{u}(\mathbf{r}) \rangle \\ &= \sum_{i\alpha, \mu, js} \frac{\delta_{\alpha 1}}{\sqrt{N}} \mathfrak{U}_{i1, \mu, js}^{\dagger} {}^{(\mu)}Q_j^s. \end{aligned} \quad (15.39)$$

Hence, we obtain

$$\langle (\text{v}), \alpha | \mathbf{u}(\mathbf{r}) \rangle = \frac{1}{\sqrt{N}} \sum_{\mu k s} \left(\sum_i \mathfrak{U}_{i\alpha, \mu k s}^{\dagger} \right) {}^{(\mu)}Q_j^s, \quad (15.40)$$

where we used the expressions

$$\begin{aligned} \langle (\text{v}), 2 | \mathbf{u}(\mathbf{r}) \rangle &= \frac{1}{\sqrt{N}} \begin{bmatrix} 0, 1, 0 & 0, 1, 0 & \dots & 0, 1, 0 \end{bmatrix}, \\ \langle (\text{v}), 3 | \mathbf{u}(\mathbf{r}) \rangle &= \frac{1}{\sqrt{N}} \begin{bmatrix} 0, 0, 1 & 0, 0, 1 & \dots & 0, 0, 1 \end{bmatrix}. \end{aligned} \quad (15.41)$$

We also express the rigid-rotation modes, which transform like Γ^a , as

$$\begin{aligned}
 \langle (a), 1 | \mathbf{u}(\mathbf{r}) \rangle &= \frac{1}{\sqrt{N'_1}} \begin{bmatrix} 0, -X_3, X_2 & 0, -X_3, X_2 & \dots & 0, -X_3, X_2 \end{bmatrix} \\
 &= \frac{1}{\sqrt{N'_1}} \sum_{i\alpha} \langle (a), 1 | i\alpha \rangle \langle i\alpha | \mathbf{u}(\mathbf{r}) \rangle \\
 &= \frac{1}{\sqrt{N'_1}} \sum_{i\alpha, \mu j s} \left(X_2(i) \delta_{3\alpha} \langle i3 | \mathbf{u}(\mathbf{r}) \rangle - X_3(i) \delta_{2\alpha} \langle i2 | \mathbf{u}(\mathbf{r}) \rangle \right) \\
 &= \frac{1}{\sqrt{N'_1}} \sum_{i, \mu k s} \left(X_2(i) \mathfrak{U}_{i3, \mu k s}^\dagger - X_3(i) \mathfrak{U}_{i2, \mu k s}^\dagger \right)^{(\mu)} Q_k^s, \quad (15.42)
 \end{aligned}$$

where $N'_1 = \left(\sum_i (X_2^2(i) + X_3^2(i)) \right)^{1/2}$. With

$$\begin{aligned}
 \langle (a), 2 | \mathbf{u}(\mathbf{r}) \rangle &= \frac{1}{\sqrt{N'_2}} \begin{bmatrix} X_3, 0, -X_1 & X_3, 0, -X_1 & \dots & X_3, 0, -X_1 \end{bmatrix}, \\
 \langle (a), 3 | \mathbf{u}(\mathbf{r}) \rangle &= \frac{1}{\sqrt{N'_3}} \begin{bmatrix} -X_2, X_1, 0 & -X_2, X_1, 0 & \dots & -X_2, X_1, 0 \end{bmatrix}. \quad (15.43)
 \end{aligned}$$

it then follows that

$$\langle (a), \alpha | \mathbf{u}(\mathbf{r}) \rangle = \frac{1}{\sqrt{N'_\alpha}} \sum_{\mu k s} \left(\sum_i \left(X_\beta(i) \mathfrak{U}_{i\gamma, \mu k s}^\dagger - X_\gamma(i) \mathfrak{U}_{i\beta, \mu k s}^\dagger \right) \right)^{(\mu)} Q_k^s, \quad (15.44)$$

where α, β, γ are cyclic, and $N'_\alpha = \sqrt{\sum_i (X_\beta^2(i) + X_\gamma^2(i))}$.

Next, we form the projection operators for the translation and rotation, or external, modes, namely,

$$P^{\text{ext}} = \sum_i \left(| (v), i \rangle \langle (v), i | + | (a), i \rangle \langle (a), i | \right). \quad (15.45)$$

The vector space for the vibrational modes can then be obtained by the internal projection operator

$$P^{\text{int}} = \mathbb{I} - \sum_\alpha \left(| (v), \alpha \rangle \langle (v), \alpha | - | (a), \alpha \rangle \langle (a), \alpha | \right). \quad (15.46)$$

The vector space of the internal, or vibrational, modes is given by

$$\begin{aligned}
 \langle \mathbf{u} | P^{\text{int}} | \mathbf{X} \rangle \langle \mathbf{X} | &= \langle \mathbf{u} | \mathbf{X} \rangle \langle \mathbf{X} | - \sum_{\alpha} \langle \mathbf{u} | (v), \alpha \rangle \langle (v), \alpha | \mathbf{X} \rangle \langle \mathbf{X} | \\
 &\quad - \sum_{\alpha} \langle \mathbf{u} | (a), \alpha \rangle \langle (a), \alpha | \mathbf{X} \rangle \langle \mathbf{X} | \\
 &= \sum_{\mu k s} {}^{(\mu)}\tilde{Q}_k^s \sum_{i\alpha} \mathfrak{U}_{\mu k s, i\alpha} \langle i\alpha | - \frac{1}{N} \sum_{\mu k s} {}^{(\mu)}\tilde{Q}_k^s \sum_{i\alpha} \mathfrak{U}_{\mu k s, i\alpha} \langle i\alpha | \\
 &\quad - \sum_{\mu k s} {}^{(\mu)}\tilde{Q}_k^s \sum_{i\alpha} \frac{X_{\beta}(i)}{N'_{\alpha}} \mathfrak{U}_{\mu k s, i\gamma} \varepsilon_{\alpha\beta\gamma} \langle i\alpha |. \tag{15.47}
 \end{aligned}$$

$$\begin{aligned}
 \langle \mathbf{u} | P^{\text{int}} | \mathbf{X} \rangle \langle \mathbf{X} | &= \sum_{\mu k s} {}^{(\mu)}\tilde{Q}_k^s \sum_{i\alpha} \mathfrak{W}_{\mu k s, i\alpha} \langle i\alpha |, \\
 \mathfrak{W}_{\mu k s, i\alpha} &= \left(1 - \frac{1}{N} - \frac{X_{\gamma}(i)}{N'_{\beta}} \varepsilon_{\beta\gamma\alpha} \right) \mathfrak{U}_{\mu k s, i\alpha}. \tag{15.48}
 \end{aligned}$$

The dynamical matrix $\mathbf{D}$

We now re-express the force constant matrix Φ in the current notation as

$$\Phi_{\alpha\beta}(ij) = \langle i\alpha | \Phi | j\beta \rangle \tag{15.49}$$

which, together with (15.15)–(15.25), allows us to write the potential energy as

$$\begin{aligned}
 \mathcal{V} &= \frac{1}{2} \sum_{\substack{i\alpha \\ j\beta}} \langle \mathbf{u} | P^{\text{int}} | \mathbf{X} \rangle \langle \mathbf{X} | \mathfrak{D} | \mathbf{X} \rangle \langle \mathbf{X} | P^{\text{int}} | \mathbf{u} \rangle \\
 &= \frac{1}{2} \sum_{\substack{\mu k s \\ \mu' k' s'}} {}^{(\mu)}\tilde{Q}_k^s D \begin{pmatrix} \mu k & \mu' k' \\ s & s' \end{pmatrix} {}^{(\mu')}Q_{k'}^{s'}, \tag{15.50}
 \end{aligned}$$

where

$$D \begin{pmatrix} \mu k & \mu' k' \\ s & s' \end{pmatrix} = \sum_{\substack{i\alpha \\ j\beta}} \mathfrak{W}_{\mu k s, i\alpha} \mathfrak{D}_{\alpha\beta}(ij) \mathfrak{W}_{j\beta, \mu' k' s'}^{\dagger}. \tag{15.51}$$

We now use the invariance of $\mathcal{V}$ under the operations of $\mathcal{G}$, together with the great orthogonality theorem, and the fact that

$$R {}^{(\mu)}Q_k^s = \sum_l {}^{(\mu)}Q_l^s {}^{(\mu)}\Gamma_{lk}(R), \tag{15.52}$$

to obtain

$$\begin{aligned}
 \mathcal{V} &= \frac{1}{2} \sum_{\substack{\mu k s \\ \mu' k' s'}}^{(\mu')} \tilde{Q}_{k'}^{s'} D \begin{pmatrix} \mu k & \mu' k' \\ s & s' \end{pmatrix}^{(\mu)} Q_k^s \\
 &\times \frac{1}{g} \sum_{\substack{R \in \mathcal{G} \\ lm}}^{(\mu')} \Gamma_{lk'}^*(R)^{(\mu)} \Gamma_{mk}(R) \\
 &= \frac{1}{2} \sum_{\substack{\mu k m s \\ \mu' k' l s'}} \delta_{\mu\mu'} \delta_{kk'} \delta_{lm}^{(\mu)} \tilde{Q}_k^s D \begin{pmatrix} \mu k \\ ss' \end{pmatrix}^{(\mu)} Q_k^{s'}, \quad (15.53)
 \end{aligned}$$

where $\mathbf{D}$ is called the *dynamical matrix*. The construction of the dynamical matrix $\mathbf{D}$ is now systematic and quite amenable to computational methods.

The Lagrangian (15.6) can now be recast as a sum of independent Lagrangians of the form

$$\begin{aligned}
 \mathcal{L} &= \sum_{\mu k} \mathcal{L}_{\mu k}, \\
 \mathcal{L}_{\mu k} &= \frac{1}{2} \sum_{ss'} \left\{ {}^{(\mu)}\tilde{Q}_k^s \dot{Q}_k^s - {}^{(\mu)}\tilde{Q}_k^s D \begin{pmatrix} \mu k \\ ss' \end{pmatrix}^{(\mu)} Q_k^{s'} \right\}, \quad (15.54)
 \end{aligned}$$

The corresponding equations of motion can be written, after some algebraic manipulations, as

$$\omega^2({}^{(\mu)}Q_k^s) = \sum_{s'} D \begin{pmatrix} \mu k \\ ss' \end{pmatrix}^{(\mu)} Q_k^{s'}. \quad (15.55)$$

We present here simple and familiar examples in order to elucidate and systematize the tensor field approach.

Example 15.5

The classical ammonia molecule

We know that the point-group of the ammonia molecule is $\mathcal{C}_{3v}$. As shown in Figure 15.2, we place the N atom at the origin, $(0, 0, 0)$, and the three H atoms at $(0, a/\sqrt{3}, -h)$, $(\pm a/2, -a/2\sqrt{3}, -h)$. It is then obvious that the subgroup of N is $\mathcal{C}_{3v}$ itself, and we find that the subgroup associated with the atom H(i) is $\mathcal{C}_s(i) = E, \sigma_i$, $i = 1, 2, 3$, with coset

representatives E, σ_j, σ_k . We obtain ${}^{(\text{perm})}\Gamma_N(R) = 1, \forall R \in \mathcal{C}_{3v}$, and

$$\begin{aligned}\Gamma_H^{\mathcal{P}}(E) &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, & \Gamma_H^{\mathcal{P}}(C_3) &= \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}, \\ \Gamma_H^{\mathcal{P}}(C_3^{-1}) &= \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}, & \Gamma_H^{\mathcal{P}}(\sigma_1) &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \\ \Gamma_H^{\mathcal{P}}(\sigma_2) &= \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}, & \Gamma_H^{\mathcal{P}}(\sigma_3) &= \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix},\end{aligned}$$

and it is then quite straightforward to construct

$$\begin{aligned}{}^{(\text{perm})}\Gamma &= \Gamma_N^{\mathcal{P}} \oplus \Gamma_H^{\mathcal{P}}, \\ \Gamma^{\text{TF}} &= {}^{(\text{perm})}\Gamma \otimes {}^{(\text{v})}\Gamma.\end{aligned}$$

The Rep Γ^{TF} is given as

$$\begin{aligned}\Gamma^{\text{TF}}(E) &= \begin{bmatrix} \mathbb{I} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbb{I} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbb{I} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbb{I} \end{bmatrix}, & \Gamma^{\text{TF}}(C_3) &= \begin{bmatrix} \mathbf{0} & \mathbf{0} & C_3 & \mathbf{0} \\ C_3 & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & C_3 & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & C_3 \end{bmatrix}, \\ \Gamma^{\text{TF}}(C_3^2) &= \begin{bmatrix} \mathbf{0} & C_3^2 & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & C_3^2 & \mathbf{0} \\ C_3^2 & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & C_3^2 \end{bmatrix}, & \Gamma^{\text{TF}}(\sigma_1) &= \begin{bmatrix} \sigma_1 & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \sigma_1 & \mathbf{0} \\ \mathbf{0} & \sigma_1 & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \sigma_1 \end{bmatrix}, \\ \Gamma^{\text{TF}}(\sigma_2) &= \begin{bmatrix} \mathbf{0} & \mathbf{0} & \sigma_2 & \mathbf{0} \\ \mathbf{0} & \sigma_2 & \mathbf{0} & \mathbf{0} \\ \sigma_2 & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \sigma_2 \end{bmatrix}, & \Gamma^{\text{TF}}(\sigma_3) &= \begin{bmatrix} \mathbf{0} & \sigma_3 & \mathbf{0} & \mathbf{0} \\ \sigma_3 & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \sigma_3 & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \sigma_3 \end{bmatrix},\end{aligned}$$

with

$$\begin{aligned}\mathbb{I} &= \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, & C_3 &= \begin{bmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}, & C_3^2 &= \begin{bmatrix} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \\ \sigma_1 &= \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, & \sigma_2 &= \begin{bmatrix} 1/2 & \sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}, & \sigma_3 &= \begin{bmatrix} 1/2 & -\sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}.\end{aligned}$$

The characters of $^{(\text{perm})}\Gamma$, $^{(v)}\Gamma$ and Γ^{TF} are:

	E	C_3, C_3^{-1}	σ_i		E	C_3, C_3^{-1}	σ_i
χ^{p}	4	1	2	$^{(1)}\chi$	1	1	1
χ^{v}	3	0	1	$^{(2)}\chi$	1	1	-1
χ^{TF}	12	0	2	$^{(3)}\chi$	2	-1	0
χ^{a}	3	0	-1				

The matrices of Irrep $^{(3)}\Gamma$ are given by

$$\begin{aligned}
 ^{(3)}\Gamma(E) &= \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}, & ^{(3)}\Gamma(C_3) &= \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{bmatrix}, \\
 ^{(3)}\Gamma(C_3^2) &= \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{bmatrix}, & ^{(3)}\Gamma(\sigma_x 1) &= \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix}, \\
 ^{(3)}\Gamma(\sigma_2) &= \begin{bmatrix} 1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{bmatrix}, & ^{(3)}\Gamma(\sigma_3) &= \begin{bmatrix} 1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{bmatrix}.
 \end{aligned}$$

We obtain the Irrep frequencies in Γ^{TF} as

$$\begin{aligned}
 \langle (\text{TF}) | (1) \rangle &= 3, & \langle (\text{TF}) | (2) \rangle &= 1, & \langle (\text{TF}) | (3) \rangle &= 4, \\
 \langle (\text{v}) | (1) \rangle &= 1, & \langle (\text{v}) | (2) \rangle &= 0, & \langle (\text{v}) | (3) \rangle &= 1, \\
 \langle (\text{a}) | (1) \rangle &= 0, & \langle (\text{a}) | (2) \rangle &= 1, & \langle (\text{a}) | (3) \rangle &= 1.
 \end{aligned}$$

Thus, the vibrational modes comprise

$$2^{(1)}\Gamma + 2^{(3)}\Gamma.$$

The Wigner projection operators for the one-dimensional irreps are

$$\begin{aligned}
 ^{(1)}\mathcal{P} &= \frac{1}{6} \begin{bmatrix} \mathbb{I} + \sigma_1 & C_3^2 + \sigma_3 & C_3 + \sigma_2 & \mathbf{0} \\ C_3 + \sigma_3 & \mathbb{I} + \sigma_2 & C_3^2 + \sigma_1 & \mathbf{0} \\ C_3^2 + \sigma_2 & C_3 + \sigma_1 & \mathbb{I} + \sigma_3 & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbb{I} + C_3 + C_3^2 + \sigma_1 + \sigma_2 + \sigma_3 \end{bmatrix} \\
 ^{(2)}\mathcal{P} &= \frac{1}{6} \begin{bmatrix} \mathbb{I} - \sigma_1 & C_3^2 - \sigma_3 & C_3 - \sigma_2 & \mathbf{0} \\ C_3 - \sigma_3 & \mathbb{I} - \sigma_2 & C_3^2 - \sigma_1 & \mathbf{0} \\ C_3^2 - \sigma_2 & C_3 - \sigma_1 & \mathbb{I} - \sigma_3 & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbb{I} + C_3 + C_3^2 - \sigma_1 - \sigma_2 - \sigma_3 \end{bmatrix}
 \end{aligned}$$

$$\begin{aligned}
{}^{(1)}\mathcal{P} &= \frac{1}{12} \begin{bmatrix} 0 & 0 & 0 & 2 & 0 & 0 & 2 & 0 & 0 \\ 0 & 4 & 0 & -2\sqrt{3} & -2 & 0 & 2\sqrt{3} & -2 & 0 \\ 0 & 0 & 4 & 0 & 0 & 4 & 0 & 0 & 4 \\ 2 & 0 & 0 & 3 & \sqrt{3} & 0 & -1 & \sqrt{3} & 0 \\ 0 & -2 & 0 & \sqrt{3} & 1 & 0 & -\sqrt{3} & 1 & 0 \\ 0 & 0 & 4 & 0 & 0 & 4 & 0 & 0 & 4 \\ 2 & 2\sqrt{3} & 0 & -1 & -\sqrt{3} & 0 & 3 & -\sqrt{3} & 0 \\ 0 & -2 & 0 & \sqrt{3} & 1 & 0 & -\sqrt{3} & 1 & 0 \\ 0 & 0 & 4 & 0 & 0 & 4 & 0 & 0 & 4 \end{bmatrix} \oplus \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \\
{}^{(2)}\mathcal{P} &= \frac{1}{12} \begin{bmatrix} 4 & 0 & 0 & -2 & 2\sqrt{3} & 0 & -2 & -2\sqrt{3} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -2 & 0 & 0 & 1 & -\sqrt{3} & 0 & 1 & \sqrt{3} & 0 \\ 2\sqrt{3} & 0 & 0 & -\sqrt{3} & 3 & 0 & -\sqrt{3} & -3 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -2 & 0 & 0 & 1 & \sqrt{3} & 0 & 1 & \sqrt{3} & 0 \\ -2\sqrt{3} & 0 & 0 & \sqrt{3} & -3 & 0 & \sqrt{3} & 3 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}
\end{aligned}$$

Diagonalizing the projection operator matrices ${}^{(1)}\mathcal{P}$ and ${}^{(2)}\mathcal{P}$ we obtain three unity eigenvalues for the former and one for the latter, with symmetry eigenvectors:

${}^{(1)}\Gamma :$

$$|1, 1\rangle = [0, -2, 0 \quad \sqrt{3}, 1, 0, \quad -\sqrt{3}, 1, 0 \quad 0, 0, 0]$$

$$|1, 2\rangle = [0, 0, 1 \quad 0, 0, 1 \quad 0, 0, 1 \quad 0, 0, 0]$$

$$|1, 3\rangle = [0, 0, 0 \quad 0, 0, 0 \quad 0, 0, 0 \quad 0, 0, 1]$$

${}^{(2)}\Gamma :$

$$|2, 1\rangle = [2, 0, 0 \quad -1, \sqrt{3}, 0 \quad -1, -\sqrt{3}, 0 \quad 0, 0, 0]$$

$${}^{(3)}\mathcal{P}_{11} = \frac{1}{12} \begin{bmatrix} 2(\mathbb{I} - \sigma_1) & \sigma_3 - C_3^2 & \sigma_2 - C_3 & \mathbf{0} \\ \sigma_3 - C_3 & 2\mathbb{I} + \sigma_2 & -(2\sigma_1 + C_3^2) & \mathbf{0} \\ \sigma_2 - C_3^2 & -(2\sigma_1 + C_3) & 2\mathbb{I} + \sigma_3 & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & 2(\mathbb{I} - \sigma_1) + \sigma_2 + \sigma_3 - C_3 - C_3^2 \end{bmatrix}$$

$${}^{(3)}\mathcal{P}_{22} = \frac{1}{12} \begin{bmatrix} 2(\mathbb{I} + \sigma_1) & -(\sigma_3 + C_3^2) & -(\sigma_2 + C_3) & \mathbf{0} \\ -(\sigma_3 + C_3) & 2\mathbb{I} - \sigma_2 & 2\sigma_1 - C_3^2 & \mathbf{0} \\ -(\sigma_2 + C_3^2) & 2\sigma_1 - C_3 & 2\mathbb{I} - \sigma_3 & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & 2(\mathbb{I} + \sigma_1) - \sigma_2 - \sigma_3 - C_3 - C_3^2 \end{bmatrix}$$

$$\begin{aligned}
{}^{(3)}\mathcal{P}_{11} &= \frac{1}{6} \begin{bmatrix} 4 & 0 & 0 & 1 & -\sqrt{3} & 0 & 1 & \sqrt{3} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 5/2 & \sqrt{3}/2 & 0 & 5/2 & -\sqrt{3}/2 & 0 \\ -\sqrt{3} & 0 & 0 & \sqrt{3}/2 & 3/2 & 0 & \sqrt{3}/2 & -3/2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 3 & 0 & 0 & -3 \\ 1 & 0 & 0 & 5/2 & \sqrt{3}/2 & 0 & 5/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3} & 0 & 0 & -\sqrt{3}/2 & -3/2 & 0 & -\sqrt{3}/2 & 3/2 & 0 \\ 0 & 0 & 0 & 0 & 0 & -3 & 0 & 0 & 3 \end{bmatrix} \oplus \frac{1}{6} \begin{bmatrix} 6 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \\
{}^{(3)}\mathcal{P}_{22} &= \frac{1}{6} \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 4 & 0 & \sqrt{3} & 1 & 0 & -\sqrt{3} & 1 & 0 \\ 0 & 0 & 4 & 0 & 0 & -2 & 0 & 0 & -2 \\ 0 & \sqrt{3} & 0 & 3/2 & -\sqrt{3}/2 & 0 & -3/2 & -\sqrt{3}/2 & 0 \\ 0 & 1 & 0 & -\sqrt{3}/2 & 5/2 & 0 & \sqrt{3}/2 & 5/2 & 0 \\ 0 & 0 & -2 & 0 & 0 & 1 & 0 & 0 & 1 \\ 0 & -\sqrt{3} & 0 & -3/2 & \sqrt{3}/2 & 0 & 3/2 & \sqrt{3}/2 & 0 \\ 0 & 1 & 0 & -\sqrt{3}/2 & 5/2 & 0 & \sqrt{3}/2 & 5/2 & 0 \\ 0 & 0 & -2 & 0 & 0 & 1 & 0 & 0 & 1 \end{bmatrix} \oplus \frac{1}{6} \begin{bmatrix} 0 & 0 & 0 \\ 0 & 6 & 0 \\ 0 & 0 & 0 \end{bmatrix}
\end{aligned}$$

${}^{(3)}\Gamma :$

$$\begin{aligned}
|3, 1, 1\rangle &= [0, 0, 0 \quad 0, 0, 0 \quad 0, 0, 0 \quad 1, 0, 0] \\
|3, 1, 2\rangle &= [0, 0, 0 \quad 0, 0, 0 \quad 0, 0, 0 \quad 0, 1, 0] \\
|3, 2, 1\rangle &= [2, 0, 0 \quad 1, -\sqrt{3}, 0 \quad 1, \sqrt{3}, 0 \quad 0, 0, 0] \\
|3, 2, 2\rangle &= [0, 2, 0 \quad \sqrt{3}, 1, 0 \quad -\sqrt{3}, 1, 0 \quad 0, 0, 0] \\
|3, 3, 1\rangle &= [1, 0, 0 \quad 5/2, \sqrt{3}/2, 0 \quad 5/2, -\sqrt{3}/2, 0 \quad 0, 0, 0] \\
|3, 3, 2\rangle &= [0, 1, 0 \quad -\sqrt{3}/2, 5/2, 0 \quad \sqrt{3}/2, 5/2, 0 \quad 0, 0, 0] \\
|3, 4, 1\rangle &= [2, 0, 0 \quad -1, -\sqrt{3}, 0 \quad -1, \sqrt{3}, 0 \quad 0, 0, 0] \\
|3, 4, 2\rangle &= [0, -2, 0 \quad -\sqrt{3}, 1, 0 \quad \sqrt{3}, 1, 0 \quad 0, 0, 0]
\end{aligned}$$

We obtain

$$\begin{aligned}
|v| (3)\rangle &= |3, 1\rangle + |3, 2\rangle + 2|3, 3\rangle \\
|a| (3)\rangle &= -|3, 1\rangle + |3, 2\rangle + 2|3, 3\rangle
\end{aligned}$$

15.2.4 Computer programs

We first describe the input data files necessary for the execution of the program. As an example we consider the ammonia molecule.

Inputs

The symmetry information for C_{3v} , namely:

- (i) number of group generators NG, and their orthogonal matrix R and permutation P
Reps;
- (ii) group order g;
- (iii) number of permutation objects NP;
- (iv) number of classes NC;
- (v) group Irreps Γ generated with the aid of Irrep programs given in Chapters 5 and 7;

is contained in file C3V.txt.

File NH3.txt has the structural information, which includes the number of simple molecules NSM, and the position vectors of representative atoms as Array RR.

SPACE GROUPS C_{3v}

```

NG=2    ⇐ number of group generators
g=6     ⇐ group order
NP=3    ⇐ number of permutation objects
(* C3,Sigma-v *) ⇐ generators
R={{{-1/2,-Sqrt3/2,0},{Sqrt3/2,-1/2,0},{0,0,1}},
   {{-1,0,0},{0,1,0},{0,0,1}}}
P={{3,1,2},{1,3,2}}
NC=3
dmu={1,2}
Γ = {{{1},{-1}},{{{ -1/2,-√3/2},{√3/2,-1/2}},{-1,0},{1,0}}}}
```

Program MOLSYM

```

<< path, file(C3V.txt) ⇔ File contains  $C_{3v}$  group information.
<< path, file(NH3.txt) ⇔ File contains necessary information
                           about the  $NH_3$  molecule.
<< DiscreteMath'Combinatorica'
<< LinearAlgebra'MatrixManipulation'
```


1. Construction of symmetry operations

```
Print["Number of Generators = ", NG, ", Group Order = ', g];
```

```
← NP is the permutation order;
```

```
P[i] are group elements in permutation form. ⇒
```

```
IRREP={}; Do[AppendTo[IRREP,1],i,1,g]; L={Range[NP]};
```

```
Do[AppendTo[L,P[[i]]],{i,1,NG}];
```

```
Array[L,{NG+1}];
```

```
nel=Length[L];
```

```
f:=Permute[L[[i]],L[[j]]];
```

```
⇒ Generate group elements via permutations.
```

```
For every new element determine the vector Rep matrix. ←
```

```
While[TrueQ[Length[L]<g],
```

```
  For[i=1,i<g,i++,
```

```
    For[j=1,j<(Length[L]+1),j++,
```

```
      Switch[FreeQ[L,f],True,
```

```
        AppendTo[L,f];nel++;
```

```
        Rot[nel]=Rot[i].Rot[j];
```

```
      ]
```

```
    ]
```

```
  ]
```

```
]
```

```
Do[
```

```
  Switch[dmu[[mu]]==1,
```

```
    True,Do[
```

```
      ch[mu,kk]=IRREP[[mu,kk]],
```

```
      {kk,1,g}
```

```
    ],
```

```
    False, Do[
```

```
      ch[mu,kk]=Tr[IRREP[[mu, kk]]],
```

```
      {kk,1,g}
```

```
    ]
```

```
  ],{mu,1,NC}
```

```
]
```

```

Rot[1] = IdentityMatrix[3];
Print["Rotation Matrices of Group Elements are : "]
Do[
  Print["R(",i,") = ",MatrixForm[Rot[i]],"; ",
    "R(",i+1,") = ",MatrixForm[Rot[i+1]]," ; ",
    "R(",i+2,") = ",MatrixForm[Rot[i+2]], " ; ",
    "R(",i+3,") = ",MatrixForm[Rot[i+3]]],
  {i,1,g-3,4}
],
m = TableForm[MultiplicationTable[L, Permute]];

```

2. Stabilizers of representative atomic positions

⇒ Information obtained from file "NH3":

- (1) number of chemical elements NCEL,
- (2) number of simple molecules NSM,
- (3) atomic positions of representative atoms array RR. ⇐

```

Print["Atomic positions in Cartesian Coordinates
NAT=0;      ⇐ Total number of atoms in molecule
PART={};   ⇐ Partitioning of NAT atoms
and Their Symmetries : "];
Do[
  Atomsym={};PRT=0;
  RRK=RR[[ik,1]];LK ={};Ltmp={};
  Cosrep={};grk=0;
  Switch[RRK=={0,0,0},
    True,grk=g;
    AppendTo[Atomsym,Range[g]];PRT=1;
    Print["[" , MOL[[ik]],",1]
      Position at = ",RR[[ik,1]],
      ", its group is the Full Point Group,"],
    False,Do[
      RK1=Rot[i].RRK;

```

```

Switch[And[RK1==RRK,FreeQ[LK,i]],
      True,grk++;AppendTo[LK,i]
      ],{i,1,g}
];AppendTo[Atomsym,LK];

];
indeks=g/grk;NAT=NAT+indeks;
AppendTo[PART,indeks];Icoset=1;
Acosrep={1};jj=1;Ltmp=LK;

⇒ Generation of coset Reps of  $\mathcal{H}(ik)$ 

While[And[Icoset<indeks,jj<g],jj++;
      Switch[FreeQ[Ltmp,jj],
            True,Icoset++;
            AppendTo[Acosrep,jj];
            Do[
                cst=LK[[ij]];
                AppendTo[Ltmp,m[[1,jj,cst]]],
                {ij,1,Length[LK]}
            ]
      ]
];

Do[
  RR[[ik,jk]]=Rot[Acosrep[jk]].RR[[ik,1]],{jk,2,indeks}
]

Switch[PRT ==0,True,
  Print["['', MOL[[ik]],'',1],
        Position at = ['',RR[[ik,1]],
        ['', its group of Order ['',grk,''], is ['',LK,
        ['', and its Coset Reps are ['',Acosrep];
  Switch[indeks>1,True,
    Print["its orbit has ['',indeks,
          '' equivalent positions:''];

```

```

        Do[
            Print[RR[[ik,jk]]],{jk,2,indeks}
        ]
    ],{ik,1,NSM}
]

```

3. Generating permutation matrices

```

PERMA={Range[NAT]};NPER={};
Do[
    NOA=0;
    Do[
        Do[
            RP=Inverse[Rot[kk]].RX[ik,jk];kx=0;park=0;
            While[And[kx<PART[[ik]],park==0],kx++;
                RDIF=RP-RX[ik,kx];
                Switch[And[RDIF·RDIF<0.01,
                    True,lx=NOA+kx;AppendTo[NPER,lx];
                    park=1
                ]
            ],{jk,1,PART[[ik]]}
        ];NOA+=PART[[ik]],{ik,1,NSM}
    ];AppendTo[PERMA,NPER];NPER={},{kk,2,g}
];
Print[MatrixForm[Partition[PERMA,8]]];

```

4. Constructing Irrep projection operators

```

ZRO=0*IdentityMatrix[3];Sympro={};Do[dmux[imu]=0,{imu,1,NC}];
Do[
    Pro={};    ⇐ Pro is initially a 3NAT×3NAT zero matrix.
    Do[
        AppendTo[Pro,ZRO],{i,1,NAT},{j,1,NAT}
    ];Pro=Partition[Pro,NAT];

```

```

⇒ Construct projection operator P( $\mu$ ) in Pro.  ⇐
Do[
  Do[
    ic=PERMA[[kk,ir]];
    Pro[[ir,ic]]=Pro[[ir,ic]]+ch[mu,kk]*Rot[kk],
    {kk,1,g}
  ],{ir,1,NAT}
];
Do[
  Do[
    Do[
      im=3*(ir-1)+i;
      Do[
        jm=3*(ic-1)+j;
        Proj[im,jm]=dmu[mu]*Pro[[ir,ic,i,j]]/g,
        {j,1,3}
      ],{ic,1,NAT}
    ],{i,1,3}
  ],{ir,1,NAT}
];
Project=Array[Proj,{3*NAT,3*NAT}];
EGV=Eigenvalues[Project];
Print["Eigenvalues[" , mu, "]" = ", EGV];
EV = Eigenvectors[Project];
Do[
  Switch[EGV[[ig]]==1,
    True,dmu[mu]++;AppendTo[Sympro,EV[[ig]]]
  ],
  {ig,1,3*NAT}],
  {mu,1,NC}
]

```

5. Determining bond vectors and their symmetries

```

MAXL = 5.0;
Print["BONDS AND THEIR GROUPS"]
BOND={};Bindx={};Bondsym={};
NB=0;ia=0;
While[ia<NSM,ia++;ja=0;
  While[ja<PART[[ia]],ja++;ib=ia-1;
    While[ib<NSM,ib++;jb=0;
      While[jb<PART[[ib]],jb++;

Generate bond:

      RB =RX[ib,jb]-RX[ia,ja];RBM =-1*RB;
      RB2=RB.RB;
      Switch[0.01<=RB2<=MAXL,True,bnd=0;
        Do[
          Switch[BOND[[kx]]==RBM,
            True,bnd=1
          ],
          {kx,1,Length[BOND]}
        ];
      Switch[bnd==0,
        True,AppendTo[BOND,RB];
        NB++;
AppendTo[Bindx,{ix,Elmnt[[ia]],ja,jx,Elmnt[[ib]],jb}];
Print["Bond Type["Elmnt[[ia]],","ja,","Elmnt[[ib]],
  ","jb,"] = ",RB," with bond length ",RB2];

Determine the group of the bond:

      Tbsym = 1; h = 1;
      Do[
        RB1=Rot[ig].RB;
      Switch[And[Or[RB1==RB,RB1==RBM],FreeQ[Tbsym,ig]],
        True,h++;AppendTo[Tbsym,ig]
      ],

```

```

        {ig,2,g}
    ];
    AppendTo[Bondsym,Tbsym];
Print["Subgroup of Bond is ",Tbsym," of Order ",h];
    indbs=g/h;Icoset=1;
    Bondcrep={1};jj=1;
    Lttmp=Tbsym;

```

Generation of coset reps of the bond group:

```

    While[And[Icoset<indbs,jj<g],jj++;
        Switch[FreeQ[Lttmp,jj],
            True,Icoset++;
            AppendTo[Bondcrep,jj];
            Do[
                cst=Tbsym[[ij]];
                AppendTo[Lttmp,m[[1,jj,cst]]],
                {ij,1,Length[Tbsym]}
            ]
        ];
    ];
Print["with Coset Representatives ",Bondcrep];

```

6. Symmetrizing force constant matrices

```

Fcm0={{f11,f12,f13},{f21,f22,f23},{f31,f32,f33}};
k=1;Fcm=Fcm0;
While[k<h,k++;ii=Tbsym[[k]];
    Fcm+=Transpose[Rot[ii]].Fcm0.Rot[ii];
];
FX=Simplify[Fcm];FX=Flatten[FX];
abc={ $\alpha$ , $\beta$ , $\gamma$ , $\delta$ , $\epsilon$ , $\zeta$ , $\eta$ , $\theta$ , $\lambda$ };
FC={};
Do[
    AppendTo[FC,i],{i,1,9}
];cnt=0;nel=0;mem={};ij=1;

```

Output

Classical NH_3

A. Point group: $\mathcal{C}_{3v}$

B. Irreps

$$\text{Irrep}[\Gamma_1] = \{1, 1, 1, 1, 1, 1\}$$

$$\text{Irrep}[\Gamma_2] = \{1, 1, -1, 1, -1, -1\}$$

$$\text{Irrep}[\Gamma_3] = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \quad \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \quad \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} \\ \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \quad \begin{bmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \quad \begin{bmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}.$$

C. Characters

$$\chi^{[\Gamma_1]} = \{1, 1, 1, 1, 1, 1\}$$

$$\chi[\Gamma_2] = \{1, 1, -1, 1, -1, -1\}$$

$$\chi[\Gamma_2] = \{2, -1, 0, -1, 0, 0\}$$

D. Rotation matrices

$$\begin{aligned}
 R(1) &= \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} & R(2) &= \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} & R(3) &= \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \\
 R(4) &= \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} & R(5) &= \begin{bmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} & R(6) &= \begin{bmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}.
 \end{aligned}$$

E. Atomic positions and their symmetries

- Molecule[1,1] is N, located at (0,0,0), its group is $\mathcal{C}_{3v}$
- Molecule[2,1] is H, located at $(0, 1/\sqrt{3}, -2.)$, its group of order 2, is $\mathcal{C}_s = \{1, 3\}$, and its Coset Reps are $\{1, 2, 4\}$

F. Total number of atoms = 4

G. Permutation matrices

$$\begin{bmatrix} 1 \\ 2 \\ 3 \\ 4 \end{bmatrix} \quad \begin{bmatrix} 1 \\ 4 \\ 2 \\ 3 \end{bmatrix} \quad \begin{bmatrix} 1 \\ 2 \\ 4 \\ 3 \end{bmatrix} \quad \begin{bmatrix} 1 \\ 3 \\ 4 \\ 2 \end{bmatrix} \quad \begin{bmatrix} 1 \\ 3 \\ 2 \\ 4 \end{bmatrix} \quad \begin{bmatrix} 1 \\ 4 \\ 3 \\ 2 \end{bmatrix}$$

H. Symmetry-adapted eigenvectors

	N	H ₁	H ₂	H ₃	
$\Gamma_1 :$	$ 1, 1\rangle = [(0 \quad 0 \quad 0)$	$(0 \quad 0 \quad 1)$	$(0 \quad 0 \quad 1)$	$(0 \quad 0 \quad 1)]$	
	$ 1, 2\rangle = [(0 \quad 0 \quad 0)$	$(0 \quad -1 \quad 0)$	$(\frac{\sqrt{3}}{2} \quad \frac{1}{2} \quad 0)$	$(-\frac{\sqrt{3}}{2} \quad \frac{1}{2} \quad 0)]$	
	$ 1, 3\rangle = [(0 \quad 0 \quad 1)$	$(0 \quad 0 \quad 0)$	$(0 \quad 0 \quad 0)$	$(0 \quad 0 \quad 0)]$	
$\Gamma_2 :$	$ 2, 1\rangle = [(0 \quad 0 \quad 0)$	$(-\frac{2}{\sqrt{3}} \quad 0 \quad 0)$	$(\frac{1}{\sqrt{3}} \quad -1 \quad 0)$	$(\frac{1}{\sqrt{3}} \quad 1 \quad 0)]$	
$\Gamma_3 :$	$ 3, 1, 1\rangle = [(0 \quad 0 \quad 0)$	$(0 \quad 0 \quad 0)$	$(0 \quad 0 \quad -1)$	$(0 \quad 0 \quad 1)]$	} Row 1
	$ 3, 1, 2\rangle = [(0 \quad 0 \quad 0)$	$(\sqrt{3} \quad 0 \quad 0)$	$(0 \quad -1 \quad 0)$	$(0 \quad 1 \quad 0)]$	
	$ 3, 1, 3\rangle = [(0 \quad 0 \quad 0)$	$(1 \quad 0 \quad 0)$	$(1 \quad 0 \quad 0)$	$(1 \quad 0 \quad 0)]$	
	$ 3, 1, 4\rangle = [(1 \quad 0 \quad 0)$	$(0 \quad 0 \quad 0)$	$(0 \quad 0 \quad 0)$	$(0 \quad 0 \quad 0)]$	
$\Gamma_3 :$	$ 3, 2, 1\rangle = [(0 \quad 0 \quad 0)$	$(0 \quad 0 \quad -2)$	$(0 \quad 0 \quad 1)$	$(0 \quad 0 \quad 1)]$	} Row 2
	$ 3, 2, 2\rangle = [(0 \quad 0 \quad 0)$	$(0 \quad 1 \quad 0)$	$(0 \quad 1 \quad 0)$	$(0 \quad 1 \quad 0)]$	
	$ 3, 2, 3\rangle = [(0 \quad 0 \quad 0)$	$(0 \quad -\sqrt{3} \quad 0)$	$(-1 \quad 0 \quad 0)$	$(1 \quad 0 \quad 0)]$	
	$ 3, 2, 4\rangle = [(0 \quad 1 \quad 0)$	$(0 \quad 0 \quad 0)$	$(0 \quad 0 \quad 0)$	$(0 \quad 0 \quad 0)]$	

Comment

For the sake of pedagogical clarity, we discuss here the connection between the symmetry-adapted vectors given above and the physical motion of the ammonia molecule. We start with identifying the translation and rotation modes. Inspection of the vectors reveals that

$$\begin{aligned}
 |\mathbf{v}, z\rangle &= |1, 1\rangle + |1, 3\rangle \\
 |\mathbf{v}, x\rangle &= |3, 1, 3\rangle + |3, 1, 4\rangle \\
 |\mathbf{v}, y\rangle &= |3, 2, 2\rangle + |3, 2, 4\rangle \\
 |\mathbf{a}, z\rangle &= |2, 1\rangle \\
 |\mathbf{a}, y\rangle &= |3, 1, 1\rangle - |3, 1, 3\rangle + |3, 1, 4\rangle \\
 |\mathbf{a}, x\rangle &= |3, 2, 1\rangle - |3, 2, 2\rangle + |3, 2, 4\rangle
 \end{aligned}$$

The normal vibrational modes can then be identified with

$$\begin{aligned}
 |\text{vib.}, \Gamma_1, 1\rangle &= |1, 1\rangle - |1, 3\rangle \\
 |\text{vib.}, \Gamma_1, 2\rangle &= |1, 2\rangle \\
 |\text{vib.}, \Gamma_3, 1, 1\rangle &= |3, 2, 2\rangle + |3, 2, 4\rangle \\
 |\text{vib.}, \Gamma_3, 1, 2\rangle &= |1, 1\rangle \\
 |\text{vib.}, \Gamma_3, 2, 1\rangle &= |3, 1, 1\rangle - |3, 1, 3\rangle + |3, 1, 4\rangle \\
 |\text{vib.}, \Gamma_3, 2, 2\rangle &= |3, 2, 1\rangle - |3, 2, 2\rangle + |3, 2, 4\rangle
 \end{aligned}$$

I. Bonds and their symmetry subgroups

- (i) – Bond type $[\text{N1-H1}] = \{0, 1/\sqrt{3}, -1.5\}$, with bond length 31/12
 - Subgroup of bond is $\{1, 3\}$ of order 2, with coset representatives $\{1, 2, 4\}$
 - Symmetry-adapted force constant matrix =
$$\begin{bmatrix} \alpha & 0 & 0 \\ 0 & \beta & \delta \\ 0 & \epsilon & \gamma \end{bmatrix}$$
- (ii) – Bond type $[\text{N1-H2}] = \{-0.5, -1/2\sqrt{3}, -1.5\}$ with bond length 31/12
 - Subgroup of bond is $\{1, 6\}$ of order 2, with coset representatives $\{1, 2, 4\}$
 - Symmetry-adapted force constant matrix =
$$\begin{bmatrix} \alpha & \beta & \gamma \\ \beta & \delta & \epsilon \\ \zeta & \eta & \theta \end{bmatrix}$$
- (iii) – Bond type $[\text{N1-H3}] = \{0.5, -1/2\sqrt{3}, -1.5\}$, with bond length 31/12.
 - Subgroup of bond is $\{1, 5\}$ of order 2, with coset representatives $\{1, 2, 3\}$
 - Symmetry-adapted force constant matrix =
$$\begin{bmatrix} \alpha & \beta & \gamma \\ \beta & \delta & \epsilon \\ \zeta & \eta & \theta \end{bmatrix}$$

- (iv) – Bond type $[\text{H1-H2}] = \{-0.5, -\sqrt{3}/2, 0\}$ with bond length 1
 - Subgroup of bond is $\{1, 5\}$ of order 2, with coset representatives $\{1, 2, 3\}$
 - Symmetry-adapted force constant matrix $= \frac{1}{4} \begin{bmatrix} \alpha + 3\beta & \sqrt{3}(\alpha - \beta) & 2\sqrt{3}\delta \\ \sqrt{3}(\alpha - \beta) & 3\alpha + \beta & -2\delta \\ 2\sqrt{3}\epsilon & -2\epsilon & 4\gamma \end{bmatrix}$
- (v) – Bond type $[\text{H1-H3}] = \{-0.5, -\sqrt{3}/2, 0\}$ with bond length 1
 - Subgroup of bond is $\{1, 6\}$ of order 2, with coset representatives $\{1, 2, 4\}$
 - Symmetry-adapted force constant matrix $= \frac{1}{4} \begin{bmatrix} \alpha + 3\beta & \sqrt{3}(\beta - \alpha) & -2\sqrt{3}\delta \\ \sqrt{3}(\beta - \alpha) & 3\alpha + \beta & -2\delta \\ -2\sqrt{3}\epsilon & -2\epsilon & 4\gamma \end{bmatrix}$
- (vi) – Bond type $[\text{H2-H3}] = \{1.0, 0, 0\}$ with bond length 1.
 - Subgroup of bond is $\{1, 3\}$ of order 2, with coset representatives $\{1, 2, 4\}$
 - Symmetry-adapted force constant matrix $= \begin{bmatrix} \alpha & 0 & 0 \\ 0 & \beta & \delta \\ 0 & \epsilon & \gamma \end{bmatrix}$

15.3 Dynamical properties of solids

Group theoretical techniques have been extensively employed in the analysis of the dynamical properties of solids since the late 1950s [93, 101, 102, 103, 104]. It was then realized that the application of group theory greatly simplifies the solution of the eigenvalue problem associated with normal modes. This is achieved by transforming the corresponding dynamical matrix into a block-diagonal form. The dynamical matrix is defined for every sampled wavevector $\mathbf{k}$ at high-symmetry points or lines inside or on the boundary of the Brillouin zone. The first application of group theory in this context was due to Yanagawa [105], who studied the vibrations of crystals of the rocksalt and diamond structures.

15.3.1 The harmonic approximation revisited

Our preceding discussion of the harmonic approximation carries over to the case of solids and liquids. However, a change in notation is necessary in the present case. The μ th atom is now labeled $\mu \equiv (l\kappa)$, according to the primitive cell it occupies, l , and its atomic-basis label, κ . The instantaneous position of the atom $(l\kappa)$ is given by

$$\mathbf{r}(l\kappa) = \mathbf{R}(l\kappa) + \mathbf{u}(l\kappa), \quad (15.56)$$

where $\mathbf{R}(l\kappa)$ is the equilibrium position and $\mathbf{u}(l\kappa)$ the *real* instantaneous displacement from equilibrium, i.e.

$$\mathbf{u}^*(l\kappa) = \mathbf{u}(l\kappa).$$

In a crystalline solid, $\mathbf{R}(l\kappa)$ is given by

$$\mathbf{R}(l\kappa) = \mathbf{t}(l) + \boldsymbol{\kappa}. \quad (15.57)$$

$\mathbf{t}(l)$ is the primitive lattice vector defining the position of the l th primitive cell, and $\boldsymbol{\kappa}$ the location of the κ th basis atom within the primitive cell. With this notation at hand, we

now expand the potential energy of the dynamical system in the harmonic approximation in terms of the displacements $\mathbf{u}(l\kappa)$ as

$$\begin{aligned}\Phi(\{\mathbf{r}(l\kappa)\}) &= \Phi(\{\mathbf{R}(l\kappa)\}) \\ &+ \frac{1}{2} \sum_{l\kappa\alpha} \sum_{l'\kappa'\beta} u_\alpha(l\kappa) \Phi_{\alpha\beta} \begin{pmatrix} l & l' \\ \kappa & \kappa' \end{pmatrix} u_\beta(l'\kappa') + \cdots, \\ \Phi_{\alpha\beta} \begin{pmatrix} l & l' \\ \kappa & \kappa' \end{pmatrix} &= \left. \frac{\partial^2 \Phi}{\partial u_\alpha(l\kappa) \partial u_\beta(l'\kappa')} \right|_{u_\alpha(l\kappa)=u_\beta(l'\kappa')=0},\end{aligned}\quad (15.58)$$

where $\Phi_{\alpha\beta} \begin{pmatrix} l & l' \\ \kappa & \kappa' \end{pmatrix}$ are called *generalized force constants*. $\mathbf{u}(l\kappa)$ may be, again, considered as a vector field $\mathbf{u}(\mathbf{r})$ whose values are only defined at the lattice sites $(l\kappa)$. Once more, we stress that the absence of terms linear in the displacement is because the expansion is carried out about the equilibrium state of the system. Second, we point out that the dots in (15.58) represent higher degree, or anharmonic, terms in the expansion. The stability of the system in the harmonic approximation requires that

$$\mathcal{V} = \frac{1}{2} \sum_{l\kappa\alpha} \sum_{l'\kappa'\beta} u_\alpha(l\kappa) \Phi_{\alpha\beta} \begin{pmatrix} l & l' \\ \kappa & \kappa' \end{pmatrix} u_\beta(l'\kappa') \geq 0. \quad (15.59)$$

We also find from the definition of $\Phi_{\alpha\beta} \begin{pmatrix} l & l' \\ \kappa & \kappa' \end{pmatrix}$ in (15.58) that its components are real and that it is a symmetric matrix with respect to its indices, namely,

$$\boxed{\Phi_{\alpha\beta} \begin{pmatrix} l & l' \\ \kappa & \kappa' \end{pmatrix} = \Phi_{\beta\alpha} \begin{pmatrix} l' & l \\ \kappa' & \kappa \end{pmatrix}.} \quad (15.60)$$

The kinetic energy associated with the lattice vibrations is expressed in terms of $\{\partial u_\alpha(l\kappa)/\partial t = \dot{u}_\alpha(l\kappa)\}$, as

$$T = \frac{1}{2} \sum_{l\kappa\alpha} M_\kappa \dot{u}_\alpha^2(l\kappa), \quad (15.61)$$

and the system Lagrangian is written as

$$\mathcal{L} = \frac{1}{2} \sum_{l\kappa\alpha} M_\kappa \dot{u}_\alpha^2(l\kappa) - \frac{1}{2} \sum_{l\kappa\alpha} \sum_{l'\kappa'\beta} u_\alpha(l\kappa) \Phi_{\alpha\beta} \begin{pmatrix} l & l' \\ \kappa & \kappa' \end{pmatrix} u_\beta(l'\kappa'). \quad (15.62)$$

The corresponding equations of motion are again obtained using

$$\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{u}_\alpha(l\kappa)} - \frac{\partial \mathcal{L}}{\partial u_\alpha(l\kappa)} = 0, \quad (15.63)$$

which yields the set of coupled equations of motion

$$M_{\kappa} \ddot{u}_{\alpha}(l\kappa) + \sum_{l'\kappa'\beta} \Phi_{\alpha\beta} \begin{pmatrix} l & l' \\ \kappa & \kappa' \end{pmatrix} u_{\beta}(l'\kappa') = 0. \quad (15.64)$$

Some consequences of translation symmetry

In the case of crystal lattice systems, the underlying periodic symmetry simplifies the structure of the generalized force constants. First, we recall that the translation operation $(E|\mathbf{t}(l))$ gives

$$(E|\mathbf{t}(m)) u_{\alpha}(l\kappa) = u_{\alpha}((l-m)\kappa). \quad (15.65)$$

Because of lattice periodicity, the potential energy should remain invariant under $(E|\mathbf{t}(m))$, and we obtain

$$\mathcal{V} = \frac{1}{2} \sum_{l\alpha} \sum_{l'\kappa'\beta} u_{\alpha}((l-m)\kappa) \Phi_{\alpha\beta} \begin{pmatrix} l-m & l'-m \\ \kappa & \kappa' \end{pmatrix} u_{\beta}((l'-m)\kappa'). \quad (15.66)$$

Since $(E|\mathbf{t}(m))$ merely shifts all atoms into equivalent positions, we must have

$$\Phi_{\alpha\beta} \begin{pmatrix} l-m & l'-m \\ \kappa & \kappa' \end{pmatrix} = \Phi_{\alpha\beta} \begin{pmatrix} l & l' \\ \kappa & \kappa' \end{pmatrix}, \quad (15.67)$$

and the force constants can only depend on the difference between $\mathbf{t}(l)$ and $\mathbf{t}(l')$, and not on $\mathbf{t}(l)$ and $\mathbf{t}(l')$ individually, so that

$$\Phi_{\alpha\beta} \begin{pmatrix} l & l' \\ \kappa & \kappa' \end{pmatrix} = \Phi_{\alpha\beta} \begin{pmatrix} l-l' & 0 \\ \kappa & \kappa' \end{pmatrix} = \Phi_{\alpha\beta} \begin{pmatrix} 0 & l'-l \\ \kappa & \kappa' \end{pmatrix}. \quad (15.68)$$

Another symmetry relation among the force constants may be obtained from (15.10) as follows: Consider the situation in which the system as a whole is given an arbitrary displacement ϵ_{β} , so that it remains in its undistorted state, and no restoring forces are activated, then (15.10) yields

$$\left(\sum_{l'\kappa'} \Phi_{\alpha\beta} \begin{pmatrix} l & l' \\ \kappa & \kappa' \end{pmatrix} \right) \epsilon_{\beta} = 0, \quad \Rightarrow \quad \sum_{l'\kappa'} \Phi_{\alpha\beta} \begin{pmatrix} 0 & l' \\ \kappa & \kappa' \end{pmatrix} = 0. \quad (15.69)$$

This sum rule is quite useful in determining the “self force constant”

$$\Phi_{\alpha\beta} \begin{pmatrix} 0 & 0 \\ \kappa & \kappa \end{pmatrix} = - \sum'_{l'\kappa'} \Phi_{\alpha\beta} \begin{pmatrix} 0 & l' \\ \kappa & \kappa' \end{pmatrix}, \quad (15.70)$$

where the prime excludes the term $l' = 0$.

15.3.2 The dynamical matrix and its symmetries

Alternative reviews of topics presented here can be found in references [41, 93, 101, 102, 104]. The first step in simplifying (15.38) is achieved by the transformation

$$u_{\alpha}(l\kappa) = \frac{1}{\sqrt{M_{\kappa}}} w_{\alpha}(l\kappa) e^{-i\omega t}, \quad (15.71)$$

which yields

$$-\omega^2 w_{\alpha}(l\kappa) + \sum_{l'\kappa'\beta} \frac{1}{\sqrt{M_{\kappa}M_{\kappa'}}} \Phi_{\alpha\beta} \begin{pmatrix} l & l' \\ \kappa & \kappa' \end{pmatrix} w_{\beta}(l'\kappa') = 0, \quad (15.72)$$

or,

$$\sum_{l'\kappa'\beta} \mathfrak{D}_{\alpha\beta} \begin{pmatrix} l & l' \\ \kappa & \kappa' \end{pmatrix} w_{\beta}(l'\kappa') = \omega^2 w_{\alpha}(l\kappa).$$

Next, we project out, with the aid of the Wigner projection operator

$$({}^{\mathbf{q}})\mathcal{P} = \frac{1}{N} \sum_{\mathbf{t}(m)} ({}^{\mathbf{q}})\Delta^*(\mathbf{t}) (E|\mathbf{t}(m)), \quad (15.73)$$

displacements that transform according to the Irrep $\mathbf{q}$ in the Brillouin zone (BZ), as

$$\begin{aligned} \mathbf{U}(\kappa, \mathbf{q}) &= ({}^{\mathbf{q}})\mathcal{P} \mathbf{w}(0\kappa) = \frac{1}{N} \sum_{\mathbf{t}(l)} ({}^{\mathbf{q}})\Delta^*(\mathbf{t}) (E|-\mathbf{t}(l)) \mathbf{w}(0\kappa) \\ &= \frac{1}{N} \sum_{\mathbf{t}(m)} e^{-i\mathbf{q}\cdot\mathbf{t}(l)} \mathbf{w}(l\kappa). \end{aligned} \quad (15.74)$$

Conversely, we write

$$\mathbf{w}(l\kappa) = \frac{1}{N} \sum_{\mathbf{q} \in BZ} e^{i\mathbf{q}\cdot\mathbf{t}(l)} \mathbf{U}(\kappa, \mathbf{q}). \quad (15.75)$$

Since $w_{\alpha}(l\kappa)$ is real, it follows that

$$U_{\alpha}^*(\kappa, \mathbf{q}) = U_{\alpha}(\kappa, -\mathbf{q}). \quad (15.76)$$

Substitution back in (15.72) yields

$$\omega^2(\mathbf{q}) U_{\alpha}(\kappa, \mathbf{q}) = \sum_{\beta\kappa'} D_{\alpha\beta}(\kappa\kappa' | \mathbf{q}) U_{\beta}(\kappa', \mathbf{q}), \quad (15.77)$$

where

$$D_{\alpha\beta}(\kappa\kappa' | \mathbf{q}) = \sum_{l'} \mathfrak{D}_{\alpha\beta} \begin{pmatrix} 0 & l' \\ \kappa & \kappa' \end{pmatrix} \exp[i\mathbf{q} \cdot \mathbf{t}(l')], \quad (15.78)$$

is identified as the *dynamical matrix*. It can also be expressed in terms of the force constant matrices as

$$D_{\alpha\beta}(\kappa\kappa' | \mathbf{q}) = \frac{1}{\sqrt{M_\kappa M_{\kappa'}}} \sum_{l'} \Phi_{\alpha\beta} \begin{pmatrix} 0 & l' \\ \kappa & \kappa' \end{pmatrix} \exp[i\mathbf{q} \cdot \mathbf{t}(l')], \quad (15.79)$$

and

$$\begin{aligned} D_{\alpha\beta}(\kappa\kappa | \mathbf{q}) &= \frac{1}{M_\kappa} \sum_{l'} \Phi_{\alpha\beta} \begin{pmatrix} 0 & l' \\ \kappa & \kappa \end{pmatrix} \left(\exp[i\mathbf{q} \cdot \mathbf{t}(l')] - 1 \right) \\ &\quad - \frac{1}{M_\kappa} \sum_{l', \kappa' \neq \kappa} \Phi_{\alpha\beta} \begin{pmatrix} 0 & l' \\ \kappa & \kappa' \end{pmatrix}, \end{aligned} \quad (15.80)$$

where we used (15.70).

If we assume that the system comprises $N \rightarrow \infty$ primitive cells and we use cyclic boundary conditions, (15.77) can be cast in the form of the matrix eigenvalue problem

$$\mathbf{D} \mathbf{U} = \omega^2 \mathbb{I} \mathbf{U} \quad \Rightarrow \quad \left\| D_{\alpha\beta}(\kappa\kappa' | \mathbf{q}) - \omega^2 \delta_{\alpha\beta} \delta_{\kappa\kappa'} \right\| = 0, \quad (15.81)$$

where $\mathbf{D}$ and $\mathbf{U}$ are $3r \times 3r$ and $3r \times 1$ matrices, respectively, where r is the number of atoms in the primitive cell. Thus, for each $\mathbf{q}$ we have $3r$ eigenvalues $\omega^2(\mathbf{q}|j)$ and corresponding normalized eigenvectors $\mathbf{e}(\mathbf{q}|j\lambda)$, with components $e_\alpha(\kappa|\mathbf{q}j\lambda)$. The index λ accounts for possible degeneracies of the eigenvalues, and $\alpha = x, y, z$.

General symmetries of the dynamical matrix and its solutions

The definition of the dynamical matrix (15.78) reveals that it is periodic in reciprocal space, namely,

$$\mathbf{D}(\kappa\kappa' | \mathbf{q} + \mathbf{G}) = \mathbf{D}(\kappa\kappa' | \mathbf{q}), \quad (15.82)$$

from which follow similar periodicities for the frequencies and the corresponding eigenvectors:

$$\begin{aligned}\omega(\mathbf{q} + \mathbf{G}|j) &= \omega(\mathbf{q}|j), \\ \mathbf{e}(\mathbf{q} + \mathbf{G}|j\lambda) &= \mathbf{e}(\mathbf{q}|j\lambda).\end{aligned}\tag{15.83}$$

We can also establish the hermiticity of $\mathbf{D}$ with the aid of (15.60) and (15.78), namely

$$\begin{aligned}D_{\beta\alpha}(\kappa\kappa' | \mathbf{q}) &= \sum_{l'} \mathfrak{D}_{\beta\alpha} \begin{pmatrix} l & l' \\ \kappa & \kappa' \end{pmatrix} \exp[i\mathbf{q} \cdot (\mathbf{t}(l) - \mathbf{t}(l'))] \\ &= \sum_{l'} \mathfrak{D}_{\alpha\beta} \begin{pmatrix} l' & l \\ \kappa' & \kappa \end{pmatrix} \exp[-i\mathbf{q} \cdot (\mathbf{t}(l') - \mathbf{t}(l))] \\ &= \sum_{l'} \mathfrak{D}_{\alpha\beta} \begin{pmatrix} l' - l & 0 \\ \kappa' & \kappa \end{pmatrix} \exp[-i\mathbf{q} \cdot (\mathbf{t}(l') - \mathbf{t}(l))] \\ &= D_{\alpha\beta}^*(\kappa'\kappa | \mathbf{q}),\end{aligned}\tag{15.84}$$

and

$$\mathbf{D}^*(\kappa\kappa' | \mathbf{q}) = \mathbf{D}(\kappa\kappa' | -\mathbf{q}),\tag{15.85}$$

thus, guaranteeing the reality of the eigenvalues $\omega^2(\mathbf{q})$; moreover, the stability condition that guarantees the positive definiteness of the force constant matrix leads to

$$\omega^2(\mathbf{q}|j) \geq 0.\tag{15.86}$$

Equation (15.85) also establishes the orthonormality and completeness of the eigenvectors

$$\begin{aligned}\mathbf{e}^*(\mathbf{q}|j\lambda) \cdot \mathbf{e}(\mathbf{q}|j'\lambda') &= \delta_{jj'} \delta_{\lambda\lambda'}, \\ \mathbf{e}_\alpha(\kappa | \mathbf{q}, j\lambda) \cdot \mathbf{e}_\beta^*(\kappa' | \mathbf{q}, j\lambda) &= \delta_{\alpha\beta} \delta_{\kappa\kappa'},\end{aligned}\tag{15.87}$$

which can be recast in component form

$$\begin{aligned}\sum_{\kappa\alpha} e_\alpha^* \left(\kappa \left| \begin{matrix} \mathbf{q} \\ j\lambda \end{matrix} \right. \right) e_\alpha \left(\kappa \left| \begin{matrix} \mathbf{q} \\ j'\lambda' \end{matrix} \right. \right) &= \delta_{jj'} \delta_{\lambda\lambda'}, \\ \sum_{j\lambda} e_\beta^* \left(\kappa' \left| \begin{matrix} \mathbf{q} \\ j\lambda \end{matrix} \right. \right) e_\alpha \left(\kappa \left| \begin{matrix} \mathbf{q} \\ j\lambda \end{matrix} \right. \right) &= \delta_{\alpha\beta} \delta_{\kappa\kappa'}.\end{aligned}\tag{15.88}$$

Finally, (15.85) and (15.77) can be used to establish the relation

$$\mathbf{e}^*(\mathbf{q}|j\lambda) = \mathbf{e}(-\mathbf{q}|j\lambda).\tag{15.89}$$

We consider the action of $S = (R|\mathbf{w}) \in \mathbb{S}$ on a component of $\mathbf{e}(j\lambda|\mathbf{q})$, namely, $e_\alpha(\kappa|\mathbf{q}j\lambda)$. We first express $e_\alpha(\kappa|\mathbf{q}j\lambda)$ in a Bloch form, namely,

$$e_\alpha(\kappa|\mathbf{q}j\lambda) = {}^{(\mathbf{q})} \mathcal{P} e_\alpha(\mathbf{0}\kappa|j\lambda)$$

and then write

$$\begin{aligned}S e_\alpha(\kappa|\mathbf{q}j\lambda) &= S {}^{(\mathbf{q})} \mathcal{P} e_\alpha(\mathbf{0}\kappa|j\lambda) \\ &= {}^{(R\mathbf{q})} \mathcal{P} S e_\alpha(\mathbf{0}\kappa|j\lambda).\end{aligned}$$

We find that since $\mathbf{e}_\alpha$ is a component of a 3D vector, then

$$\hat{S} \mathbf{e}_\alpha = \sum_{\beta} {}^{(\nu)}\Gamma_{\alpha\beta}(R) \mathbf{e}_\beta, \quad (15.90)$$

where ${}^{(\nu)}\Gamma$ is the 3D vector Rep. It will also take site κ into site $\bar{\kappa}$, such that

$$S \boldsymbol{\kappa} = R \boldsymbol{\kappa} - R \mathbf{w} = \mathbf{t}[\kappa, S] + \bar{\boldsymbol{\kappa}} = S \boldsymbol{\kappa} \pmod{\mathbf{t}},$$

which engenders a permutation among the atomic bases of the primitive cell. We then have

$$\begin{aligned} \hat{S} \mathbf{e}_\alpha(\kappa|j\lambda, \mathbf{q}) &= {}^{(R\mathbf{q})} \mathcal{P} \sum_{\beta} {}^{(\nu)}\Gamma_{\alpha\beta}(S) \mathbf{e}_\beta(\mathbf{t}[\kappa, S] + \bar{\boldsymbol{\kappa}}|j\lambda) \\ &= \sum_{\beta\bar{\kappa}} {}^{(\nu)}\Gamma_{\alpha\beta}(S) e^{iR\mathbf{q} \cdot \mathbf{t}[\kappa, S]} \mathbf{e}_\beta(\bar{\kappa}|R\mathbf{q}j\lambda) \delta(\hat{S}\kappa, \bar{\kappa}) \\ &= \sum_{\beta\bar{\kappa}} e^{iR\mathbf{q} \cdot \mathbf{t}[\kappa, S]} {}^{(\nu)}\Gamma_{\alpha\beta}(S) {}^{(\text{perm})}\Gamma_{\kappa\bar{\kappa}}(S) \mathbf{e}_\beta(\bar{\kappa}|R\mathbf{q}j\lambda). \end{aligned} \quad (15.91)$$

Writing $\mathbf{t}[\kappa, S] = R^{-1}\boldsymbol{\kappa} - \bar{\boldsymbol{\kappa}}$, we obtain

$$\begin{aligned} \hat{S} \mathbf{e}_\alpha(\kappa|\mathbf{q}j\lambda) &= \sum_{\beta\bar{\kappa}} e^{iR\mathbf{q} \cdot (R\boldsymbol{\kappa} - \bar{\boldsymbol{\kappa}})} {}^{(\nu)}\Gamma_{\alpha\beta}(S) {}^{(\text{perm})}\Gamma_{\kappa\bar{\kappa}}(S) \mathbf{e}_\beta(\bar{\kappa}|R\mathbf{q}j\lambda) \\ &= \sum_{\beta\bar{\kappa}} e^{i\mathbf{q} \cdot (\boldsymbol{\kappa} - R^{-1}\bar{\boldsymbol{\kappa}})} {}^{(\nu)}\Gamma_{\alpha\beta}(S) {}^{(\text{perm})}\Gamma_{\kappa\bar{\kappa}}(S) \mathbf{e}_\beta(\bar{\kappa}|R\mathbf{q}j\lambda). \end{aligned} \quad (15.92)$$

Or

$$S \mathbf{e}(j\lambda|\mathbf{q}) = {}^{(\mathbf{q}, j)} \Gamma(S) \mathbf{e}(j\lambda|\mathbf{q}), \quad (15.93)$$

where

$${}^{(\mathbf{q}, j)} \Gamma_{\kappa\bar{\kappa}}(S) = e^{i\mathbf{q} \cdot (\boldsymbol{\kappa} - R\bar{\boldsymbol{\kappa}})} {}^{(\nu)}\Gamma(R) {}^{(\text{perm})}\Gamma_{\kappa\bar{\kappa}}(S) \quad (15.94)$$

Representation of $\mathbb{G}_{\mathbf{q}}$ engendered by the set $\mathbf{e}(j\lambda|R_s\mathbf{q})$.

The analysis presented here parallels references [102, 104]. We now focus on the action of $S = (R|\mathbf{w}) \in \mathbb{G}_{\mathbf{q}}$ on $\mathbf{e}_\alpha(\kappa|j\lambda, \mathbf{q})$. With the aid of (15.92) we find that

$$\hat{S} \mathbf{e}_\alpha(\kappa|\mathbf{q}j\lambda) = \sum_{\beta\kappa'} e^{i\mathbf{q} \cdot (\boldsymbol{\kappa} - R\boldsymbol{\kappa}')} {}^{(\nu)}\Gamma_{\alpha\beta}(S) {}^{(\text{perm})}\Gamma_{\kappa\kappa'}(S) \mathbf{e}_\beta(\kappa'|R\mathbf{q}j\lambda). \quad (15.95)$$

Setting

$$\bar{\mathbf{e}}_\alpha(\kappa|\mathbf{q}j\lambda) = e^{-i\mathbf{q} \cdot \boldsymbol{\kappa}} \mathbf{e}_\alpha(\kappa|j\lambda, \mathbf{q}),$$

(15.92) yields

$$\hat{S} \bar{e}_\alpha(\kappa|\mathbf{q}j\lambda) = \sum_{\beta\kappa'}^{(\nu)} \Gamma_{\alpha\beta}(S) \Gamma_{\kappa\kappa'}^{(\text{perm})}(S) \bar{e}_\beta(\kappa'|\mathbf{q}j\lambda). \quad (15.96)$$

The engendered Rep is just the outer-product

$$^{(\mathbf{q},j)}\bar{\Gamma} = ^{(\nu)}\Gamma(S) \otimes ^{(\text{perm})}\Gamma(S). \quad (15.97)$$

The eigenvalue equations in the $\bar{\mathbf{e}}$ representation are written as

$$\omega^2(\mathbf{q}j) \bar{e}_\alpha(\kappa|\mathbf{q}j\lambda) = \sum_{\kappa'\beta} C_{\alpha\beta}(\kappa\kappa'|\mathbf{q}) \bar{e}_\beta(\kappa'|\mathbf{q}j\lambda), \quad (15.98)$$

where the eigenvalues of the $\mathbf{C}(\mathbf{q})$ and $\mathbf{D}(\mathbf{q})$ matrices are the same, since they are related by a unitary transformation

$$C_{\alpha\beta}(\kappa\kappa'|\mathbf{q}) = e^{-i\mathbf{q}\cdot(\kappa-\kappa')} D_{\alpha\beta}(\kappa\kappa'|\mathbf{q}). \quad (15.99)$$

By definition, symmetry operations $S \in \mathbb{G}_{\mathbf{q}}$ leave the dynamical matrix $\mathbf{D}(\mathbf{q})$ unchanged, so that for a given frequency solution $\omega(\mathbf{q}|j)$ we have

$$S \mathbf{D}(\mathbf{q}) S^{-1} S \mathbf{e}(\mathbf{q}, j\lambda) = \mathbf{D}(\mathbf{q}) S \mathbf{e}(\mathbf{q}, j\lambda) = \omega^2(\mathbf{q}, j) S \mathbf{e}(\mathbf{q}, j\lambda). \quad (15.100)$$

Taking the matrix elements of (15.100) we get

$$\omega^2(\mathbf{q}, j) S e_\alpha(\kappa|\mathbf{q}, j\lambda) = \sum_{\beta\kappa'} \mathbf{D} \begin{pmatrix} \mathbf{q} \\ \alpha\kappa, \beta\kappa' \end{pmatrix} S e_\beta(\kappa'|\mathbf{q}, j\lambda),$$

and with the aid of (15.91) and (15.97) we can write

$$\begin{aligned} & \sum_{\bar{\beta}\bar{\kappa}} ^{(\mathbf{q},j)}\Gamma_{\alpha\kappa, \bar{\beta}\bar{\kappa}}(S) \left(\omega^2(\mathbf{q}, j) e_{\bar{\beta}}(\bar{\kappa}'|\mathbf{q}, j\lambda) \right) \\ &= \sum_{\bar{\beta}\bar{\kappa}} ^{(\mathbf{q},j)}\Gamma_{\alpha\kappa, \bar{\beta}\bar{\kappa}}(S) \sum_{\bar{\beta}'\bar{\kappa}'} \mathbf{D} \begin{pmatrix} \mathbf{q} \\ \bar{\beta}\bar{\kappa}, \bar{\beta}'\bar{\kappa}' \end{pmatrix} e_{\bar{\beta}'}(\bar{\kappa}'|\mathbf{q}, j\lambda) \\ &= \sum_{\beta\kappa'} \sum_{\gamma\kappa''} \mathbf{D} \begin{pmatrix} \mathbf{q} \\ \alpha\kappa, \beta\kappa' \end{pmatrix} ^{(\mathbf{q},j)}\Gamma_{\beta\kappa', \gamma\kappa''}(S) e_\gamma(\kappa''|\mathbf{q}, j\lambda). \end{aligned}$$

The hermiticity of $\mathbf{D}(\mathbf{q})$ implies that

$$\mathbf{D} \begin{pmatrix} \mathbf{q} \\ \alpha\kappa, \beta\kappa' \end{pmatrix} = \mathbf{D}^* \begin{pmatrix} \mathbf{q} \\ \beta\kappa', \alpha\kappa \end{pmatrix},$$

which leads to

$$\begin{aligned} & \sum_{\bar{\beta}\bar{\kappa}} \sum_{\bar{\beta}'\bar{\kappa}'} \mathbf{D}^* \begin{pmatrix} \mathbf{q} \\ \bar{\beta}'\bar{\kappa}', \bar{\beta}\bar{\kappa} \end{pmatrix} ^{(\mathbf{q},j)}\Gamma_{\alpha\kappa, \bar{\beta}\bar{\kappa}}(S) e_{\bar{\beta}'}(\bar{\kappa}'|\mathbf{q}, j\lambda) \\ &= \sum_{\beta\kappa'} \sum_{\gamma\kappa''} ^{(\mathbf{q},j)}\Gamma_{\beta\kappa', \gamma\kappa''}(S) \mathbf{D}^* \begin{pmatrix} \mathbf{q} \\ \beta\kappa', \alpha\kappa \end{pmatrix} e_\gamma(\kappa''|\mathbf{q}, j\lambda), \end{aligned}$$

which can be recast as

$$\begin{aligned} & \sum_{\bar{\beta}' \bar{\kappa}'} \left[\mathbf{D}^* \left(\begin{array}{c} \mathbf{q} \\ \bar{\beta}' \bar{\kappa}', \bar{\beta} \bar{\kappa} \end{array} \right) \cdot {}^{(\mathbf{q},j)}\Gamma_{\alpha\kappa, \bar{\beta}\bar{\kappa}}(S) \right]_{\bar{\beta}' \bar{\kappa}', \alpha\kappa} e_{\bar{\beta}'}(\bar{\kappa}'|\mathbf{q}, j\lambda) \\ &= \sum_{\gamma\kappa''} \left[{}^{(\mathbf{q},j)}\Gamma_{\beta\kappa', \gamma\kappa''}(S) \cdot \mathbf{D}^* \left(\begin{array}{c} \mathbf{q} \\ \beta\kappa' \alpha\kappa \end{array} \right) \right]_{\gamma\kappa'', \alpha\kappa} e_{\gamma}(\kappa''|\mathbf{q}, j\lambda). \end{aligned}$$

Matching the summation indices on both sides demonstrates that this relation is derived from the commutation

$$\mathbf{D}(\mathbf{q}) {}^{(\mathbf{q},j)}\Gamma(S) = {}^{(\mathbf{q},j)}\Gamma(S) \mathbf{D}(\mathbf{q}), \quad \forall S \in \mathbb{G}(\mathbf{q}). \quad (15.101)$$

Since the dynamical matrix is not a scalar, ${}^{(\mathbf{q},j)}\Gamma$ must be reducible according to Schur's lemma.

Relation between the Irreps ${}^{(\mathbf{q}\sigma)}\Gamma$ of $\mathbb{G}_{\mathbf{q}}$ and ${}^{(\mathbf{q},j)}\Gamma$

We write the reduction of ${}^{(\mathbf{q},j)}\Gamma$ as a CG series in the Irreps ${}^{(\mathbf{q}\sigma)}\Gamma$ of $\mathbb{G}_{\mathbf{q}}$ as

$${}^{(\mathbf{q},j)}\Gamma = \sum_{\sigma} \langle \mathbf{q}j|\sigma \rangle {}^{(\mathbf{q}\sigma)}\Gamma. \quad (15.102)$$

This allows us to relabel the eigenvectors and write (15.100) as

$$\mathbf{D}(\mathbf{q}) S \epsilon(\mathbf{q}, \sigma\ell) = \omega^2(\mathbf{q}, \sigma) S \epsilon(\mathbf{q}, \sigma\ell) \quad (15.103)$$

where $\ell = 1, \dots, d_{\sigma}$. Exhausting all the elements $S \in \mathbb{G}_{\mathbf{q}}$ will produce a subset of d_{σ} eigenvectors of $\mathbf{D}(\mathbf{q})$ that are degenerate and complete with respect to the symmetry of $\mathbb{G}_{\mathbf{q}}$. This completeness allows us to construct a Rep of $\mathbb{G}_{\mathbf{q}}$ of dimension d_{σ} as

$$S \epsilon(\mathbf{q}, \sigma\ell) = \sum_{m=1}^{d_{\sigma}} {}^{(\mathbf{q}\sigma)}\Gamma_{m\ell}(S) \epsilon(\mathbf{q}, \sigma m).$$

We determine the matrix elements ${}^{(\mathbf{q}\sigma)}\Gamma_{m\ell}(S)$ by considering the action of S on the $(\alpha\kappa)$ component of $\epsilon(\mathbf{q}, \sigma\ell)$, namely,

$$\begin{aligned} S \epsilon_{\alpha}(\kappa|\mathbf{q}, \sigma\ell) &= \sum_{m=1}^{d_{\sigma}} {}^{(\mathbf{q}\sigma)}\Gamma_{m\ell}(S) \epsilon_{\alpha}(\kappa|\mathbf{q}, \sigma m) \\ &= \sum_{\beta\kappa'} {}^{(\nu)}\Gamma_{\alpha\beta}(S) e^{i\mathbf{q} \cdot \mathbf{t}[\kappa, S]} \epsilon_{\beta}(\kappa'|\mathbf{q}\sigma\ell) \delta(\hat{S}\kappa, \kappa'), \end{aligned} \quad (15.104)$$

where the last line of (15.104) was obtained with the aid of (15.91). Multiplying the two left-sides of (15.104) by $\epsilon_{\alpha}^*(\kappa|\mathbf{q}, \sigma m)$, summing over $(\alpha\kappa)$ and using the orthogonality relation (15.88), we obtain

$${}^{(\mathbf{q}\sigma)}\Gamma_{m\ell}(S) = \sum_{\alpha\beta, \kappa\kappa'} \epsilon_{\alpha}^*(\kappa|\mathbf{q}, \sigma m) {}^{(\nu)}\Gamma_{\alpha\beta}(S) e^{i\mathbf{q} \cdot \mathbf{t}[\kappa, S]} \delta(\hat{S}\kappa, \kappa') \epsilon_{\beta}(\kappa'|\mathbf{q}\sigma\ell). \quad (15.105)$$

Notice that the vector $\epsilon_\alpha(\mathbf{q}, \sigma\ell)$ is a $3r$ of the form

$$\epsilon_\alpha(\kappa|\mathbf{q}, \sigma\ell) = [\epsilon_\alpha(\kappa|\mathbf{q}, \sigma_1 1), \epsilon_\alpha(\kappa|\mathbf{q}, \sigma_1 2), \dots, \epsilon_\alpha(\kappa|\mathbf{q}, \sigma_1 d_{\sigma_1}), \dots, \epsilon_\alpha(\kappa|\mathbf{q}, \sigma_n d_{\sigma_n}), \dots]$$

and the action of S merely permutes the entries within each Irrep σ_i .

Normal coordinates

The lattice displacements $u_\alpha(l\kappa)$ may now be expanded in terms of the eigenvectors of the dynamical matrix as

$$u_\alpha(l\kappa) = \frac{1}{\sqrt{NM_\kappa}} \sum_{j\lambda, \mathbf{q}} e_\alpha(j\lambda|\mathbf{q}) Q_{j\lambda}(\mathbf{q}, t) e^{i\mathbf{q} \cdot \mathbf{R}_l}. \quad (15.106)$$

The reality of $u_\alpha(l\kappa)$ requires

$$Q_{j\lambda}^*(\mathbf{q}, t) = Q_{j\lambda}(-\mathbf{q}, t). \quad (15.107)$$

Particular symmetries of the dynamical matrix

As we have demonstrated in Section 15.2.2, the invariance of the potential energy $\mathcal{V}$ under the operations of the symmetry group of a system, here $\mathbb{S}$, leads to similar invariance of the force constant matrix Φ , and the modified force constant matrix $\mathfrak{D}$. These arguments carry over to the case of solids. Thus, we may write for a space-group operation $S = (R | \mathbf{t}(m) + \boldsymbol{\tau}) \in \mathbb{S}$ that

$$\mathfrak{D} = \tilde{S} \mathfrak{D} S, \quad (15.108)$$

where

$$\begin{aligned} \tilde{S} \mathfrak{D} \begin{pmatrix} l & l' \\ \kappa & \kappa' \end{pmatrix} S &= \mathfrak{D} \begin{pmatrix} l_S & l'_S \\ \kappa_S & \kappa'_S \end{pmatrix}, \\ S(\mathbf{t}(l) + \mathbf{r}_\kappa) &= R^{-1} [\mathbf{t}(l) - \mathbf{t}(m) + \mathbf{r}_\kappa - \boldsymbol{\tau}] \\ &= \mathbf{t}(l_S) + \mathbf{r}_{\kappa_S}, \quad \kappa_S \sim \kappa. \end{aligned} \quad (15.109)$$

Summary

(i) $\mathbf{D}(\mathbf{q})$ is Hermitian,

$$D_{\beta\alpha}(\kappa'\kappa|\mathbf{q}) = D_{\alpha\beta}^*(\kappa\kappa'|\mathbf{q}).$$

(ii) $\mathbf{D}(\mathbf{q})$ is periodic in the reciprocal lattice,

$$D_{\alpha\beta}(\kappa\kappa'|\mathbf{q} + \mathbf{G}) = D_{\alpha\beta}(\kappa\kappa'|\mathbf{q}).$$

If the point-group of the space-group contains the inversion operation, the following simplifications arise:

- (a) If every atom is at an inversion center, $\mathbf{D}(\mathbf{q})$ can be cast as a real symmetric matrix with real eigenvectors, with the aid of the transformation

$$\begin{aligned} C_{\alpha\beta}(\kappa\kappa'|\mathbf{q}) &= \exp[-i\mathbf{q} \cdot (\boldsymbol{\kappa} - \boldsymbol{\kappa}')] D_{\alpha\beta}(\kappa\kappa'|\mathbf{q}), \\ e_{\alpha}(\kappa|\mathbf{q}j) &= \exp[-i\mathbf{q} \cdot \boldsymbol{\kappa}] u_{\alpha}(\kappa|\mathbf{q}j). \end{aligned}$$

The real form of $\mathbf{C}(\mathbf{q})$ is very convenient from a computation view-point. If we wish to keep the Hermitian form of $\mathbf{D}(\mathbf{q})$ we may still apply the following simplifications

$$\begin{aligned} D_{\alpha\beta}^*(\kappa\kappa|\mathbf{q}) &= D_{\alpha\beta}(\kappa\kappa|\mathbf{q}), \\ D_{\beta\alpha}(\kappa'\kappa|\mathbf{q}) &= \exp[-i\mathbf{q} \cdot (\mathbf{r}_{\kappa} - \mathbf{r}_{\kappa'})] D_{\alpha\beta}(\kappa\kappa'|\mathbf{q}). \end{aligned}$$

- (b) When only some of the atoms are located at centers of inversion, then the above simplifications apply to the corresponding values of κ and κ' .
 (c) If two atoms are interchanged by the inversion operation $S_I = (I|\boldsymbol{\tau} + \mathbf{t})$, then

$$D_{\alpha\beta}(S_I(\kappa)S_I(\kappa)|\mathbf{q}) = D_{\beta\alpha}(\kappa\kappa|\mathbf{q})$$

and

$$D_{\alpha\beta}(S_I(\kappa)\kappa|\mathbf{q}) = D_{\alpha\beta}^*(\kappa S_I(\kappa)|\mathbf{q}) = D_{\beta\alpha}(S_I(\kappa)\kappa|\mathbf{q}).$$

- (iii) A relation between the matrix elements of $\mathbf{D}$ at equivalent wavevectors, $\mathbf{q}$ and $R\mathbf{q}$, can be established, using (15.92), as

$$\begin{aligned} D_{\alpha\beta}(\bar{\kappa}\bar{\kappa}'|R\mathbf{q}) &= \exp[iR\mathbf{q} \cdot (\boldsymbol{\kappa} - S\bar{\boldsymbol{\kappa}} - \boldsymbol{\kappa}' - S\bar{\boldsymbol{\kappa}}')] \\ &\times \sum_{\gamma\delta} R_{\alpha\gamma} R_{\beta\delta} D_{\gamma\delta}(\kappa\kappa'|\mathbf{q}), \end{aligned} \quad (15.110)$$

where $\bar{\kappa} = S^{-1}\boldsymbol{\kappa} \bmod \mathbf{t}$.

- (iv) The form of the force constant matrices $\Phi(l\kappa; l'\kappa')$, which enter in the construction of $\mathbf{D}(\mathbf{q})$, can be determined using the group of the bond discussed earlier. These matrices may be associated with first, second, and higher neighbor interactions. The general relations used to obtain the simplified forms of the force constant matrices are

$$\begin{aligned} \Phi_{\alpha\beta}(S(l\kappa); S(l'\kappa')) &= \sum_{\gamma\delta} S_{\alpha\gamma} S_{\beta\delta} \Phi_{\gamma\delta}(l\kappa; l'\kappa'), \\ \Phi_{\beta\alpha}(l'\kappa'; l\kappa) &= \Phi_{\alpha\beta}(l\kappa; l'\kappa'). \end{aligned}$$

15.3.3 Displacement tensor field and its symmetry decomposition

We are concerned here with a system possessing the symmetry of a space-group $\mathbb{S}$. We presented in Section 13.4 the method of decomposition of tensor fields and their tensor field Reps into Irreps of $\mathbb{S}$. This method is summarized as follows:

- (i) The system is decomposed into simple crystals; each can be identified in terms of a Wyckoff position (ρ) and its associated subgroup $\mathbb{H}_\rho(\mathbf{r})$. $\mathbb{H}_\rho(\mathbf{r})$ comprises elements $(R|\boldsymbol{\tau} + \mathbf{t})\mathbf{r}_\rho = \mathbf{r}_\rho$, and is isomorphic to the point-group $\mathbb{P}_\rho$.
- (ii) The permutation Rep, $^{(\text{Perm})}\Gamma_\rho(\mathbf{r})$, for each of the constituent simple crystals is constructed. $^{(\text{Perm})}\Gamma_\rho(\mathbf{r})$ is just the ground Rep of $\mathbb{S}$ with respect to $\mathbb{H}_\rho(\mathbf{r})$.
- (iii) The complete tensor field Rep is then given by

$$\mathfrak{F} = \sum_{\rho} \mathfrak{F}_{\rho} = \sum_{\rho}^{\oplus} {}^{(\text{Perm})}\Gamma_{\rho}(\mathbf{r}) \otimes {}^{\mathcal{T}}\Gamma, \quad (15.111)$$

where ${}^{\mathcal{T}}\Gamma$ is the Rep of the physical tensor under investigation. Here, ${}^{\mathcal{T}}\Gamma = {}^{(\nu)}\Gamma$, the polar-vector Rep of atomic displacements.

- (iv) The reduction of each $\mathfrak{F}_{\rho}$ in terms of the space-group Irreps $^{(*\mathbf{q},\mu)}\Gamma$ was described in Section 13.4.2, where we found that

$$\begin{aligned} \mathfrak{F}_{\rho}(\mathbf{r}) &= \sum_{*\mathbf{q},\mu}^{\oplus} \langle \mathfrak{F}_{\rho}(\mathbf{r}) | *\mathbf{q},\mu \rangle {}^{(*\mathbf{q}',\nu)}\Gamma, \\ \langle \mathfrak{F}_{\rho}(\mathbf{r}) | *\mathbf{q},\mu \rangle &= \sum_{(\mathbf{q}',\nu)} \langle {}^{(\text{Perm})}\Gamma_{\rho}(\mathbf{r}) | *\mathbf{q}',\nu \rangle \\ &\quad \times \langle {}^{(*\mathbf{q}',\nu)}\Gamma \otimes \Gamma^{\mathcal{T}} | *\mathbf{q},\mu \rangle. \end{aligned} \quad (15.112)$$

For tensor fields belonging to $\mathbf{q} = \mathbf{0}$, such as $^{(\nu)}\Gamma$, we have

$$\begin{aligned} \langle \mathfrak{F}_{\rho}(\mathbf{r}) | *\mathbf{q},\mu \rangle &= \sum_{\nu} \langle {}^{(\text{Perm})}\Gamma_{\rho}(\mathbf{r}) | *\mathbf{q},\nu \rangle \\ &\quad \times \langle {}^{(*\mathbf{q},\nu)}\Gamma \otimes {}^{(\nu)}\Gamma | *\mathbf{q},\mu \rangle. \end{aligned} \quad (15.113)$$

- (v) Complete reduction of the tensor field Rep is then obtained by substituting (15.112) and (15.113) back into (15.111).

Construction of symmetry-adapted displacements

One of the important applications of the tensor field Rep is in the construction of symmetry projection operators associated with the dynamical space of the system. These symmetry projection operators, when applied to a displacement vector of the constituent atoms, produce symmetry-adapted displacement vectors that transform according to Irreps of the space-group $\mathbb{S}$ of the system. In turn, the complete set of symmetry coordinates, or displacements, forms a unitary transformation that block-diagonalizes the corresponding dynamical matrix into submatrices, each transforms according to a specific row of a specific Irrep.

According to (6.12) and (6.14), we may write the Wigner and Irrep projection operators associated with the μ -Irrep as

$$\begin{aligned} {}^{(\mu)}\hat{P}_{ii} &= \frac{d_\mu}{g} \sum_R {}^{(\mu)}\Gamma_{ii}^{-1}(R) \mathfrak{F}(R), \\ {}^{(\mu)}P &= \frac{d_\mu}{g} \sum_{R \in \mathcal{G}} {}^{(\mu)}\chi(R) \mathfrak{F}(R), \end{aligned} \tag{15.114}$$

where we substituted $\mathfrak{F}(R)$ for $\hat{R}$.

Example 15.8

Symmetry-adapted lattice vibrations in TiO_2

Titanium dioxide, TiO_2 , has the rutile structure, with space-group $\mathbb{S} = P \frac{4_2}{mnm} (\mathbb{D}_{4h}^{14})$, or the detailed notation $P \frac{4_2}{m} \frac{2_1}{n} \frac{2}{m}$. The system consists of two simple crystals:

- (i) A simple crystal of Ti atoms at the 2(a) Wyckoff positions,
 $\mathbf{r}_1 = (0, 0, 0)$, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, with site-symmetry $\mathcal{D}_{2h}^{(z,xy,\bar{x}y)}$, and coset expansion
 $\mathcal{D}_{4h} = (E + C_4) \mathcal{D}_{2h}^{(z,xy,\bar{x}y)}.$

The permutation Rep induced from $\mathcal{D}_{2h}^{(z,xy,\bar{x}y)}$,

$${}^{(\text{perm})}\Gamma_1 = {}^{(1)}\Gamma \left(\mathcal{D}_{2h}^{(z,xy,\bar{x}y)} \right) \uparrow \mathcal{D}_{4h},$$

is simply the corresponding 2×2 ground Rep, namely,

$${}^{(\text{perm})}\Gamma_{\text{Ti}} \left(E, C_2^{(z)}, I, \sigma_h, C_2^{(xy)}, C_2^{(\bar{x}y)}, \sigma_{xy}, \sigma_{\bar{x}y} \right) = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix},$$

while the remaining elements of $\mathcal{D}_{4h}$ are represented by

$${}^{(\text{perm})}\Gamma_{\text{Ti}} \left(C_4, C_4^3, S_4, S_4^3, C_2^{(x)}, C_2^{(y)}, \sigma_x, \sigma_y \right) = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}.$$

The corresponding tensor field Rep is of dimension 6, where the representative matrix of operator R is obtained by replacing each entry of 1 in $^{(\text{perm})}\Gamma_{\text{Ti}}(R)$ by $^{(\text{v})}\Gamma(R)$.

- (ii) A simple crystal of O atoms at the 4(f) Wyckoff positions, $\mathbf{r}_2 = (x, x, 0)$, $(-x, -x, 0)$, $(\frac{1}{2} + x, \frac{1}{2} - x, \frac{1}{2})$, $(\frac{1}{2} - x, \frac{1}{2} + x, \frac{1}{2})$, with site-symmetry $\mathcal{C}_{2v}^{(\bar{x}y)}$, and coset expansion

$$\mathcal{D}_{4h} = (E + I + C_4 + C_2^{(x)})\mathcal{C}_{2v}^{(\bar{x}y)}.$$

The construction of the second induced Rep

$$^{(\text{perm})}\Gamma_2 = {}^{(1)}\Gamma\left(\mathcal{C}_{2v}^{(\bar{x}y)}\right) \uparrow \mathcal{D}_{4h}$$

is slightly more involved, although it is also derived with the aid of the ground Rep. We find that

$$^{(\text{perm})}\Gamma_{\text{O}}\left(\begin{matrix} E \\ \sigma_h \end{matrix}\right) = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}, \quad ^{(\text{perm})}\Gamma_{\text{O}}\left(\begin{matrix} C_2^{(z)} \\ I \end{matrix}\right) = \begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix},$$

$$^{(\text{perm})}\Gamma_{\text{O}}\left(\begin{matrix} C_2^{(xy)} \\ \sigma_{\bar{x}y} \end{matrix}\right) = \begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}, \quad ^{(\text{perm})}\Gamma_{\text{O}}\left(\begin{matrix} C_2^{(\bar{x}y)} \\ \sigma_{xy} \end{matrix}\right) = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix},$$

$$^{(\text{perm})}\Gamma_{\text{O}}\left(\begin{matrix} C_4 \\ S_4^3 \end{matrix}\right) = \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix}, \quad ^{(\text{perm})}\Gamma_{\text{O}}\left(\begin{matrix} C_4^3 \\ S_4 \end{matrix}\right) = \begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix},$$

$$^{(\text{perm})}\Gamma_{\text{O}}\left(\begin{matrix} C_2^{(x)} \\ \sigma_y \end{matrix}\right) = \begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix}, \quad ^{(\text{perm})}\Gamma_{\text{O}}\left(\begin{matrix} C_2^{(y)} \\ \sigma_x \end{matrix}\right) = \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}.$$

Here, the corresponding tensor field Rep is of dimension 12. The representative matrix of operator R is obtained by replacing each entry of 1 in $^{(\text{perm})}\Gamma_{\text{O}}(R)$ by $^{(\text{v})}\Gamma(R)$.

Table 15.1. *Irreps of $\mathcal{D}_{4h}$.*

		E	U	C_2	C_4	U^d	I	σ	σ_h	S_4	σ_d
A_{1g}	Γ_1^+	1	1	1	1	1	1	1	1	1	1
B_{1g}	Γ_2^+	1	1	1	-1	-1	1	1	1	-1	-1
A_{2g}	Γ_3^+	1	-1	1	1	-1	1	-1	1	1	-1
B_{2g}	Γ_4^+	1	-1	1	-1	1	1	-1	1	-1	1
E_g	Γ_5^+	2	0	-2	0	0	2	0	-2	0	0
A_{1u}	Γ_1^-	1	1	1	1	1	-1	-1	-1	-1	-1
B_{1u}	Γ_2^-	1	1	1	-1	-1	-1	-1	-1	1	1
A_{2u}	Γ_3^-	1	-1	1	1	-1	-1	1	-1	-1	1
B_{2u}	Γ_4^-	1	-1	1	-1	1	-1	1	-1	1	-1
E_u	Γ_5^-	2	0	-2	0	0	-2	0	2	0	0
	$(\text{perm})\Gamma_{Ti}$	2	0	2	0	2	2	0	2	0	2
	$(\text{perm})\Gamma_O$	4	0	0	0	2	0	0	4	0	2
	$(v)\Gamma$	3	-1	-1	1	-1	-3	1	1	-1	1
	$(a)\Gamma$	3	-1	-1	1	-1	3	-1	-1	1	-1

At the Γ -point, the group of the wavevector is $\mathcal{D}_{4h}$, its Irreps are given in Table 15.1. In this table we also list the characters of $(\text{perm})\Gamma_{Ti}$, $(\text{perm})\Gamma_O$, $(v)\Gamma$, and $(a)\Gamma$. We obtain the following decompositions

$$\begin{aligned}
 (\text{perm})\Gamma_{Ti} &= \Gamma_1^+ + \Gamma_4^+, \\
 (\text{perm})\Gamma_O &= \Gamma_1^+ + \Gamma_4^+ + \Gamma_5^-, \\
 (v)\Gamma &= \Gamma_3^- + \Gamma_5^-, \\
 (a)\Gamma &= \Gamma_3^+ + \Gamma_5^+.
 \end{aligned}$$

With the aid of Tables 15.1 and 15.2, and (15.113), we get

$$\begin{aligned}
 \langle \mathfrak{F}_{Ti} \mid \mathbf{0}\mu \rangle &= \langle (1+) \otimes (3-) \mid \mathbf{0}\mu \rangle + \langle (4+) \otimes (3-) \mid \mathbf{0}\mu \rangle \\
 &\quad + \langle (1+) \otimes (5-) \mid \mathbf{0}\mu \rangle + \langle (4+) \otimes (5-) \mid \mathbf{0}\mu \rangle \\
 &= \langle (3-) \mid \mathbf{0}\mu \rangle + \langle (2-) \mid \mathbf{0}\mu \rangle + 2 \langle (5-) \mid \mathbf{0}\mu \rangle,
 \end{aligned}$$

Table 15.2. *Decomposition of direct-outer-products of $\mathcal{D}_{4h}$ Irreps.*

	Γ_1^+	Γ_2^+	Γ_3^+	Γ_4^+	Γ_5^+	Γ_1^-	Γ_2^-	Γ_3^-	Γ_4^-	Γ_5^-
	Γ_1^+	Γ_2^+	Γ_3^+	Γ_4^+	Γ_5^+	Γ_1^-	Γ_2^-	Γ_3^-	Γ_4^-	Γ_5^-
Γ_2^+	Γ_2^+	Γ_1^+	Γ_4^+	Γ_3^+	Γ_5^+	Γ_2^-	Γ_1^-	Γ_4^-	Γ_3^-	Γ_5^-
Γ_3^+	Γ_3^+	Γ_4^+	Γ_1^+	Γ_2^+	Γ_5^+	Γ_3^-	Γ_4^-	Γ_1^-	Γ_2^-	Γ_5^-
Γ_4^+	Γ_4^+	Γ_3^+	Γ_2^+	Γ_1^+	Γ_5^+	Γ_4^-	Γ_3^-	Γ_2^-	Γ_1^-	Γ_5^-
Γ_5^+	Γ_5^+	Γ_5^+	Γ_5^+	Γ_5^+	$(\Gamma_1^+ + \Gamma_2^+ + \Gamma_3^+ + \Gamma_4^+)$	Γ_5^-	Γ_5^-	Γ_5^-	Γ_5^-	$(\Gamma_1^- + \Gamma_2^- + \Gamma_3^- + \Gamma_4^-)$
Γ_1^-	Γ_1^-	Γ_2^-	Γ_3^-	Γ_4^-	Γ_5^-	Γ_1^+	Γ_2^+	Γ_3^+	Γ_4^+	Γ_5^+
Γ_2^-	Γ_2^-	Γ_1^-	Γ_4^-	Γ_3^-	Γ_5^-	Γ_2^+	Γ_1^+	Γ_4^+	Γ_3^+	Γ_5^+
Γ_3^-	Γ_3^-	Γ_4^-	Γ_1^-	Γ_2^-	Γ_5^-	Γ_3^+	Γ_4^+	Γ_1^+	Γ_2^+	Γ_5^+
Γ_4^-	Γ_4^-	Γ_3^-	Γ_2^-	Γ_1^-	Γ_5^-	Γ_4^+	Γ_3^+	Γ_2^+	Γ_1^+	Γ_5^+
Γ_5^-	Γ_5^-	Γ_5^-	Γ_5^-	Γ_5^-	$(\Gamma_1^- + \Gamma_2^- + \Gamma_3^- + \Gamma_4^-)$	Γ_5^+	Γ_5^+	Γ_5^+	Γ_5^+	$(\Gamma_1^+ + \Gamma_2^+ + \Gamma_3^+ + \Gamma_4^+)$

and

$$\begin{aligned}
 \langle \mathfrak{F}_O \mid \mathbf{0}\mu \rangle &= \langle (1+) \otimes (3-) \mid \mathbf{0}\mu \rangle + \langle (4+) \otimes (3-) \mid \mathbf{0}\mu \rangle + \langle (5-) \otimes (3-) \mid \mathbf{0}\mu \rangle \\
 &\quad + \langle (1+) \otimes (5-) \mid \mathbf{0}\mu \rangle + \langle (4+) \otimes (5-) \mid \mathbf{0}\mu \rangle + \langle (5-) \otimes (5-) \mid \mathbf{0}\mu \rangle \\
 &= \langle (3-) \mid \mathbf{0}\mu \rangle + \langle (2-) \mid \mathbf{0}\mu \rangle + \langle (5+) \mid \mathbf{0}\mu \rangle + 2 \langle (5-) \mid \mathbf{0}\mu \rangle \\
 &\quad + \langle (1+) \mid \mathbf{0}\mu \rangle + \langle (2+) \mid \mathbf{0}\mu \rangle + \langle (3+) \mid \mathbf{0}\mu \rangle + \langle (4+) \mid \mathbf{0}\mu \rangle,
 \end{aligned}$$

The final decomposition is

$$\begin{aligned}
 \mathfrak{F}_{Ti} &= \Gamma_2^- + \Gamma_3^- + 2\Gamma_5^-, \\
 \mathfrak{F}_O &= \Gamma_1^+ + \Gamma_2^+ + \Gamma_3^+ + \Gamma_4^+ + \Gamma_5^+ + \Gamma_2^- + \Gamma_3^- + 2\Gamma_5^-, \\
 \mathfrak{F}_{TiO_2} &= \mathfrak{F}_{Ti} \oplus \mathfrak{F}_O \\
 &= \Gamma_1^+ + \Gamma_2^+ + \Gamma_3^+ + \Gamma_4^+ + \Gamma_5^+ + 2\Gamma_2^- + 2\Gamma_3^- + 4\Gamma_5^-.
 \end{aligned}$$

The symmetry-adapted normal mode vectors are obtained after eliminating the translation and rotation modes with the aid of the decompositions of $^{(v)}\Gamma$ and $^{(a)}\Gamma$, namely,

$$\Gamma_1^+ + \Gamma_2^+ + \Gamma_4^+ + 2\Gamma_2^- + \Gamma_3^- + 3\Gamma_5^-.$$

Example 15.9

CsCl structure

The CsCl structure belongs to the simple cubic lattice system, and has the symmetry of the symmorphic space-group $Pm\bar{3}m$ ($\mathcal{O}_h^1$), with the point-group $\mathcal{O}_h \equiv m\bar{3}m$. It is decomposable into two simple crystals, with Wyckoff positions (a) $\rightarrow \mathbf{r}_{\text{Cs}} = (0, 0, 0)$ and (b) $\rightarrow \mathbf{r}_{\text{Cl}} = (1/2, 1/2, 1/2)$, both invariant under point-group $m\bar{3}m$.

Consequently, both $^{(\text{perm})}\Gamma$ s are just the invariant Irrep of dimension 1, and the tensor field Rep can be written as

$$\mathfrak{F} = {}^{(\text{v})}\Gamma \oplus {}^{(\text{v})}\Gamma = {}^{(\text{v})}\Gamma \times \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}.$$

q-independent symmetries of $\mathbf{D}$ Since both atomic sites are centers of inversion, we choose to use the $\mathbf{C}$ matrix. The direct-sum form of the tensor field gives $\kappa \rightarrow \kappa$ and $\kappa' \rightarrow \kappa'$, and we write the modified form of (15.110) as

$$C_{\alpha\beta}(\kappa\kappa'|R\mathbf{q}) = \sum_{\gamma\delta} R_{\alpha\gamma} R_{\beta\delta} C_{\gamma\delta}(\kappa\kappa'|\mathbf{q}).$$

Using the operation $C_3^{(xyz)} = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}$, we obtain the following relations among the elements of $\mathbf{D}$, which are $\mathbf{q}$ -independent:

$$\begin{aligned} C_{22}(\kappa\kappa'|q_1, q_2, q_3) &= C_{33}(\kappa\kappa'|q_3, q_1, q_2), & C_{33}(\kappa\kappa'|q_1, q_2, q_3) &= C_{11}(\kappa\kappa'|q_3, q_1, q_2), \\ C_{23}(\kappa\kappa'|q_1, q_2, q_3) &= C_{31}(\kappa\kappa'|q_3, q_1, q_2), & C_{31}(\kappa\kappa'|q_1, q_2, q_3) &= C_{12}(\kappa\kappa'|q_3, q_1, q_2), \\ C_{13}(\kappa\kappa'|q_1, q_2, q_3) &= C_{21}(\kappa\kappa'|q_3, q_1, q_2), & C_{32}(\kappa\kappa'|q_1, q_2, q_3) &= C_{13}(\kappa\kappa'|q_3, q_1, q_2). \end{aligned}$$

One additional independent relation may be obtained using $U^{(x\bar{y})}$:

$$C_{21}(\kappa\kappa'|q_1, q_2, q_3) = C_{12}(\kappa\kappa'|q_2, q_1, q_3).$$

The remaining operations give no new information. The above relations are sufficient to show that there are only two independent terms, which we may choose as $C_{11}(\kappa\kappa'|\mathbf{q})$ and $C_{12}(\kappa\kappa'|\mathbf{q})$. For given values of κ and κ' , the remaining seven components can be expressed in terms of $C_{11}(\kappa\kappa'|\mathbf{q})$ and $C_{12}(\kappa\kappa'|\mathbf{q})$ by cyclic permutations and interchanges of the $\mathbf{q}$ -components, as

$$\begin{aligned} C_{22}(\kappa\kappa'|\mathbf{q}) &= C_{11}(\kappa\kappa'|q_2, q_3, q_1), & C_{33}(\kappa\kappa'|\mathbf{q}) &= C_{11}(\kappa\kappa'|q_3, q_1, q_2), \\ C_{23}(\kappa\kappa'|\mathbf{q}) &= C_{12}(\kappa\kappa'|q_2, q_3, q_1), & C_{31}(\kappa\kappa'|\mathbf{q}) &= C_{12}(\kappa\kappa'|q_3, q_1, q_2), \\ C_{13}(\kappa\kappa'|\mathbf{q}) &= C_{12}(\kappa\kappa'|q_1, q_3, q_2), & C_{32}(\kappa\kappa'|\mathbf{q}) &= C_{12}(\kappa\kappa'|q_3, q_2, q_1). \\ C_{21}(\kappa\kappa'|\mathbf{q}) &= C_{12}(\kappa\kappa'|q_2, q_1, q_3), & & \end{aligned} \tag{15.115}$$

These relations apply also to the real dynamical matrix $\mathbf{C}(\mathbf{q})$. We also use the hermiticity (symmetry) of $\mathbf{D}$ ($\mathbf{C}$) to obtain the relations

$$\begin{aligned} C_{11}(21|\mathbf{q}) &= C_{11}^*(12|\mathbf{q}), & C_{11}(21|\mathbf{q}) &= C_{11}(21|\mathbf{q}), \\ C_{12}(21|\mathbf{q}) &= C_{12}^*(21|\mathbf{q}), & C_{11}(21|\mathbf{q}) &= C_{11}(21|\mathbf{q}). \end{aligned}$$

Thus, these relations leave, in all, six independent terms in either $\mathbf{D}$ or $\mathbf{C}$.

Symmetries of Φ First, we consider the nearest-neighbor (nn) Φ , namely $\Phi \begin{pmatrix} 000 & 000 \\ 1 & 2 \end{pmatrix}$, which has the general form

$$\Phi \begin{pmatrix} 000 & 000 \\ 1 & 2 \end{pmatrix} = - \begin{pmatrix} \alpha & \beta & \gamma \\ \delta & \epsilon & \zeta \\ \eta & \theta & \iota \end{pmatrix}.$$

The group of the bond is $3m = \{E, C_3^{(xyz)}, C_3^{(\bar{x}\bar{y}\bar{z})}, U^{(x\bar{y})}, U^{(\bar{x}z)}, U^{(y\bar{z})}\}$. $C_3^{(xyz)}$ yields the relations

$$\alpha = \epsilon = \iota, \quad \eta = \zeta = \beta, \quad \theta = \delta = \gamma;$$

while $U^{(x\bar{y})}$ gives

$$\epsilon = \alpha, \quad \zeta = \beta, \quad \delta = \gamma, \quad \eta = \theta.$$

These relations lead to

$$\Phi \begin{pmatrix} 000 & 000 \\ 1 & 2 \end{pmatrix} = - \begin{pmatrix} \alpha & \beta & \beta \\ \beta & \alpha & \beta \\ \beta & \beta & \alpha \end{pmatrix} = \Phi \begin{pmatrix} 000 & 000 \\ 2 & 1 \end{pmatrix},$$

where we used the flipping operator symmetry to obtain the right-side. The force constant matrices of the remaining seven nn bonds are obtained with the aid of the coset representative of $\mathcal{O}_h$ in $3m$.

There are six second nn, with a typical Φ given, in general, by

$$\Phi \begin{pmatrix} 000 & 100 \\ 1 & 1 \end{pmatrix} = - \begin{pmatrix} \lambda & \mu & \nu \\ \sigma & \rho & \xi \\ \tau & v & \phi \end{pmatrix}.$$

The point-group of the bond is $4mm$. The operation $C_4^{(x)} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}$ exhausts all possible relations, giving

$$\mu = \nu = \sigma = \tau = \xi = v = 0, \quad \phi = \rho.$$

Table 15.3. *Symmetries of the simple cubic Brillouin zone.*

q -vector ($a_0\mathbf{q}/\pi$)	BSW notation	$G_{\mathbf{q}}$	Principal axis	Equivalent points	Star of $\mathbf{q}$
$(q, q, 0)$	Σ	$mm2$	$[110]$	$(q, q, 0)$	$(\pm q, \pm q, 0), (\pm q, 0, \pm q), (0, \pm q, \pm q)$
$(1, q, q,)$	S	$mm2$	$[011]$	$(\pm 1, q, q)$	$(1, \pm q, \pm q), (\pm q, 1, \pm q), (\pm q, \pm q, 1)$
$(1, q, 0)$	Z	$mm2$	$[010]$	$(\pm 1, q, 0)$	$(0, \pm q, 1), (1, 0, \pm q), (0, 1, \pm q)$
(q, q, q)	Λ	$3m$	$[111]$	(q, q, q)	$(\pm q, \pm q, \pm q)$
$(1, 1, q)$	T	$4mm$	$[001]$	$(\pm 1, \pm 1, q)$	$(1, 1, \pm q), (1, \pm q, 1), (\pm q, 1, 1)$
$(q, 0, 0)$	Δ	$4mm$	$[100]$	$(q, 0, 0)$	$(\pm q, 0, 0), (0, \pm q, 0), (0, 0, \pm q)$
$(1, 0, 0)$	X	$4/mmm$	$[100]$	$(\pm 1, 0, 0)$	$(1, 0, 0), (0, 1, 0), (0, 0, 1)$
$(1, 1, 0)$	M	$4/mmm$	$[001]$	$(\pm 1, \pm 1, 0)$	$(1, 1, 0), (0, 1, 0), (0, 1, 1)$
$(1, 1, 1)$	R	$m3m$	$[111]$	$(\pm 1, \pm 1, \pm 1)$	$(1, 1, 1)$
$(0, 0, 0)$	Γ	$m3m$	$[000]$	$(0, 0, 0)$	$(0, 0, 0)$

Thus, we have

$$\Phi \begin{pmatrix} 000 & 100 \\ 1 & 1 \end{pmatrix} = - \begin{pmatrix} \lambda & 0 & 0 \\ 0 & \rho & 0 \\ 0 & 0 & \rho \end{pmatrix} = \Phi \begin{pmatrix} 100 & 000 \\ 1 & 1 \end{pmatrix} = \Phi \begin{pmatrix} 000 & -100 \\ 1 & 1 \end{pmatrix}.$$

Again, the remaining four force constant matrices are obtained with the aid of coset representatives.

Dispersion relations at high symmetry points and directions

(i) The Γ -point, $\mathbf{q} = \mathbf{0}$

We obtain

$$\begin{aligned} C_{11}(11|\mathbf{0}) &= C_{22}(11|\mathbf{0}) = C_{33}(11|\mathbf{0}) = A = \frac{8\alpha}{M_1}, \\ C_{11}(22|\mathbf{0}) &= C_{22}(22|\mathbf{0}) = C_{33}(22|\mathbf{0}) = B = \frac{8\alpha}{M_2}, \\ C_{11}(12|\mathbf{0}) &= C_{22}(12|\mathbf{0}) = C_{33}(12|\mathbf{0}) = C = -\frac{8\alpha}{\sqrt{M_1 M_2}} = -\sqrt{AB}. \end{aligned}$$

The $m3m$ symmetry leads to the vanishing of all $C_{12}(\kappa\kappa'|\mathbf{0})$ components. The dynamical matrix at Γ becomes

$$\mathbf{D}(\mathbf{0}) = \begin{bmatrix} A & 0 & 0 & C & 0 & 0 \\ 0 & A & 0 & 0 & C & 0 \\ 0 & 0 & A & 0 & 0 & C \\ C & 0 & 0 & B & 0 & 0 \\ 0 & C & 0 & 0 & B & 0 \\ 0 & 0 & C & 0 & 0 & B \end{bmatrix}.$$

We find that $^{(\nu)}\Gamma \equiv \Gamma_{15}$ of $m3m$, and write

$$\mathfrak{F}_1, \mathfrak{F}_2 \Rightarrow \Gamma_{15}; \quad \mathfrak{F} \Rightarrow \Gamma_{15} \oplus \Gamma_{15}.$$

This decomposition indicates that the phonon modes separate into the two triply degenerate manifolds of acoustic and optic modes, respectively, each belonging to Γ_{15} . To demonstrate this result in a systematic way, we construct the projection operator

$$P_{11}^{(15)} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix},$$

and apply it to $\mathbf{D}(\mathbf{0})$ to obtain

$$P_{11}^{(15)} \mathbf{D}(\mathbf{0}) P_{11}^{(15)} = \begin{bmatrix} A & C \\ C & B \end{bmatrix},$$

with eigenvalues

$$\omega^2(\mathbf{0}, \pm) = \frac{A+B}{2} \pm \sqrt{\left(\frac{A-B}{2}\right)^2 + C^2} \Rightarrow \begin{cases} \omega(\mathbf{0}, +) = \sqrt{A+B} \text{ (optic),} \\ \omega(\mathbf{0}, -) = 0 \text{ (acoustic),} \end{cases}$$

and corresponding eigenvectors

$$\begin{aligned} \tilde{\mathbf{e}}(\mathbf{0}|(15)1-) &= \frac{1}{\sqrt{C^2 + A^2}} \begin{bmatrix} -C & 0 & 0 & A & 0 & 0 \end{bmatrix}, \\ \tilde{\mathbf{e}}(\mathbf{0}|(15)1+) &= \frac{1}{\sqrt{C^2 + B^2}} \begin{bmatrix} -C & 0 & 0 & -B & 0 & 0 \end{bmatrix}. \end{aligned}$$

It is appropriate here to note that the optic mode degeneracy is reduced due to the macroscopic electric field, which increases the frequency of the longitudinal optic mode.

The R-point, $\mathbf{q} = \frac{\pi}{a_0}(1, 1, 1)$: $\mathcal{P}_R = m3m$ With the aid of (15.94), we find that the Reps at the R-point are given by

$$\begin{aligned} {}^{(\mu)}\mathbf{R}(S) &= e^{i\mathbf{q} \cdot (\mathbf{r}_{Cs} - S\mathbf{r}_{Cs})} {}^{(\nu)}\Gamma(R) \oplus e^{i\mathbf{q} \cdot (\mathbf{r}_{Cl} - S\mathbf{r}_{Cl})} {}^{(\nu)}\Gamma(R) \\ &= {}^{(\nu)}\Gamma(R) \begin{bmatrix} 1 & 0 \\ 0 & \theta \end{bmatrix}, \end{aligned}$$

where

$$\theta = \exp[i\mathbf{q} \cdot (\mathbf{r}_{\text{Cl}} - S\mathbf{r}_{\text{Cl}})] = \begin{cases} +1 & \text{if } R \in \bar{4}3m, \\ -1 & \text{if } R \in \mathcal{I} \otimes \bar{4}3m, \end{cases}$$

which gives the decomposition

$$\mathfrak{F}_1 \Rightarrow {}^{(15)}R, \quad \mathfrak{F}_2 \Rightarrow {}^{(25')}R; \quad \mathfrak{F} \Rightarrow {}^{(15)}R \oplus {}^{(25')}R.$$

Again, (15.79) and (15.80) give

$$\begin{aligned} C_{11}(11|\mathbf{R}) &= C_{22}(11|\mathbf{R}) = C_{33}(11|\mathbf{R}) = A = -\frac{8\alpha + 2\lambda_1 + 8\rho_1}{M_1}, \\ C_{11}(22|\mathbf{R}) &= C_{22}(22|\mathbf{R}) = C_{33}(22|\mathbf{R}) = B = \frac{8\alpha + 2\lambda_2 + 8\rho_2}{M_2}, \\ C_{11}(12|\mathbf{R}) &= C_{22}(12|\mathbf{R}) = C_{33}(12|\mathbf{R}) = 0, \\ C_{12}(\kappa\kappa'|\mathbf{R}) &= 0, \quad \forall \kappa, \kappa'. \end{aligned}$$

The eigenvalues obtained are

$$\omega^2(111|(15)) = A, \quad \omega^2(111|(25')) = B.$$

The M -point, $\mathbf{q} = \frac{\pi}{a_0}(1, 1, 0)$; $\mathcal{P}_M = 4/mmm$ ($\mathcal{D}_{4h}$) Again, using (15.94) we find that

$${}^{(\mu)}M(S) = {}^{(\nu)}\Gamma(R) \begin{bmatrix} 1 & 0 \\ 0 & \theta' \end{bmatrix},$$

where

$$\theta' = \begin{cases} 1 & \text{for } E, C_2^z, \sigma^z, C_2^{xy}, C_2^{x\bar{y}}, I, \sigma^{xy}, \sigma^{x\bar{y}}, \\ -1 & \text{for } C_2^x, C_2^y, \sigma^x, \sigma^y, C_4^z, \bar{C}_4^z, S_4^z, \bar{S}_4^z, \end{cases}$$

and we obtain from table (2)

$$\begin{aligned} {}^{(\text{perm})}\Gamma_1 &= M_1^+; & {}^{(\text{perm})}\Gamma_2 &= M_4^+, \\ {}^{(\nu)}\Gamma &= M_2^- \oplus M_5^- \end{aligned}$$

where we substituted M for Γ . Next, we obtain with the aid of Table 15.2

$$\mathfrak{F} = (M_1^+ \oplus M_4^+) \otimes (M_2^- \oplus M_5^-) = 2M_2^- \oplus 2M_5^-$$

with symmetry projection operators

$$\begin{aligned} P(M_2^-) &= \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 & 0 & 0 \end{bmatrix}, \\ P_{11}(M_5^-) &= \begin{bmatrix} 0 & 0 & 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}, & P_{22}(M_5^-) &= \begin{bmatrix} 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \end{bmatrix}. \end{aligned}$$

The application of (15.79) and (15.80) gives

$$\begin{aligned} C_{11}(11|\mathbf{M}) &= C_{22}(11|\mathbf{M}) = -\frac{8\alpha + 4(\lambda_1 + \rho_1)}{M_1} = A, & C_{33}(11|\mathbf{M}) &= -8\frac{\alpha + \rho_1}{M_1} = D, \\ C_{11}(22|\mathbf{M}) &= C_{22}(22|\mathbf{M}) = -\frac{8\alpha + 4(\lambda_2 + \rho_2)}{M_2} = B, & C_{33}(22|\mathbf{M}) &= -8\frac{\alpha + \rho_2}{M_2} = E, \\ C_{12}(12|\mathbf{M}) &= C_{21}(12|\mathbf{M}) = \frac{8\beta}{\sqrt{M_1 M_2}} = C. \end{aligned}$$

We write

$$\mathbf{D}(\mathbf{M}) = \begin{bmatrix} A & 0 & 0 & 0 & C & 0 \\ 0 & A & 0 & C & 0 & 0 \\ 0 & 0 & D & 0 & 0 & 0 \\ 0 & C & 0 & B & 0 & 0 \\ C & 0 & 0 & 0 & B & 0 \\ 0 & 0 & 0 & 0 & 0 & E \end{bmatrix}.$$

Application of the projection operators gives

$$D^{(1)}(M_2^-) = [D]; \quad D^{(2)}(M_2^-) = [E]; \quad D(M_5^-) = \begin{bmatrix} A & C \\ C & B \end{bmatrix}.$$

Example 15.10

Rocksalt structure

The symmetry of the rocksalt structure belongs to the space-group $Fm\bar{3}m$, and it has an f.c.c. primitive cell, with lattice vectors

$$\frac{1}{2} \begin{pmatrix} 1 & 1 & 0 \\ 0 & 1 & 1 \\ 1 & 0 & 1 \end{pmatrix}.$$

It has two atoms, of different chemical species, occupying Wyckoff positions (a) ($m\bar{3}m$) and (e) ($4m \cdot m$).

Symmetrized force constant matrices First, we consider the nearest-neighbor (nn)

Φ , namely $\Phi \begin{pmatrix} 000 & 000 \\ 1 & 2 \end{pmatrix}$, which has the general form

$$\Phi \begin{pmatrix} 000 & 000 \\ 1 & 2 \end{pmatrix} = - \begin{pmatrix} \alpha & \delta & \epsilon \\ \zeta & \beta & \eta \\ \theta & \iota & \gamma \end{pmatrix}.$$

The group of the bond $(0, 0, 1/2)$ is $\mathcal{C}_{4v}$. Operating with σ_x , we obtain $\delta = \epsilon = \zeta = \theta = 0$. Next we operate with C_4 and obtain $\iota = \eta = 0$ and $\alpha = \beta$. We write the ensuing matrices

as

$$\begin{aligned}\Phi \begin{pmatrix} 000 & 000 \\ 1 & 2 \end{pmatrix} &= \begin{pmatrix} \alpha & 0 & 0 \\ 0 & \alpha & 0 \\ 0 & 0 & \beta \end{pmatrix} = \Phi \begin{pmatrix} 000 & 1\bar{1}\bar{1} \\ 1 & 2 \end{pmatrix}, \\ \Phi \begin{pmatrix} 000 & 1\bar{1}\bar{1} \\ 1 & 2 \end{pmatrix} &= \begin{pmatrix} \alpha & 0 & 0 \\ 0 & \beta & 0 \\ 0 & 0 & \alpha \end{pmatrix} = \Phi \begin{pmatrix} 000 & \bar{1}\bar{1}1 \\ 1 & 2 \end{pmatrix}, \\ \Phi \begin{pmatrix} 000 & \bar{1}\bar{1}1 \\ 1 & 2 \end{pmatrix} &= \begin{pmatrix} \beta & 0 & 0 \\ 0 & \alpha & 0 \\ 0 & 0 & \alpha \end{pmatrix} = \Phi \begin{pmatrix} 000 & \bar{1}\bar{1}\bar{1} \\ 1 & 2 \end{pmatrix}.\end{aligned}$$

The contributions of this force constant matrix type to the dynamical matrix are

$$\begin{aligned}D_{11}(12|\mathbf{q}) &= \frac{2}{\sqrt{M_1 M_2}} \left[\alpha (1 + \cos[\pi q_2]) + \beta \cos[\pi q_1] \right] \exp[-i\pi q_3], \\ D_{22}(12|\mathbf{q}) &= \frac{2}{\sqrt{M_1 M_2}} \left[\alpha (1 + \cos[\pi q_1]) + \beta \cos[\pi q_2] \right] \exp[-i\pi q_3], \\ D_{33}(12|\mathbf{q}) &= \frac{2}{\sqrt{M_1 M_2}} \left[\alpha (\cos[\pi q_1] + \cos[\pi q_2]) + \beta \right] \exp[-i\pi q_3], \\ D_{12}(12|\mathbf{q}) &= D_{12}(12|\mathbf{q}) = D_{12}(12|\mathbf{q}) = 0.\end{aligned}$$

There are twelve second nn, with a typical Φ given, in general, by

$$\Phi \begin{pmatrix} 000 & 100 \\ 1 & 1 \end{pmatrix} = - \begin{pmatrix} \lambda & \mu & \nu \\ \sigma & \rho & \xi \\ \tau & v & \phi \end{pmatrix}.$$

We symmetrize it for the bond $(1/2, 1/2, 0)$ with point-group $4mm$. We start with σ_{xy} , and we find that $\lambda = \rho$, $\mu = \sigma$, $\nu = \xi$, and $\tau = v$. When we operate with σ_z we obtain $\nu = \xi = v = \tau = 0$. The second nn matrices have the form

$$\begin{aligned}\Phi \begin{pmatrix} 000 & 100 \\ 1 & 1 \end{pmatrix} &= \begin{pmatrix} \lambda & \mu & 0 \\ \mu & \lambda & 0 \\ 0 & 0 & \rho \end{pmatrix}, \\ \Phi \begin{pmatrix} 000 & 010 \\ 1 & 1 \end{pmatrix} &= \begin{pmatrix} \rho & 0 & 0 \\ 0 & \lambda & \mu \\ 0 & \mu & \lambda \end{pmatrix}, \quad [0\bar{1}1], [01\bar{1}] = \begin{pmatrix} \rho & 0 & 0 \\ 0 & \lambda & -\mu \\ 0 & -\mu & \lambda \end{pmatrix}, \\ \Phi \begin{pmatrix} 000 & 001 \\ 1 & 1 \end{pmatrix} &= \begin{pmatrix} \lambda & 0 & \mu \\ 0 & \rho & 0 \\ \mu & 0 & \lambda \end{pmatrix}, \quad [\bar{1}01], [10\bar{1}] = \begin{pmatrix} \lambda & 0 & -\mu \\ 0 & \rho & 0 \\ -\mu & 0 & \lambda \end{pmatrix}.\end{aligned}$$

Contributions to the dynamical matrix have the form

$$\begin{aligned}
 D_{11}(11|\mathbf{q}) &= \frac{2}{\sqrt{M_1 M_2}} [\lambda (\cos[\pi(q_1 + q_2)] + \cos[\pi(q_1 - q_2)] + \cos[\pi(q_1 + q_3)] \\
 &\quad + \cos[\pi(q_1 - q_3)]) + \rho (\cos[\pi(q_2 + q_3)] + \cos[\pi(q_2 - q_3)])] \\
 D_{22}(11|\mathbf{q}) &= \frac{2}{\sqrt{M_1 M_2}} [\lambda (\cos[\pi(q_1 + q_2)] + \cos[\pi(q_1 - q_2)] + \cos[\pi(q_2 + q_3)] \\
 &\quad + \cos[\pi(q_2 - q_3)]) + \rho (\cos[\pi(q_1 + q_3)] + \cos[\pi(q_1 - q_3)])] \\
 D_{33}(11|\mathbf{q}) &= \frac{2}{\sqrt{M_1 M_2}} [\lambda (\cos[\pi(q_1 + q_3)] + \cos[\pi(q_1 - q_3)]) + \cos[\pi(q_2 + q_3)] \\
 &\quad + \cos[\pi(q_2 - q_3)]) + \rho (\cos[\pi(q_1 + q_2)] + \cos[\pi(q_1 - q_2)])] \\
 D_{12}(11|\mathbf{q}) &= \mu \left[\cos[\pi(q_1 + q_2)] - \cos[\pi(q_1 - q_2)] \right] = D_{21}(11|\mathbf{q}) \\
 D_{13}(11|\mathbf{q}) &= \mu \left[\cos[\pi(q_1 + q_3)] - \cos[\pi(q_1 - q_3)] \right] = D_{31}(11|\mathbf{q}) \\
 D_{23}(11|\mathbf{q}) &= \mu \left[\cos[\pi(q_2 + q_3)] - \cos[\pi(q_2 - q_3)] \right] = D_{32}(11|\mathbf{q})
 \end{aligned}$$

Example 15.11

Sr₂CuO₂Cl₂ with I4/mmm ($\mathbb{D}_{4h}^{17}$) symmetry

This crystal has a body-centered tetragonal structure, with lattice constants: $a = b = 3.972 \text{ \AA}$, $c = 15.613 \text{ \AA}$.

Lattice basis vectors	Reciprocal lattice basis vectors
$\frac{1}{2} \begin{pmatrix} a & a & -c \\ a & -a & c \\ -a & a & c \end{pmatrix}$	$\frac{2\pi}{ac} \begin{pmatrix} c & c & 0 \\ c & 0 & a \\ 0 & c & a \end{pmatrix}.$

Table 15.4. *Atomic coordinates and Wyckoff positions.*

	x/a	y/b	z/c	Wyckoff position	Primitive cell multiplicity	Symmetry
Cu	0	0	0	a	1	4/mmm
O	0.5	0	0	c	2	mmm
		0	0.5			
Sr	0	0	± 0.392	e	2	4mm
Cl	0	0	± 0.183	e	2	4mm

The space-group $I4/mmm$ is symmorphic, and its point-group is $\frac{4}{mmm} (\mathcal{D}_{4h})$.

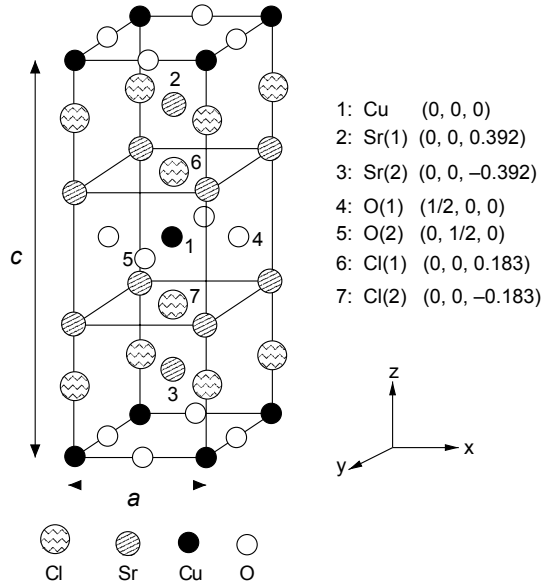


Fig. 15.3. Unit cell of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$.

Table 15.5. *Bond types and their symmetries.*

Bond	x/a	y/b	z/c	Bond group	Force constant matrix
Cu–O	0.5	0	0	$\{E, C_{2x}, \sigma_h, \sigma_y\}$	$\begin{bmatrix} \alpha & 0 & 0 \\ 0 & \beta & 0 \\ 0 & 0 & \gamma \end{bmatrix}$
Cu–Cl	0	0	0.183	$\left\{ \begin{matrix} E, & C_{4z}, & C_{2z} & C_{4z}^- \\ \sigma_x, & \sigma_y, & \sigma_{xy}, & \sigma_{\bar{xy}} \end{matrix} \right\}$	$\begin{bmatrix} \alpha & 0 & 0 \\ 0 & \alpha & 0 \\ 0 & 0 & \beta \end{bmatrix}$
Sr–Cl	0	0	-0.209		$\begin{bmatrix} \alpha & \gamma & \delta \\ \gamma & \alpha & \delta \\ \epsilon & \epsilon & \beta \end{bmatrix}$
Sr–Cl	0.5	0.5	-0.075	$\{E, \sigma_{\bar{xy}}\}$	$\begin{bmatrix} \alpha & 0 & 0 \\ 0 & \beta & \epsilon \\ 0 & \delta & \gamma \end{bmatrix}$
Sr–O	0	-0.5	-0.108	$\{E, \sigma_x\}$	

Table 15.6. *Symmetries of the body-centered tetragonal Brillouin zone.*

$\mathbf{q}$ -vector $\left(\frac{a(c)\mathbf{q}}{2\pi}\right)$	BSW notation	$\mathcal{G}_{\mathbf{q}}$	Principal axis	Equivalent points	Star of $\mathbf{q}$
$(\frac{1}{2}, q, \frac{1}{2})$	Q	2	$[1\alpha 1]$	$(\pm\frac{1}{2}, q, \pm\frac{1}{2})$	$(\frac{1}{2}, \pm q, \frac{1}{2}), (-\frac{1}{2}, \pm q, \frac{1}{2}),$ $(\pm q, \frac{1}{2}, \frac{1}{2}), (\pm q, -\frac{1}{2}, \frac{1}{2})$
$(\frac{1}{2}, \frac{1}{2}, q)$	W	m	$[001]$	$(\pm\frac{1}{2}, \pm\frac{1}{2}, q)$	$(1, 1, 0), (0, 1, 0), (0, 1, 1)$
$(\frac{1}{2}, 0, \frac{1}{2})$	N	$2/m$	$[101]$	$(\pm\frac{1}{2}, 0, \pm\frac{1}{2})$	$(\pm\frac{1}{2}, 0, \frac{1}{2}), (0, \pm\frac{1}{2}, \frac{1}{2})$
$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	P	$2mm$	$[111]$	$(\pm\frac{1}{2}, \pm\frac{1}{2}, \frac{1}{2})$	$(\frac{1}{2}, \frac{1}{2}, \pm\frac{1}{2}), (\frac{1}{2}, -\frac{1}{2}, \pm\frac{1}{2})$
$(q, q, 0)$	Σ	$2mm$	$[110]$	$(q, q, 0)$	$(\pm q, q, 0), (\pm q, -q, 0)$
$(q, 0, 0)$	Δ	$2mm$	$[100]$	$(q, 0, 0)$	$(\pm q, 0, 0), (0, \pm q, 0)$
$(\frac{1}{2}, \frac{1}{2}, 0)$	X	mmm	$[110]$	$(\pm\frac{1}{2}, \pm\frac{1}{2}, 0)$	$(\pm\frac{1}{2}, \frac{1}{2}, 0)$
$(0, 0, q)$	Λ	$4mm$	$[001]$	$(0, 0, q)$	$(0, 0, \pm q)$
$(0, 0, 1)$	Z	$4/mmm$	$[010]$	$(0, 0, \pm 1)$	$(0, 0, 1)$
$(0, 0, 0)$	Γ	$4/mmm$	$[000]$	$(0, 0, 0)$	$(0, 0, 0)$

*Example 15.12***Orthorhombic potassium selenate, with $Pnam$ ($\mathbb{D}_{2h}^{16}$) space-group**

We are interested in this system because it undergoes two phase transitions, first, from a paraelectric phase with an orthorhombic lattice, which we consider here, to an incommensurate phase, with incommensurate modulation along the a -axis at 130 K, and then to a ferroelectric below 93 K.

The orthorhombic structure has a $Pnam$ space-group symmetry; its unit cell, shown schematically in Figure 15.4, has four formula K_2SeO_4 : eight oxygens O(1) are in general position (d), all other atoms are at Wyckoff positions (c): O(2), O(3), K_α , K_β and Se, namely,

$$\left(x, y, \frac{1}{4}\right), \quad \left(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{4}\right), \quad \left(\bar{x}, \bar{y}, \frac{3}{4}\right), \quad \left(\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{4}\right).$$

given in Table 15.7. The Se atoms are located at the centers of O tetrahedra. The coset representatives of $Pnam$ are given in Table 15.8.

Since each formula consists of seven atoms, there is a total of 84 normal modes. Among these modes, 60 belong to the SeO_4 tetrahedra. We do not consider the internal-vibrations of these tetrahedra, which are treated as rigid structures; we are then left with their rotation and COM translations which comprise 24 modes. Thus, in all, we consider 48 normal modes.

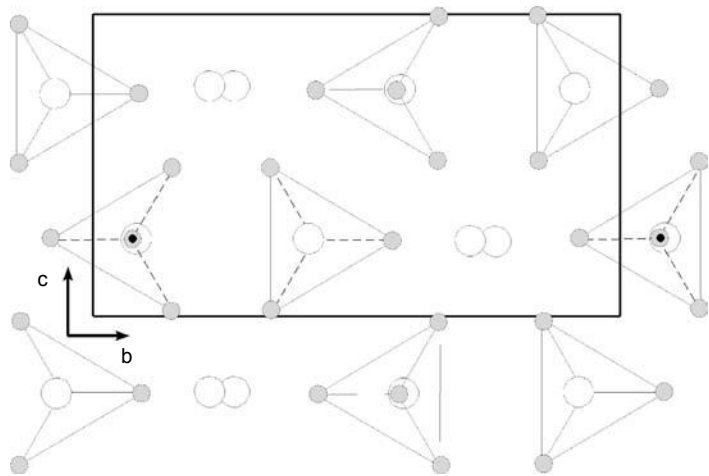


Fig. 15.4. Projection of the unit cell of K_2SeO_4 along the $[100]$ direction. Se (solid black circles), O (solid gray circles), and K (white circles). Hidden atoms are not shown.

Table 15.7. Atomic coordinates.

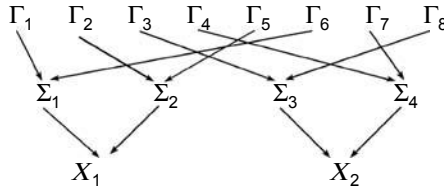
	x/a	y/b	z/c	Wyckoff position
Se	0.2242	0.4200	$1/4$	c
K(1)	0.1705	0.0843	$1/4$	c
K(2)	-0.0057	-0.2905	$1/4$	c
O(1)	0.2931	0.3471	0.0271	d
O(2)	0.3024	-0.4356	$1/4$	c
O(3)	0.0126	0.4251	$1/4$	c

Table 15.8. Symmetry operations of the space-group $Pnam (\mathcal{D}_{2h}^{16})$.

Symmetry operation	Action	Symmetry operation	Action
$(E \mathbf{0})$	x, y, z	$(\mathcal{I} \mathbf{0})$	$\bar{x}, \bar{y}, \bar{z}$
$(C_{2x} \frac{1}{2}\mathbf{a} + \frac{1}{2}\mathbf{b} + \frac{1}{2}\mathbf{c})$	$\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$	$(\sigma_x \frac{1}{2}\mathbf{a} + \frac{1}{2}\mathbf{b} + \frac{1}{2}\mathbf{c})$	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$
$(C_{2y} \frac{1}{2}\mathbf{a} + \frac{1}{2}\mathbf{b})$	$\frac{1}{2} - x, \frac{1}{2} + y, \bar{z}$	$(\sigma_y \frac{1}{2}\mathbf{a} + \frac{1}{2}\mathbf{b})$	$\frac{1}{2} + x, \frac{1}{2} - y, z$
$(C_{2z} \frac{1}{2}\mathbf{c})$	$\bar{x}, \bar{y}, \frac{1}{2} + z$	$(\sigma_z \frac{1}{2}\mathbf{c})$	$x, y, \frac{1}{2} - z$

Table 15.9. *Irreps of $\mathcal{D}_{2h}$ and $\mathcal{C}_{2v}^{(x)}$.*

$\mathcal{D}_{2h}$	E	C_{2x}	C_{2y}	C_{2z}	$\mathcal{I}$	σ_x	σ_y	σ_z	$\mathcal{C}_{2v}^{(x)}$	E	C_{2x}	σ_y	σ_z
$\Gamma_1 (A_g)$	1	1	1	1	1	1	1	1	Σ_1	1	1	1	1
$\Gamma_2 (B_{3g})$	1	1	-1	-1	1	1	-1	-1	Σ_2	1	1	-1	-1
$\Gamma_3 (B_{1g})$	1	-1	1	-1	1	-1	1	-1	Σ_3	1	-1	1	-1
$\Gamma_4 (B_{2g})$	1	-1	-1	1	1	-1	-1	1	Σ_4	1	-1	-1	1
$\Gamma_5 (A_u)$	1	1	1	1	-1	-1	-1	-1					
$\Gamma_6 (B_{3u})$	1	1	-1	-1	-1	-1	1	1					
$\Gamma_7 (B_{1u})$	1	-1	1	-1	-1	1	-1	1					
$\Gamma_8 (B_{2u})$	1	-1	-1	1	-1	1	1	-1					
X_1	2	2	0	0	0	0	0	0					
X_2	2	-2	0	0	0	0	0	0					

Fig. 15.5. Compatibility relations along $\Gamma - \Sigma - X$.

Since symmetry operations interchange equivalent atoms only, each symmetry-adapted displacement vector can be written as $[\vec{K}_\alpha, \vec{K}_\beta, \vec{T}, \vec{R}]$, where the last two entries represent tetrahedral COM displacements and rotations, respectively. Each entry comprises four 3D vectors, for example we have $\vec{K}_\alpha \equiv (\mathbf{u}_\alpha^{(1)}, \mathbf{u}_\alpha^{(2)}, \mathbf{u}_\alpha^{(3)}, \mathbf{u}_\alpha^{(4)})$.

The effective permutations of the point-group action are:

$$\begin{aligned}
 E &\equiv (1)(2)(3)(4), & \mathcal{I} &\equiv (13)(24) & C_{2x} &\equiv (12)(34), & C_{2y} &\equiv (14)(23), \\
 C_{2z} &\equiv (13)(24), & \sigma_x &\equiv (14)(23), & \sigma_y &\equiv (12)(34), & \sigma_z &\equiv (1)(2)(3)(4).
 \end{aligned}$$

We confine our analysis to the Σ -direction ($\Gamma \rightarrow X$, with wavevectors $(q, 0, 0)$), the direction of the incommensurate modulation. The Γ -point has a point-group $\mathcal{D}_{2h}$ with eight classes, and hence eight 1D Irreps given in Table 15.9.

Compatibility The 48 normal modes considered here decompose into the following CG series:

$$\begin{aligned} \Gamma\text{-point } & 7\left(\begin{smallmatrix} \Gamma_1 \\ A_{1g} \end{smallmatrix}\right) + 5\left(\begin{smallmatrix} \Gamma_2 \\ B_{3g} \end{smallmatrix}\right) + 5\left(\begin{smallmatrix} \Gamma_3 \\ B_{2g} \end{smallmatrix}\right) + 7\left(\begin{smallmatrix} \Gamma_4 \\ B_{1g} \end{smallmatrix}\right) \\ & + 5\left(\begin{smallmatrix} \Gamma_5 \\ A_{1u} \end{smallmatrix}\right) + 7\left(\begin{smallmatrix} \Gamma_6 \\ B_{3u} \end{smallmatrix}\right) + 7\left(\begin{smallmatrix} \Gamma_7 \\ B_{2u} \end{smallmatrix}\right) + 5\left(\begin{smallmatrix} \Gamma_8 \\ B_{1u} \end{smallmatrix}\right) \\ \Sigma\text{-line } & 14\Sigma_1 + 10\Sigma_2 + 10\Sigma_3 + 14\Sigma_4 \\ \mathbf{X}\text{-point } & 14X_1 + 10X_2. \end{aligned}$$

Rotation and COM translation modes of a tetrahedron From Table 15.10, we find that the rotations transform as Γ_4 , while the COM translations transform as Γ_5 . First, we find that the tetrahedral symmetry-adapted rotation Γ_4 and translation Γ_5 subduce onto $\Gamma_2 + \Gamma_3 + \Gamma_4$ and $\Gamma_6 + \Gamma_7 + \Gamma_8$ of $\mathcal{D}_{2h}$, respectively, and thus $4\Gamma_2 + 4\Gamma_3 + 4\Gamma_4$ are associated with the rotations of the four tetrahedra, and $4\Gamma_6 + 4\Gamma_7 + 4\Gamma_8$ are associated with their COM translations.

Table 15.10. *Subduction of tetrahedral modes on Irreps of T_d .*

Irrep	E	$8C_3$	$3C_2$	$6S_4$	6σ	
$\Gamma_1 (A_1)$	1	1	1	1	1	$ \mathbf{r} $
$\Gamma_2 (A_2)$	1	1	1	-1	-1	
$\Gamma_3 (E)$	2	-1	2	0	0	
$\Gamma_4 (T_1)$	3	0	-1	1	-1	R_x, R_y, R_z
$\Gamma_5 (T_2)$	3	0	-1	-1	1	$\mathbf{r}$
Γ	15	0	-1	-1	3	

15.3.4 Elastic equations of motion

Elastic waves can be set in a medium by first applying an inhomogeneous stress to the medium and then releasing the stress. Elastic restoring forces set up relative motions of the different parts of the crystal. The net force acting in the α -direction on an element of volume $\Delta v = \Delta x \Delta y \Delta z$ at a point $\bar{r}$ inside the crystal is given by

$$\begin{aligned} F_\alpha &= \sum_\gamma \frac{\partial S_{\alpha\gamma}}{\partial x_\gamma} \Delta a_\gamma \Delta x_\gamma = \sum_\gamma \frac{\partial}{\partial x_\gamma} \left(\frac{\partial \mathcal{V}}{\partial \epsilon_{\alpha\gamma}} \right) \Delta v \\ &= \sum_{\gamma\beta\lambda} C_{\alpha\gamma,\beta\lambda} \frac{\partial \epsilon_{\beta\lambda}}{\partial x_\gamma} \Delta v = \sum_{\gamma\beta\lambda} C_{\alpha\gamma,\beta\lambda} \frac{\partial}{\partial x_\gamma} \left(\frac{u_{\beta\lambda} + u_{\lambda\beta}}{2} \right) \Delta v \\ &= \sum_{\gamma\beta\lambda} C_{\alpha\gamma,\beta\lambda} \frac{\partial^2 u_\beta}{\partial x_\gamma \partial x_\lambda} \Delta v, \end{aligned} \tag{15.116}$$

where $\Delta a_\gamma = \Delta x_\beta \Delta x_\lambda$; $\lambda \neq \beta \neq \gamma$ is the element of area of the face whose normal is along the γ -direction. We have used the property $C_{\alpha\gamma,\beta\lambda} = C_{\alpha\gamma,\lambda\beta}$ to arrive at the last line.

Using the fact that the mass inside the volume element is given by $m = \rho \Delta \Omega$, where ρ is the crystal density, we obtain the equation of motion

$$\rho \ddot{u}_\alpha = \sum_{\gamma\beta\lambda} C_{\alpha\gamma,\beta\lambda} \frac{\partial^2 u_\beta}{\partial x_\gamma \partial x_\lambda}. \quad (15.117)$$

For a crystal with cubic symmetry and density ρ_0 we get

$$\rho \ddot{u}_x = c_{11} \frac{\partial^2 u_x}{\partial x^2} + c_{44} \left(\frac{\partial^2 u_x}{\partial y^2} + \frac{\partial^2 u_x}{\partial z^2} \right) + (c_{12} + c_{44}) \left(\frac{\partial^2 u_y}{\partial x \partial y} + \frac{\partial^2 u_z}{\partial x \partial z} \right). \quad (15.118)$$

Further manipulations of (15.118) yield

$$\begin{aligned} \rho \ddot{u}_x &= (c_{11} - c_{12} - 2c_{44}) \frac{\partial^2 u_x}{\partial x^2} + c_{44} \nabla^2 u_x \\ &\quad + (c_{12} + c_{44}) \frac{\partial}{\partial x} \left(\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} \right) \\ &= (c_{11} - c_{12} - 2c_{44}) \frac{\partial^2 u_x}{\partial x^2} + c_{44} \nabla^2 u_x + (c_{12} + c_{44}) \frac{\partial}{\partial x} \operatorname{div} \mathbf{u}. \end{aligned} \quad (15.119)$$

Using the translational invariance of the continuum elastic equations we can diagonalize the equations of motion by taking the space and time Fourier components of the displacement field

$$\mathbf{u}(\mathbf{r}) = \frac{1}{\Omega} \int d\mathbf{q} dt \mathbf{u}(\mathbf{q}, \omega) e^{i(\mathbf{q} \cdot \mathbf{r} - \omega(\mathbf{q})t)}, \quad (15.120)$$

where Ω is crystal volume. This gives in general

$$\rho \omega^2(\mathbf{q}) \mathbf{u}(\mathbf{q}) = \mathcal{D}(\mathbf{q}) \mathbf{u}(\mathbf{q}), \quad (15.121)$$

where

$$\mathcal{D}_{\alpha\beta}(\mathbf{q}) = \sum_{\gamma\lambda} C_{\alpha\gamma,\beta\lambda} q_\gamma q_\lambda. \quad (15.122)$$

Example 15.13

For the case of cubic crystals we find that we can simplify this procedure by introducing either a longitudinal or a transverse wave component. The former has the functional dependence $u_x = u_0 e^{i(qx - \omega t)}$, which upon substitution in (15.118) gives

$$\omega^2 \rho = c_{11} q^2, \quad (15.123)$$

so that the wave velocity is

$$v = \omega/q = \left(\frac{c_{11}}{\rho_0} \right)^{1/2}. \quad (15.124)$$

The transverse solution will have the form $u_x = u_0 e^{i(ky - \omega t)}$, giving

$$\omega^2 \rho_0 = c_{44} q^2, \quad (15.125)$$

with velocity

$$v = \left(\frac{c_{44}}{\rho_0} \right)^{1/2}. \quad (15.126)$$

Elastic isotropy

If we set

$$c_{11} - c_{12} = 2c_{44}, \quad (15.127)$$

we find that the first term in (15.119) drops out, and including similar equations for $\ddot{u}_y$ and $\ddot{u}_z$ we write

$$\begin{aligned} \rho_0 \ddot{\mathbf{u}} &= c_{44} \nabla^2 \mathbf{u} + (c_{12} + c_{44}) \text{grad div } \mathbf{u} \\ &= c_{11} \text{grad div } \mathbf{u} - c_{44} \text{curl curl } \mathbf{u}, \end{aligned} \quad (15.128)$$

where we have used the identity $\text{curl curl } \mathbf{A} = \text{grad div } \mathbf{A} - \nabla^2 \mathbf{A}$. Equation (15.128) is invariant under arbitrary rotations, thus the relation (15.127) is the condition that the crystal should be *elastically isotropic*, so that longitudinal and transverse waves should propagate in all directions with the same velocities. This is clearly seen if we set $\text{curl } \mathbf{u} = 0$, the term *grad div* gives rise to a longitudinal wave; and the $\text{div } \mathbf{u} = 0$, the *curl curl* term gives rise to two independent orthogonal transverse wave solutions of equal frequencies.

The anisotropy factor A in a cubic crystal is defined as the square of the ratio of velocities of the shear (transverse) waves propagating in the $\langle 100 \rangle$ and $\langle 110 \rangle$ directions:

$$A = \frac{2c_{44}}{c_{11} - c_{12}}. \quad (15.129)$$

Cauchy relations

If certain conditions are satisfied, there exist among the elastic constants relations first obtained by Cauchy. The relations reduce to

$$c_{12} = c_{44}, \quad (15.130)$$

in a crystal with cubic symmetry. If this is satisfied the isotropy condition (15.127) becomes $c_{11} = 3c_{44}$, and the velocity of longitudinal waves will equal $\sqrt{3}$ that of the transverse waves. The conditions for the validity of the Cauchy relations are:

- All interatomic forces must be central, i.e. act along lines joining the atomic centers. This is not generally true of covalent and metallic bindings.
- Every atom must be at a center of inversion symmetry.
- The crystal should be initially under no stress.

Connection between the microscopics and macroscopics: the method of long-waves

So far in this section we have considered the theory of lattice dynamics from a microscopic and a macroscopic perspective. Here, we establish the connection between the two pictures [101, 103, 106]. In order to achieve this end, and for pedagogical simplicity, we shall adopt the approach given by Lax [101], and consider a monatomic crystal. Since there is only one atom per primitive cell, we relate the density to the atomic mass M by

$$\rho_0 = \frac{M}{\Omega_0},$$

where Ω_0 is the primitive cell volume. Moreover, the dynamical matrix,

$$D_{\alpha\beta}(\mathbf{q}) = \sum_{\ell\ell'} \Phi_{\alpha\beta}(\ell\ell') e^{i\mathbf{q} \cdot (\mathbf{t}(\ell) - \mathbf{t}(\ell'))},$$

in this case is real and symmetric, since each atomic site is centrosymmetric. Expanding $D(\mathbf{q})$ in powers of $\mathbf{q}$, and including only bilinear terms, we obtain

$$\begin{aligned} \rho_0 \omega^2(\mathbf{q}) U_\alpha &= \frac{1}{\Omega_0} \sum_{\alpha\beta} D_{\alpha\beta}(\mathbf{q}) U_\beta \\ &= \sum_{\gamma\lambda\beta} \mathcal{C}_{\alpha\gamma\beta\lambda} q_\gamma q_\lambda U_\beta, \end{aligned} \quad (15.131)$$

where

$$\mathcal{C}_{\alpha\gamma\beta\lambda} = -\frac{1}{2\Omega_0} \sum_{\ell\ell'} \Phi_{\alpha\beta}(\ell\ell') (\mathbf{t}(\ell) - \mathbf{t}(\ell'))_\gamma (\mathbf{t}(\ell) - \mathbf{t}(\ell'))_\lambda,$$

which possesses the symmetries

$$\mathcal{C}_{\alpha\gamma\beta\lambda} = \mathcal{C}_{\alpha\lambda\beta\gamma} = \mathcal{C}_{\beta\gamma\alpha\lambda}, \quad (15.132)$$

where the last relation was obtained with the aid of bond-flip symmetry. Next we use the relation

$$u_\alpha(\mathbf{X}, t) = U_\alpha e^{i(\mathbf{q} \cdot \mathbf{X}_\ell - \omega t)}$$

to rewrite (15.131) as

$$\rho_0 \ddot{u}_\alpha = \sum_{\gamma\lambda\beta} \mathcal{C}_{\alpha\gamma\beta\lambda} \frac{\partial^2 u_\beta}{\partial X_\gamma \partial X_\lambda}. \quad (15.133)$$

However, when we compare (15.133) with (15.117), namely,

$$\rho \ddot{u}_\alpha = \sum_{\gamma\beta\lambda} C_{\alpha\gamma,\beta\lambda} \frac{\partial^2 u_\beta}{\partial x_\gamma \partial x_\lambda},$$

we realize that in contrast to $\mathcal{C}_{\alpha\gamma\beta\lambda}$, $C_{\alpha\gamma,\beta\lambda}$ is not symmetric with respect to interchanging γ and λ . $C_{\alpha\gamma,\beta\lambda}$ satisfies (13.67), namely

$$C_{\alpha\gamma,\beta\lambda} = C_{\beta\lambda,\alpha\gamma}, \quad C_{\alpha\gamma,\beta\lambda} = C_{\gamma\alpha,\beta\lambda}, \quad C_{\alpha\gamma,\beta\lambda} = C_{\alpha\gamma,\lambda\beta}.$$

It is possible, however, to obtain a relation between the two sets by manipulating the inherent symmetries of each. Manipulating these symmetry relations, including (15.132),

we obtain

$$2C_{\alpha\gamma\beta\lambda} = C_{\alpha\gamma\beta\lambda} + C_{\alpha\lambda\beta\gamma}, \quad (15.134)$$

$$2C_{\gamma\alpha\beta\lambda} = C_{\gamma\lambda\beta\alpha} + C_{\alpha\gamma\beta\lambda}, \quad (15.135)$$

after interchanging α and γ in (15.134); next, we interchange α and β in (15.135) and obtain

$$2\mathcal{C}_{\gamma\beta\alpha\lambda} = C_{\beta\gamma\alpha\lambda} + C_{\gamma\lambda\alpha\beta}. \quad (15.136)$$

Next, we add (15.134) and (15.135), subtract (15.135) and divide by 2; we get

$$C_{\alpha\gamma\beta\lambda} = C_{\alpha\gamma\beta\lambda} + C_{\gamma\alpha\beta\lambda} - C_{\gamma\beta\alpha\lambda}. \quad (15.137)$$

Finally, we should note that the relations between the $\mathcal{C}$ s and the C s must satisfy all symmetries required by the C s if relations like (15.137) be reliable in computing the elastic constants. To this end we show that actually the $\mathcal{C}$ s satisfy one extra symmetry by interchanging α and γ as well as β and λ in (15.134) to obtain

$$2\mathcal{C}_{\gamma\alpha\lambda\beta} = C_{\gamma\alpha\lambda\beta} + C_{\gamma\beta\lambda\alpha}, \quad (15.138)$$

where, in fact, the right-hand sides of (15.138) and (15.134) are equal, hence

$$C_{\gamma\alpha\lambda\beta} = C_{\alpha\gamma\beta\lambda}. \quad (15.139)$$

Internal shifts in crystals with sublattices When stress is applied to a crystal comprised of two or more sublattices, the ensuing strain involves two component types: the ordinary elastic strain as well as an internal shift by each sublattice from its equilibrium position. We follow Lax [101], section 11.10, and write

$$u_{\alpha}(\ell\kappa) = v_{\alpha}(\kappa) + \sum_{\beta} u_{\alpha\beta} X_{\beta}(\ell\kappa), \quad (15.140)$$

where $u_{\alpha}(\kappa)$ is the shift of sublattice κ , and the second term is just the elastic strain. Substitution in (15.59) and division by the crystal volume gives

$$\begin{aligned} \phi &= \frac{1}{2\Omega} \sum_{\ell\kappa\alpha} \sum_{\ell'\kappa'\beta} u_{\alpha}(\ell\kappa) \Phi_{\alpha\beta} \begin{pmatrix} \ell & \ell' \\ \kappa & \kappa' \end{pmatrix} u_{\beta}(\ell'\kappa') \\ &= \frac{1}{2} \sum_{\substack{\alpha\beta \\ \kappa\kappa'}} \left(v_{\alpha}(\kappa) \phi \begin{pmatrix} \kappa\kappa' \\ \alpha\beta \end{pmatrix} v_{\beta}(\kappa') + 2 \sum_{\gamma} v_{\alpha}(\kappa) \psi \begin{pmatrix} \kappa \\ \alpha\beta\gamma \end{pmatrix} u_{\beta\gamma} \right. \\ &\quad \left. + \sum_{\gamma\lambda} u_{\alpha\gamma} \{ \alpha\beta, \gamma\lambda \} u_{\beta\lambda} \right), \end{aligned} \quad (15.141)$$

where

$$\begin{aligned}
 \phi \begin{pmatrix} \kappa \kappa' \\ \alpha \beta \end{pmatrix} &= \frac{1}{\Omega} \sum_{\ell \ell'} \Phi_{\alpha \beta} \begin{pmatrix} \ell & \ell' \\ \kappa & \kappa' \end{pmatrix} = \frac{1}{\Omega_0} \sum_{\ell'} \Phi_{\alpha \beta} \begin{pmatrix} 0 & \ell' \\ \kappa & \kappa' \end{pmatrix} \\
 \psi \begin{pmatrix} \kappa \\ \alpha \beta \gamma \end{pmatrix} &= \frac{1}{\Omega} \sum_{\ell \ell' \kappa'} \Phi_{\alpha \beta} \begin{pmatrix} \ell & \ell' \\ \kappa & \kappa' \end{pmatrix} X_{\gamma}(\ell' \kappa') \\
 &= \frac{1}{\Omega_0} \sum_{\ell' \kappa'} \Phi_{\alpha \beta} \begin{pmatrix} 0 & \ell' \\ \kappa & \kappa' \end{pmatrix} X_{\gamma}(\ell' \kappa') = \sum_{\kappa'} \bar{\psi} \begin{pmatrix} \kappa \kappa' \\ \alpha \beta \gamma \end{pmatrix} \\
 \{\alpha \beta, \gamma \lambda\} &= \frac{1}{2\Omega} \sum_{\ell \ell' \kappa \kappa'} X_{\gamma}(\ell \kappa) \Phi_{\alpha \beta} \begin{pmatrix} \ell & \ell' \\ \kappa & \kappa' \end{pmatrix} X_{\lambda}(\ell \kappa)
 \end{aligned} \tag{15.142}$$

The second term in (15.141) allows for lowering the potential energy through adjustments of the internal sublattice shifts. The magnitudes of these shifts in terms of the external strain $u_{\beta\gamma}$ can be determined from

$$\frac{\partial \phi}{\partial v_{\alpha}(\kappa)} = \sum_{\beta \kappa'} \left(\phi \begin{pmatrix} \kappa \kappa' \\ \alpha \beta \end{pmatrix} v_{\beta}(\kappa') + \sum_{\gamma} \bar{\psi} \begin{pmatrix} \kappa \kappa' \\ \alpha \beta \gamma \end{pmatrix} u_{\beta\gamma} \right) = 0. \tag{15.143}$$

We then use these results to express ϕ in terms of the strain as

$$\phi = \frac{1}{2} \sum C_{\alpha\gamma\beta\lambda} u_{\alpha\gamma} u_{\beta\lambda}, \tag{15.144}$$

where

$$C_{\alpha\gamma\beta\lambda} = \{\alpha\beta, \gamma\lambda\} + (\alpha\gamma, \beta\lambda), \tag{15.145}$$

where the last term is the contribution from the internal shifts. The term $\{\alpha\beta, \gamma\lambda\}$ is boundary sensitive, to avoid this problem Lax shows that by defining

$$\mathcal{C}_{\alpha\gamma\beta\lambda}^{\text{ext}} = \frac{1}{2} (\{\alpha\beta, \gamma\lambda\} + \{\alpha\lambda, \beta\gamma\}) = [\alpha\beta, \gamma\lambda],$$

which is symmetric with respect to $(\gamma\lambda)$ exchange, it can be expressed in the boundary-insensitive form

$$\mathcal{C}_{\alpha\gamma\beta\lambda}^{\text{ext}} = \frac{1}{2\Omega_0} \sum_{\ell \kappa \kappa'} (\mathbf{X}(\ell \kappa') - \mathbf{X}(0\kappa))_{\gamma} \Phi_{\alpha\beta} \begin{pmatrix} 0 & \ell' \\ \kappa & \kappa' \end{pmatrix} (\mathbf{X}(\ell \kappa') - \mathbf{X}(0\kappa))_{\lambda}. \tag{15.146}$$

With expressions like (15.146) we obtain the boundary-insensitive form

$$\{\alpha\gamma, \beta\lambda\} = [\alpha\gamma, \beta\lambda] + [\gamma\alpha, \beta\lambda] - [\gamma\beta, \alpha\lambda] \tag{15.147}$$

using a procedure similar to that for the monatomic lattice.

Rewriting (15.143) as

$$\sum_{\beta \kappa'} \phi \begin{pmatrix} \kappa \kappa' \\ \alpha \beta \end{pmatrix} v_{\beta}(\kappa') = - \sum_{\beta \gamma} \psi \begin{pmatrix} \kappa \\ \alpha \beta \gamma \end{pmatrix} u_{\beta\gamma}, \tag{15.148}$$

which form a set of $3r \times 3r$ linear equations, where r is the number of sublattices, and solving these equations yields

$$v_\alpha(\kappa) = - \sum_{\substack{\kappa'\beta \\ \delta\lambda}} \phi \left(\frac{\kappa\kappa'}{\alpha\beta} \right)^{-1} \psi \left(\frac{\kappa'}{\beta\delta\lambda} \right) u_{\delta\lambda}.$$

Substituting for the vs in (15.141), we get

$$(\alpha\gamma, \beta\lambda) = - \sum_{\substack{\kappa\kappa' \\ \rho\delta}} \psi \left(\frac{\kappa}{\rho\alpha\gamma} \right) \phi \left(\frac{\kappa\kappa'}{\rho\delta} \right)^{-1} \psi \left(\frac{\kappa'}{\delta\beta\lambda} \right). \quad (15.149)$$

15.4 Dynamical properties of surfaces

Surface acoustic waves have been a subject of scientific interest for more than a hundred years. Lord Rayleigh showed in 1887 that a semi-infinite, isotropic, elastic medium, bounded by a single stress-free planar surface, can support propagating modes that are wavelike in directions parallel to the surface. These dynamical excitations are identified as surface elastic waves because they are characterized by acoustic fields that decay exponentially with distance into the medium from the surface, and by a frequency that is linearly proportional to a two-dimensional wavevector, which lies in the plane of the surface. The displacements of the medium lie in the sagittal plane, which is defined by the normal to the surface and the direction of propagation of the wave. In honor of their discoverer, they are known as *Rayleigh waves*. Detailed presentations of the properties of surfaces are found in references [107, 108].

15.4.1 Surface modes of an elastic medium

We consider an elastic medium occupying the upper half-space $x_3 > 0$. The surface $x_3 = 0$ is assumed to be stress free. According to (15.117) the elastic equations of motion are given by

$$\rho \ddot{u}_\alpha = \sum_{\gamma\beta\lambda} C_{\alpha\gamma,\beta\lambda} \frac{\partial^2 u_\beta}{\partial x_\gamma \partial x_\lambda} = \sum_\gamma \frac{\partial S_{\alpha\gamma}}{\partial x_\gamma}.$$

Since the stress tensor $S_{\alpha\beta}$ is defined as

$$S_{\alpha\gamma} = \sum_{\beta\lambda} C_{\alpha\gamma\beta\lambda} \frac{\partial u_\beta}{\partial x_\lambda}, \quad (15.150)$$

we must supplement (15.117) by the conditions of a stress-free surface

$$S_{\alpha 3} \Big|_{x_3=0} = \sum_{\beta\lambda} C_{\alpha 3\beta\lambda} \frac{\partial u_\beta}{\partial x_\lambda} \Big|_{x_3=0} = 0, \quad (15.151)$$

which for a cubic medium gives

$$\begin{aligned} S_{13} &= c_{44} \left(\frac{\partial u_1}{\partial x_3} + \frac{\partial u_3}{\partial x_1} \right) = 0, \\ S_{23} &= c_{44} \left(\frac{\partial u_2}{\partial x_3} + \frac{\partial u_3}{\partial x_2} \right) = 0, \\ S_{33} &= c_{12} \left(\frac{\partial u_1}{\partial x_1} + \frac{\partial u_2}{\partial x_2} \right) + c_{11} \frac{\partial u_3}{\partial x_3} = 0. \end{aligned} \quad (15.152)$$

We impose the isotropy condition, namely $c_{11} - c_{12} = 2c_{44}$, and place the propagation vector along the x -direction, so that the xz -plane becomes a symmetry mirror plane, known as the *sagittal plane*. This, in turn, identifies even and odd polarizations, the former consists of x and z , and the latter, y displacements.

We focus on the even polarizations, which give rise to the celebrated surface Rayleigh waves. We set $u_2 = 0$, so that the relevant equations of motion are

$$\begin{aligned} -\rho \omega^2 u_1 &= c_{11} \frac{\partial^2 u_1}{\partial x_1^2} + c_{44} \frac{\partial^2 u_1}{\partial x_3^2} + (c_{11} - c_{44}) \frac{\partial^2 u_3}{\partial x_1 \partial x_3}, \\ -\rho \omega^2 u_3 &= c_{11} \frac{\partial^2 u_3}{\partial x_3^2} + c_{44} \frac{\partial^2 u_3}{\partial x_1^2} + (c_{11} - c_{44}) \frac{\partial^2 u_1}{\partial x_3 \partial x_1}, \end{aligned} \quad (15.153)$$

where we introduced periodic time dependence. Inserting the first condition of (15.152) into (15.153), we decouple the equations of motion, and obtain

$$-\rho \omega^2 u_1 = c_{11} \frac{\partial^2 u_1}{\partial x_1^2} - c_{12} \frac{\partial^2 u_1}{\partial x_3^2}. \quad (15.154)$$

Since the surface wave decays into the bulk of the elastic medium, we write $u_1 = U \exp[-\kappa z + i(kx - \omega t)]$, and we obtain

$$q^2 = \left(3 - 2 \frac{c_{44}}{c_{11}} \right) - \frac{\rho c^2}{c_{44}}, \quad (15.155)$$

where $c = \omega/k$ and $q = \kappa/k$.

15.4.2 Surface modes of a crystalline solid

Traditionally, the problem of calculating surface-phonon dispersion relations has been approached by two methods. The first employs a slab geometry, where the slab has infinite extension in planes parallel to the surface, xy -planes, and a finite extent along the z -direction. The second method is based on a Green function approach. We only consider the former here, since it is the preferred method for many calculations.

The slab method [109]

In slab geometries, the number of slab layers in the z -direction is usually taken to be odd, in order to maintain odd and even parity with respect to the central layer. The number of layers is then increased until the odd and even branches merge, indicating that the interaction between the two boundary surfaces of the slab has vanished. At this point,

each of the boundary surfaces becomes a bona fide independent surface of the crystalline material system.

In the slab geometry, the instantaneous position of a given particle (κ) is defined as

$$\mathbf{r}(\ell, L, \kappa) = \ell c \hat{\mathbf{z}} + l_1 \mathbf{a}_1 + l_2 \mathbf{a}_2 + \boldsymbol{\kappa} + \mathbf{u}(\ell, L, \kappa) \quad (15.156)$$

where c is the interlayer separation, ℓ indicates the layer, $L \equiv (l_1, l_2)$ indexes the 2D primitive cell and κ the position within the cell.

The equations of motion are written as

$$M_\kappa \ddot{\mathbf{u}}_\alpha(\ell, L, \kappa) = \sum_{\ell', L', \kappa', \beta} \Phi_{\alpha\beta} \begin{pmatrix} \ell & 0 \\ \kappa & \kappa' \end{pmatrix} \begin{pmatrix} \ell' & L' \\ \kappa' & \kappa' \end{pmatrix} \mathbf{u}_\beta(\ell', L', \kappa'). \quad (15.157)$$

Writing

$$\mathbf{u}_\alpha(\ell, L, \kappa) = \frac{1}{\sqrt{NM_\kappa}} \mathbf{U}_\alpha(\ell\kappa) e^{i\mathbf{q} \cdot \mathbf{R}(L) - \omega t}, \quad (15.158)$$

where $\mathbf{R}(L) = l_1 \mathbf{a}_1 + l_2 \mathbf{a}_2$, and substituting in (15.157) we obtain

$$\omega^2(\mathbf{q}) \mathbf{U}_\alpha(\ell\kappa|p) = \sum_{\ell', \kappa', \beta} D_{\alpha\beta} \begin{pmatrix} \ell & \ell' \\ \kappa & \kappa' \end{pmatrix} \mathbf{U}_\beta(\ell'\kappa'|p), \quad (15.159)$$

where p is a phonon branch index. The dynamical matrix is defined by

$$D_{\alpha\beta} \begin{pmatrix} \ell & \ell' \\ \kappa & \kappa' \end{pmatrix} = \frac{1}{\sqrt{M_\kappa M_{\kappa'}}} \sum_{L'} \Phi_{\alpha\beta} \begin{pmatrix} \ell & 0 \\ \kappa & \kappa' \end{pmatrix} \begin{pmatrix} \ell' & L' \\ \kappa' & \kappa' \end{pmatrix} e^{i\mathbf{q} \cdot (\mathbf{R}(L) - \mathbf{R}(L'))}. \quad (15.160)$$

Appendix 1 Coulomb interactions and the method of Ewald summations

Because the Coulomb interaction potential is $\propto 1/r$, and the number of ions at a distance r , interacting with an ion at the origin is $\propto r^2$, the summation over such contributions diverges. To avoid such divergence when calculating Coulomb forces, Ewald proposed a mathematical trick whereby the contributions from nearby neighbors can be summed in configuration space, while contributions from far neighbors are summed in reciprocal space. (See also references [103, 110, 111].)

The Coulomb contribution to the dynamical matrix of a crystal is written as

$$\begin{aligned} C_{\alpha\beta} \begin{pmatrix} \mathbf{q} \\ \kappa\kappa' \end{pmatrix} &= \sum_{l'} \Phi_{\alpha\beta}^C \begin{pmatrix} 0 & l' \\ \kappa & \kappa' \end{pmatrix} e^{i\mathbf{q} \cdot \mathbf{x}(l')}, \\ \Phi_{\alpha\beta}^C \begin{pmatrix} 0 & l' \\ \kappa & \kappa' \end{pmatrix} &= -Z_\kappa Z_{\kappa'} e^2 \lim_{\mathbf{r} \rightarrow 0} \left[\frac{\partial^2}{\partial x_\alpha \partial x_\beta} \frac{1}{|\mathbf{r} - [\mathbf{x}(l'\kappa') - \mathbf{x}(0\kappa)]|} \right] \\ &= Z_\kappa Z_{\kappa'} e^2 \left[\frac{\delta_{\alpha\beta}}{r^3} - \frac{3x_\alpha x_\beta}{r^5} \right]_{r=|\mathbf{x}(l'\kappa') - \mathbf{x}(0\kappa)|}, \quad (l'\kappa') \neq (0\kappa). \end{aligned} \quad (15.161)$$

The self term is given by

$$\Phi_{\alpha\beta}^C \begin{pmatrix} 0 & 0 \\ \kappa & \kappa \end{pmatrix} = - \sum_{l'\kappa'} \Phi_{\alpha\beta}^C \begin{pmatrix} 0 & l' \\ \kappa & \kappa' \end{pmatrix}. \quad (15.162)$$

The method of Ewald summation yields

$$\begin{aligned} \sum_{l'} \frac{\exp[i\mathbf{q} \cdot \mathbf{x}(l')]}{|\mathbf{r} - [\mathbf{x}(l'\kappa') - \mathbf{x}(0\kappa)]|} &= \frac{4\pi}{v} \sum_{\mathbf{G}} \frac{1}{|\mathbf{G} + \mathbf{q}|^2} e^{i(\mathbf{G} + \mathbf{q}) \cdot [\mathbf{r} + \mathbf{x}(\kappa) - \mathbf{x}(\kappa')]} \\ &\times e^{-(\mathbf{G} + \mathbf{q})^2 / 4\eta^2} \\ &+ \sum_{l'} e^{i\mathbf{q} \cdot \mathbf{x}(l')} \left(\frac{\operatorname{erfc}(\eta x)}{x} \right)_{x = |\mathbf{r} - \mathbf{x} \begin{pmatrix} l' & 0 \\ \kappa' & \kappa \end{pmatrix}|}. \end{aligned} \quad (15.163)$$

When this is substituted back in (15.161) we obtain

$$\begin{aligned} C_{\alpha\beta} \begin{pmatrix} \mathbf{q} \\ \kappa\kappa' \end{pmatrix} &= Z_{\kappa} Z_{\kappa'} e^2 \left[\mathcal{B}_{\alpha\beta} \begin{pmatrix} \mathbf{q} \\ \mathbf{x}(\kappa) - \mathbf{x}(\kappa') \end{pmatrix} \right. \\ &\left. - \mathcal{C}_{\alpha\beta} \begin{pmatrix} \mathbf{q} \\ \mathbf{x}(\kappa) - \mathbf{x}(\kappa') \end{pmatrix} \right], \quad \kappa \neq \kappa', \end{aligned} \quad (15.164)$$

where

$$\mathcal{B}_{\alpha\beta} \begin{pmatrix} \mathbf{q} \\ \mathbf{x} \end{pmatrix} = \frac{4\pi}{v} \sum_{\mathbf{G}} \frac{(\mathbf{G} + \mathbf{q})_{\alpha} (\mathbf{G} + \mathbf{q})_{\beta}}{|\mathbf{G} + \mathbf{q}|^2} e^{i(\mathbf{G} + \mathbf{q}) \cdot \mathbf{x}} e^{-(\mathbf{G} + \mathbf{q})^2 / 4\eta^2} \quad (15.165)$$

and

$$\begin{aligned} \mathcal{C}_{\alpha\beta} \begin{pmatrix} \mathbf{q} \\ \mathbf{x} \end{pmatrix} &= \sum_{l'} e^{i\mathbf{q} \cdot \mathbf{x}(l')} \left[\frac{(\mathbf{x}(l') - \mathbf{x})_{\alpha} (\mathbf{x}(l') - \mathbf{x})_{\beta}}{|\mathbf{x}(l') - \mathbf{x}|^5} \right] \\ &\times \left(\operatorname{erfc}(y) + \frac{\exp[-y^2]}{\sqrt{\pi}} (4y^3 + 6y) \right) - \frac{\delta_{\alpha\beta}}{|\mathbf{x}(l') - \mathbf{x}|^3} \\ &\times \left(\operatorname{erfc}(y) + \frac{2y}{\sqrt{\pi}} \exp[-y^2] \right), \end{aligned} \quad (15.166)$$

$$y = \eta |\mathbf{x}(l') - \mathbf{x}|. \quad (15.167)$$

Rapid convergence of the $\mathcal{B}$ and $\mathcal{C}$ series is obtained by proper choice of η , in practice,

$$\eta \sim \frac{1}{\text{unit-cell dimension}}.$$

The leading term in $\mathcal{B}$ is of the form

$$\frac{4\pi}{v} \frac{q_{\alpha} q_{\beta}}{|\mathbf{q}|^2} \exp(-q^2 / 4\eta^2).$$

The factor $q_\alpha q_\beta / |\mathbf{q}|^2$ has no unique limit for $\mathbf{q} \rightarrow 0$. Its value depends on the direction of $\mathbf{q}$ as it approaches zero. To understand the physics behind this peculiarity we write

$$\begin{aligned} B_{\alpha\beta} \left(\frac{\mathbf{q}}{\mathbf{x}} \right) &= \frac{4\pi}{v} \left[\sum_{\mathbf{G}}' \frac{(\mathbf{G} + \mathbf{q})_\alpha (\mathbf{G} + \mathbf{q})_\beta}{|\mathbf{G} + \mathbf{q}|^2} e^{i(\mathbf{G} + \mathbf{q}) \cdot \mathbf{x}} e^{-(\mathbf{G} + \mathbf{q})^2 / 4\eta^2} \right. \\ &\quad \left. + \frac{q_\alpha q_\beta}{|\mathbf{q}|^2} [\exp(-q^2 / 4\eta^2) - 1] + \frac{q_\alpha q_\beta}{|\mathbf{q}|^2} \right]. \end{aligned} \quad (15.168)$$

The term

$$\frac{q_\alpha q_\beta}{|\mathbf{q}|^2} [1 - \exp(-q^2 / 4\eta^2)]$$

vanishes at $\mathbf{q} = 0$. If we multiply the last term by $Z_\kappa Z_{\kappa'} e^2$ we find that

$$\lim_{\mathbf{q} \rightarrow 0} Z_\kappa Z_{\kappa'} \frac{4\pi e^2}{v} \frac{q_\alpha q_\beta}{|\mathbf{q}|^2},$$

is just the Fourier transform of a macroscopic electric field, its value will depend on the direction $\mathbf{q}$ approaches zero. This is just the electric field associated with the array of dipoles associated with an optic mode of $\mathbf{q} = 0$.

To understand the source of this field, we consider a dipolar array, where a dipole is placed at each site ($l\kappa$) with moment

$$\mathbf{p}(l\kappa) = \mathbf{p}(\kappa) e^{i\mathbf{q} \cdot \mathbf{x}(l\kappa)}$$

with $|\mathbf{q}|$ approaching zero. We express the polarization density as

$$P(\mathbf{x}) = \sum_{l\kappa} \mathbf{p}(l\kappa) \delta(\mathbf{x} - \mathbf{x}(l\kappa)) = \sum_{\mathbf{G}} \mathbf{p}(\mathbf{G}) e^{i(\mathbf{q} + \mathbf{G}) \cdot \mathbf{x}}.$$

The macroscopic polarization is just the $\mathbf{G} = \mathbf{0}$ term, namely,

$$P(\mathbf{x}) = \mathbf{p}(0) e^{i\mathbf{q} \cdot \mathbf{x}}, \quad \mathbf{p}(0) = \frac{1}{\Omega_0} \sum_{\kappa} \mathbf{p}(\kappa). \quad (15.169)$$

From Maxwell's equations we obtain

$$\nabla \times \nabla \times \mathbf{E} = -\frac{1}{c^2} \frac{\partial \mathbf{D}}{\partial t}, \quad \mathbf{D} = \mathbf{E} + 4\pi \mathbf{P}$$

or

$$\nabla \times \nabla \times \mathbf{E} + \frac{1}{c^2} \frac{\partial \mathbf{E}}{\partial t} = -\frac{1}{c^2} \frac{\partial \mathbf{P}}{\partial t}.$$

With $\mathbf{E} = \mathbf{E}^0 e^{i\mathbf{q} \cdot \mathbf{x} - \omega t}$, $\mathbf{P} = \mathbf{P}^0 e^{i\mathbf{q} \cdot \mathbf{x} - \omega t}$ we get

$$\sum_{\beta} \left[\delta_{\alpha\beta} - \frac{q_\alpha q_\beta}{|\mathbf{q}|^2} - \frac{\omega^2}{c^2 q^2} \delta_{\alpha\beta} \right] E_{\beta}^0 = \frac{4\pi\omega^2}{c^2 q^2} P_{\alpha}^0,$$

with solution

$$E_{\alpha}^0 = -4\pi \sum_{\beta} \frac{q_\alpha q_\beta}{|\mathbf{q}|^2} P_{\beta}^0 + \frac{4\pi}{n^2 - 1} \sum_{\beta} \left(\delta_{\alpha\beta} - \frac{q_\alpha q_\beta}{|\mathbf{q}|^2} \right) P_{\beta}^0,$$

where $n = cq/\omega$. Taking the electrostatic limit, by setting $c \rightarrow \infty$, we obtain

$$E_\alpha^0 = -4\pi \sum_\beta \frac{q_\alpha q_\beta}{|\mathbf{q}|^2} P_\beta^0. \quad (15.170)$$

Substituting (15.169) in (15.170) yields

$$E_\alpha^0 = -\frac{4\pi}{\Omega_0} \sum_{\kappa\beta} \frac{q_\alpha q_\beta}{|\mathbf{q}|^2} p_\beta(\kappa).$$

For a normal mode ($\mathbf{q}j$) the displacement at site ($l\kappa$) is $u_\alpha(l\kappa) = M_\kappa^{-1/2} \mathbf{e}_\alpha(\kappa|\mathbf{q}j) e^{i\mathbf{q}\cdot\mathbf{x}}(l\kappa)$, so that

$$p_\alpha(l\kappa) = Z_\kappa e u_\alpha(l\kappa) = Z_\kappa e M_\kappa^{-1/2} \mathbf{e}_\alpha(\kappa|\mathbf{q}j) e^{i\mathbf{q}\cdot\mathbf{x}}(l\kappa)$$

and, hence

$$p_\alpha(\kappa) = Z_\kappa e M_\kappa^{-1/2} \mathbf{e}_\alpha(\kappa|\mathbf{q}j).$$

Finally, the self term can be written as

$$\begin{aligned} C_{\alpha\beta} \begin{pmatrix} \mathbf{q} \\ \kappa\kappa \end{pmatrix} &= \sum_{l'}^l \Phi_{\alpha\beta}^C \begin{pmatrix} 0 & l' \\ \kappa & \kappa \end{pmatrix} e^{i\mathbf{q}\cdot\mathbf{x}}(l') + \Phi_{\alpha\beta}^C \begin{pmatrix} 0 & 0 \\ \kappa & \kappa \end{pmatrix} \\ &= \sum_{l'}^l \Phi_{\alpha\beta}^C \begin{pmatrix} 0 & l' \\ \kappa & \kappa \end{pmatrix} \left(e^{i\mathbf{q}\cdot\mathbf{x}}(l') - 1 \right) \\ &\quad - \sum_{\kappa'}^l \sum_{l'}^l \Phi_{\alpha\beta}^C \begin{pmatrix} 0 & l' \\ \kappa & \kappa' \end{pmatrix}. \end{aligned} \quad (15.171)$$

By adding and subtracting $\Phi_{\alpha\beta}^C \begin{pmatrix} 0 & 0 \\ \kappa & \kappa \end{pmatrix}$ we obtain

$$\begin{aligned} C_{\alpha\beta} \begin{pmatrix} \mathbf{q} \\ \kappa\kappa \end{pmatrix} &= \sum_{l'}^l \Phi_{\alpha\beta}^C \begin{pmatrix} 0 & l' \\ \kappa & \kappa \end{pmatrix} e^{i\mathbf{q}\cdot\mathbf{x}}(l') - \sum_{l'}^l \Phi_{\alpha\beta}^C \begin{pmatrix} 0 & l' \\ \kappa & \kappa \end{pmatrix} \\ &\quad - \sum_{\kappa'}^l \sum_{l'}^l \Phi_{\alpha\beta}^C \begin{pmatrix} 0 & l' \\ \kappa & \kappa' \end{pmatrix} \\ &= (Z_\kappa e)^2 \left(\mathcal{B}(\mathbf{q}, 0) - \mathcal{C}(\mathbf{q}, 0) \right) \\ &\quad - (Z_\kappa e)^2 \left(\mathcal{B}(\mathbf{q} \equiv 0, 0) - \mathcal{C}(\mathbf{q} \equiv 0, 0) \right) \\ &\quad - \sum_{\kappa'}^l Z_\kappa Z_{\kappa'} e^2 \left(\mathcal{B}(\mathbf{q} \equiv 0, \mathbf{x}(\kappa) - \mathbf{x}(\kappa')) - \mathcal{C}(\mathbf{q} \equiv 0, \mathbf{x}(\kappa) - \mathbf{x}(\kappa')) \right). \end{aligned} \quad (15.172)$$

The ill-defined terms in (15.172), namely

$$\begin{aligned} \frac{4\pi}{v} \left[\frac{G_\alpha G_\beta}{G^2} \right]_{\mathbf{G}=\mathbf{0}} &\Rightarrow \mathcal{B}(\mathbf{q} \equiv 0, 0), \\ \left[\frac{x_\alpha(l)x_\beta}{|\mathbf{x}(l)|^5} \left(3 + \frac{4\eta^3 |\mathbf{x}(l)|^3 + 6\eta |\mathbf{x}(l)|}{\sqrt{\pi}} \right) \right. \\ &\quad \left. - \frac{\delta_{\alpha\beta}}{|\mathbf{x}(l)|^3} \left(1 + \frac{2\eta |\mathbf{x}(l)|}{\sqrt{\pi}} \right) \right]_{l=0} \Rightarrow \mathcal{C}(\mathbf{q}, 0). \end{aligned} \quad (15.173)$$

The total contribution of the $\mathcal{B}$ terms is $-Z_\kappa e (\sum_{\kappa'} Z_{\kappa'} e) \sum \frac{4\pi}{v} \left[\frac{G_\alpha G_\beta}{G^2} \right]_{\mathbf{G}=\mathbf{0}}$ which vanishes because of charge neutrality. Similar arguments apply to the $\mathcal{C}$ contributions. Thus, we can omit these terms from the outset and we write

$$\begin{aligned} C_{\alpha\beta} \left(\begin{matrix} \mathbf{q} \\ \kappa\kappa \end{matrix} \right) &= (Z_\kappa e)^2 \left(\mathcal{B}'(\mathbf{q}, 0) - \mathcal{C}'(\mathbf{q}, 0) \right) \\ &\quad - (Z_\kappa e)^2 \left(\mathcal{B}'(\mathbf{q} \equiv 0, 0) - \mathcal{C}'(\mathbf{q} \equiv 0, 0) \right) \\ &\quad - \sum_{\kappa'} Z_\kappa Z_{\kappa'} e^2 \left(\mathcal{B}'(\mathbf{q} \equiv 0, \mathbf{x}(\kappa) - \mathbf{x}(\kappa')) - \mathcal{C}'(\mathbf{q} \equiv 0, \mathbf{x}(\kappa) - \mathbf{x}(\kappa')) \right) \end{aligned} \quad (15.174)$$

where the primes on $\mathcal{B}$ and $\mathcal{C}$ indicate omission of the ill-defined terms. We now define the dynamical matrix $\mathbf{M}^C$ as

$$\begin{aligned} M_{\alpha\beta}^C \left(\begin{matrix} \mathbf{q} \\ \kappa\kappa' \end{matrix} \right) &= \exp[-i\mathbf{q} \cdot [\mathbf{x}(\kappa) - \mathbf{x}(\kappa')]] C_{\alpha\beta} \left(\begin{matrix} \mathbf{q} \\ \kappa\kappa' \end{matrix} \right) \\ &= \bar{M}_{\alpha\beta}^C \left(\begin{matrix} \mathbf{q} \\ \kappa\kappa' \end{matrix} \right) + Z_\kappa Z_{\kappa'} \frac{4\pi e^2}{v} \frac{q_\alpha q_\beta}{|\mathbf{q}|^2}. \end{aligned} \quad (15.175)$$

Appendix 2 Electronic effects on phonons in insulators and semiconductors

In ionic and covalent crystals the electronic charge is concentrated at the ionic sites or at the site of the covalent bond. Significant deviations in the measured phonon spectra from those obtained from a point ion (or electron) model have been observed, which can only be explained by displacements (or deformations) of the electronic charges from their equilibrium positions (or distributions) due to the motion of the ions. This led to the proposition and formulation of several phenomenological microscopic models aimed at explaining the origin of these deviations.

To describe the physics of these phenomenological models we start by considering the solid as consisting of an ion and an electron system. Electronic structure calculations provide us with the ground-state electronic density, $n^{(0)}(\mathbf{r})$, which is established in response

to the electron-ion potential corresponding to the ion equilibrium configuration, which we write as

$$V_{\text{ei}}^{(0)}(\mathbf{r}) = \sum_{\mathbf{R}_L} v(\mathbf{r} - \mathbf{R}_L),$$

where $L \equiv (l, \kappa)$. $n^{(0)}(\mathbf{r})$ has to belong to the invariant Irrep. The infinitesimal displacements of the ions from their equilibrium gives rise to an extra contribution to V_{ei} ,

$$V_{\text{ei}}^{(1)} = \sum_L \nabla_{\mathbf{R}_L} v(\mathbf{r} - \mathbf{R}_L) \cdot \mathbf{u}_L = - \sum_L \nabla v(\mathbf{r} - \mathbf{R}_L) \cdot \mathbf{u}_L. \quad (15.176)$$

The first-order change in the electron density is, by perturbation theory, of the form

$$n^{(1)}(\mathbf{r}) = \int d\mathbf{r}' \chi(\mathbf{r}, \mathbf{r}') V_{\text{ei}}^{(1)}(\mathbf{r}'), \quad (15.177)$$

where $\chi(\mathbf{r}, \mathbf{r}')$ is known as the static density-density response function. It measures the change in density when a perfect crystal is subject to a small perturbing potential. It is a property of the perfect system. The translational invariance symmetry of the crystal ensures that

$$\chi(\mathbf{r} + \mathbf{t}, \mathbf{r}' + \mathbf{t}) = \chi(\mathbf{r}, \mathbf{r}'). \quad (15.178)$$

The change in the total electron energy to second order in $V^{(1)\text{ei}}$ is then put in the following form:

$$\begin{aligned} E^{(2)} = & - \sum_{l\kappa\alpha} \int d\mathbf{r} n^{(1)}(\mathbf{r}) \frac{\partial v(\mathbf{r} - \mathbf{R}_{l\kappa})}{\partial r_\alpha} u_{l\kappa\alpha} \\ & + \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' n^{(1)}(\mathbf{r}) [v_c(\mathbf{r} - \mathbf{r}') + K(\mathbf{r}, \mathbf{r}')] n^{(1)}(\mathbf{r}'), \end{aligned} \quad (15.179)$$

where $v_c(\mathbf{r} - \mathbf{r}')$ is the electron-electron Coulomb potential and $K(\mathbf{r}, \mathbf{r}')$ is the exchange-correlation potential.

Since the electrons are fairly well localized on the ionic (or covalent) sites, we can attribute the first-order change in the electron density to various sites,

$$n^{(1)}(\mathbf{r}) = \sum_{l\kappa} \rho^{(1)}(\mathbf{r}, l\kappa), \quad (15.180)$$

where $\rho^{(1)}(\mathbf{r}, l\kappa)$ vanishes for $\mathbf{r}$ more than one or two cells from the site $(l\kappa)$; it is reminiscent of Wannier functions. We now expand $\rho^{(1)}(\mathbf{r}, l\kappa)$ in terms of a complete set of functions $^{(\mu)}\phi_j(\mathbf{r})$ which are bases of Irreps of the local site-symmetry group:

$$\rho^{(1)}(\mathbf{r}, l\kappa) = \sum_{\mu, j} ^{(\mu)}\phi_j(\mathbf{r} - \mathbf{R}_{l\kappa}) P_{\mu, j}(l\kappa). \quad (15.181)$$

We are leaving the basis functions general for the time being, restricting them only to the requirement of the existence of any set of functions ϕ_n such that $\int d\mathbf{r} ^{(\mu)}\phi_j(\mathbf{r}) ^{(\nu)}$

$\phi_{jj'}(\mathbf{r}) = \delta_{\mu\nu} \delta_{jj'}$. Substituting (15.181) into (15.180), we get

$$\begin{aligned}
 E^{(2)} = & - \sum_{l\kappa\alpha, l'\kappa'; \mu j} \int d\mathbf{r}^{(\mu)} \phi_j(\mathbf{r} - \mathbf{R}_{l'\kappa'}) \frac{\partial v(\mathbf{r} - \mathbf{R}_{l\kappa})}{\partial r_\alpha} u_{l\kappa\alpha} P_{\mu j}(l'\kappa') \\
 & + \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}'^{(\mu)} \phi_j(\mathbf{r}) [v_c(\mathbf{r} - \mathbf{r}' + \mathbf{R}_{l\kappa} - \mathbf{R}_{l'\kappa'}) \\
 & + K(\mathbf{r} + \mathbf{R}_{l\kappa}, \mathbf{r}' + \mathbf{R}_{l'\kappa'})]^{(\mu)} \phi_j(\mathbf{r}') P_{\mu j}(l\kappa) P_{\mu j}(l'\kappa') \\
 = & \mathbf{u} \cdot \bar{T} \cdot \mathbf{P} + \frac{1}{2} \mathbf{P} \cdot \bar{S} \cdot \mathbf{P}
 \end{aligned} \tag{15.182}$$

This is the most general form of the electronic contribution to the potential energy. If we choose only three functions ϕ_n with p -symmetry, we get the dipolar shell model. If we take an additional s -like function for the basis, we include the effect of a “breathing-shell” model. In a similar fashion, if we choose the functions to be Gaussians centered on the covalent bond charge sites of semiconductors, we have the “bond-charge” model. $P_{\mu j}(l\kappa)$ are some kind of moments of the change of local electronic charge density,

$$P_{\mu j}(l\kappa) = \int d\mathbf{r}^{(\mu)} \phi_j(\mathbf{r} - \mathbf{R}_{l\kappa}) \rho^{(1)}(\mathbf{r}, l\kappa). \tag{15.183}$$

Finally, we should emphasize the fact that we still have to include direct ion-ion interactions, which, as we know by now, have the form

$$\frac{1}{2} \mathbf{U} \cdot [\overleftrightarrow{C} + \overleftrightarrow{R}] \cdot \mathbf{U},$$

where $\overleftrightarrow{C}$ and $\overleftrightarrow{R}$ are the dynamical matrix contributions from Coulomb and short-range interactions, respectively.

The shell model

If we neglect the electronic contributions to the phonon dispersion relations, we have the equations of motion for the rigid ion model, namely,

$$\omega^2 \overleftrightarrow{M}_d \mathbf{U} = [\overleftrightarrow{R} + \overleftrightarrow{Z}_d \overleftrightarrow{C} \overleftrightarrow{Z}_d] \mathbf{U}, \tag{15.184}$$

where the subscript d indicates diagonal matrices. The components of the matrix $\overleftrightarrow{C}$ are calculated using the Ewald summation method.

The shell model allows for the inclusion of the electronic contributions as follows: Each ion is visualized as consisting of a positive core, with charge X , and a negative outer shell of valence electrons, with charge Y . Each electron shell is coupled to its core by a harmonic potential, with force constant K , and is allowed to be displaced, without deformation relative to it, thus giving rise to ion *polarizability*. The polarization may arise either through harmonic forces involving its neighbors or in the presence of an electric field. In the shell model the electronic shell is not allowed to deform, it is only allowed to have a displacement vector; this model corresponds to a vector Rep of the electronic degrees of freedom. If the shell is allowed to deform, the deformation must be a symmetry-adapted one. The *breathing-shell* model allows for a deformation that belongs to the invariant Irrep, and so on.

For a diatomic crystal, charge neutrality constraints require that

$$X_1 + Y_1 = Z_1, \quad X_2 + Y_2 = Z_2, \quad Z_1 + Z_2 = 0, \quad (15.185)$$

where Z_i is the total static charge of ion i . We extend the particle labeling to the ionic shells, namely:

	κ	Charge	Displacement	Force constants	
+ve core	1	$X_1 e$	u_1^c	core-core	D
-ve core	2	$X_2 e$	u_1^s	+ve core-shell	K_1
+ve shell	3	$Y_1 e$	u_2^c	-ve core-shell	K_2
-ve shell	4	$Y_2 e$	u_2^s	shell-shell	S

We further define

$$W_i = u_i^s - u_i^c,$$

as the relative core-shell displacement. We consider the simple case of a polarizable negative ion and a rigid positive ion. Writing the equation of motion for the negative shell, we obtain

$$K W_2 - S [u_2^c + W_2 - u_1^c] + Y_2 e \mathcal{E} = 0,$$

where $\mathcal{E}$ is the local electric field. The dipole moment of an ion pair is

$$Ze [u_1^c - u_2^c] + Y_2 e W_2, \quad Z = |Z_1| = |Z_2|,$$

which after eliminating W_2 becomes

$$\left(Ze + \frac{Y_2 e S}{K + S} \right) [u_1^c - u_2^c] + \frac{(Y_2 e)^2}{K + S} \mathcal{E}.$$

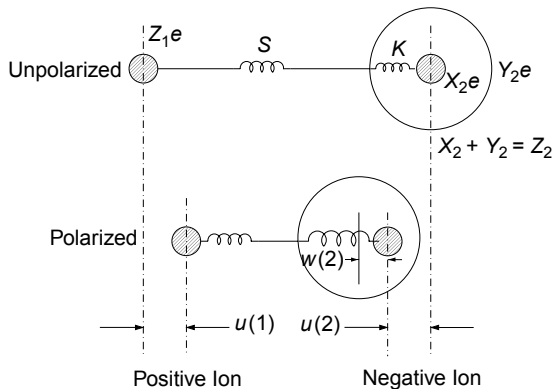


Fig. 15.6. Schematic of a pair of ions where only the negative ion is polarizable.

We now define the negative ion polarizability as

$$\alpha_- = \frac{(Y_2 e)^2}{K + S},$$

and the additional dipole moment $((Y_2 e S)/(K + S)) [u_1^c - u_2^s]$ arises from the short-range mechanical polarizability d , defined as

$$d = -\frac{Y_2 e S}{K + S}.$$

Equations of motion

Following Cochran *et al.*, we define the potential energy of the core-shell model as

$$\begin{aligned} \mathcal{V} &= \Phi^{(2)} + \sum_{l\kappa, \alpha\beta} K_{\alpha\beta}(\kappa) [u_\alpha^c(l\kappa) - u_\alpha^s(l\kappa)] [u_\beta^c(l\kappa) - u_\beta^s(l\kappa)] \\ &= \Phi^{(2)} + \sum_{l\kappa, \alpha\beta} K_{\alpha\beta}(\kappa) w_\alpha(l\kappa) w_\beta(l\kappa). \end{aligned} \quad (15.186)$$

For the case K is a scalar, the last term reduces to $\sum_{l\kappa, \alpha} K(\kappa) w_\alpha^2(l\kappa)$. The first term is given by

$$\begin{aligned} \Phi^{(2)} &= \sum_{\substack{l l', \kappa \kappa' \\ \alpha \beta}} \left[\Phi_{\alpha\beta}^{(cc)} \begin{pmatrix} l & l' \\ \kappa & \kappa' \end{pmatrix} u_\alpha^c(l\kappa) u_\beta^c(l'\kappa') + \Phi_{\alpha\beta}^{(cs)} \begin{pmatrix} l & l' \\ \kappa & \kappa' \end{pmatrix} u_\alpha^c(l\kappa) u_\beta^s(l'\kappa') \right. \\ &\quad \left. + \Phi_{\alpha\beta}^{(sc)} \begin{pmatrix} l & l' \\ \kappa & \kappa' \end{pmatrix} u_\alpha^s(l\kappa) u_\beta^c(l'\kappa') + \Phi_{\alpha\beta}^{(ss)} \begin{pmatrix} l & l' \\ \kappa & \kappa' \end{pmatrix} u_\alpha^s(l\kappa) u_\beta^s(l'\kappa') \right]. \end{aligned} \quad (15.187)$$

Making the substitution $\mathbf{u}(l\kappa) = \mathbf{u}^c(l\kappa)$, $\mathbf{w}(l\kappa) = \mathbf{u}^s(l\kappa) - \mathbf{u}^c(l\kappa)$, we obtain

$$\begin{aligned} \Phi^{(2)} &= \sum_{\substack{l l', \kappa \kappa' \\ \alpha \beta}} \left[\Phi_{\alpha\beta}^{(R)} \begin{pmatrix} l & l' \\ \kappa & \kappa' \end{pmatrix} u_\alpha(l\kappa) u_\beta(l'\kappa') + \Phi_{\alpha\beta}^{(T)} \begin{pmatrix} l & l' \\ \kappa & \kappa' \end{pmatrix} u_\alpha(l\kappa) w_\beta(l'\kappa') \right. \\ &\quad \left. + \Phi_{\alpha\beta}^{(T')} \begin{pmatrix} l & l' \\ \kappa & \kappa' \end{pmatrix} w_\alpha(l\kappa) u_\beta(l'\kappa') + \Phi_{\alpha\beta}^{(S)} \begin{pmatrix} l & l' \\ \kappa & \kappa' \end{pmatrix} w_\alpha(l\kappa) w_\beta(l'\kappa') \right]. \end{aligned} \quad (15.188)$$

The adiabatic approximation here means that we set the electron mass to zero, and after taking temporal and spatial Fourier transformations we obtain

$$\omega^2(\mathbf{q}) \mathbf{M}_d \mathbf{U} = \left[\mathbf{R} + \mathbf{Z}_d \mathbf{C} \mathbf{Z}_d \right] \mathbf{U} + \left[\mathbf{T} + \mathbf{Z}_d \mathbf{C} \mathbf{Y}_d \right] \mathbf{W}, \quad (15.189)$$

$$\mathbf{0} = \left[\mathbf{T}^\dagger + \mathbf{Y}_d \mathbf{C} \mathbf{Z}_d \right] \mathbf{U} + \left[\boldsymbol{\zeta} + \mathbf{Y}_d \mathbf{C} \mathbf{Y}_d \right] \mathbf{W}. \quad (15.190)$$

$$\omega^2(\mathbf{q}) \mathbf{M} \mathbf{U} = \left[\mathbf{R} + \mathbf{Z}_d \mathbf{C} \mathbf{Z}_d \right] \mathbf{U} - \left[\mathbf{T} + \mathbf{Z}_d \mathbf{C} \mathbf{Y}_d \right] \left[\boldsymbol{\zeta} + \mathbf{Y}_d \mathbf{C} \mathbf{Y}_d \right]^{-1} \left[\mathbf{T}^\dagger + \mathbf{Y}_d \mathbf{C} \mathbf{Z}_d \right] \mathbf{U}. \quad (15.191)$$

Exercises

- 15.1 NaCl belongs to the space-group $Fm\bar{3}m$ (O_h^5). The $\text{Na}^+ - \text{Cl}^-$ bond has C_{4v} symmetry, while the Na–Na and Cl–Cl bonds have mm . Determine the forms of the force constant matrices corresponding to these two bond types.
- 15.2 **The rigid ion model:** One of the early models for the dynamics of alkali halides, proposed by Born, considers an interionic potential of the form

$$\Phi(\kappa\kappa'|r) = \frac{Z_\kappa Z_{\kappa'} e^2}{r} + a_{\kappa\kappa'} e^{-br} = \Phi^{(C)}(r) + \Phi^{(R)}(r),$$

where the last term is the short-range Born–Mayer type nearest-neighbor repulsive potential. Consider, here, the case of NaCl, $\text{Na}^{+1}(\kappa = 1)$ and $\text{Cl}^{-1}(\kappa = 2)$, with $Z_1 = 1$ and $Z_2 = -1$.

- (i) Show that the energy per primitive cell is given by

$$\Phi_0 = -\alpha \frac{e^2}{r_0} + 6\Phi^{(R)},$$

where $r_0 = 2.1 \text{ \AA}$ is the nearest-neighbor distance in NaCl, and

$$\alpha = \sum_j \frac{\pm 1}{\rho_{0j}}$$

is the Madelung constant. The $+$ sign involves even neighbors and the $-$ sign odd ones, and $\rho_{0j} = r_{0j}/r_0$.

- (ii) The equilibrium value r_0 is obtained by setting $\left. \frac{d\Phi(r)}{dr} \right|_{r_0} = 0$. Writing

$$\left(\frac{1}{r} \frac{d\Phi^{(R)}(r)}{dr} \right)_{r_0} = \frac{e^2}{2r_0^3} B,$$

where $2r_0^3 = v_a$ is the primitive cell volume, use the equilibrium condition to express B in terms of α .

- (iii) Calculate α for NaCl with the aid of a simple program.
- (iv) Given that the pressure is expressed as

$$P = -\frac{\partial \Phi}{\partial v_a} = -\frac{1}{6r^2} \frac{\partial \Phi}{\partial r},$$

show that the compressibility κ_B is given by

$$\frac{1}{\kappa_B} = -v_a \left. \frac{\partial P}{\partial v_a} \right|_{r_0} = \frac{1}{18r_0} \left[-2\alpha \frac{e^2}{r_0^3} + \frac{3}{2} A \frac{e^2}{r_0^3} \right] = \frac{1}{12r_0^4} [A + 2B],$$

where we set

$$\left. \frac{d^2 \Phi^{(R)}}{dr^2} \right|_{r_0} = \frac{e^2}{v_a} A.$$

Express A in terms of α and κ_B .

- (v) Given that $\kappa_B = 4.16 \times 10^{-12} \text{ cm}^2/\text{dyne}$, and the value you obtained for α , evaluate A .

- 15.3 (i) Derive expressions for the force constants

$$\Phi_{\alpha\beta}^{(R)} \begin{pmatrix} 0l \\ \kappa\kappa' \end{pmatrix} = \frac{\partial^2 \Phi^{(R)}(0\kappa; l\kappa')}{\partial x_\alpha \partial x_\beta}$$

in terms of A and B defined in Exercise 15.1.

- (ii) Obtain an expression for $R_{\alpha\beta}(\kappa\kappa'|\mathbf{q})$, the short-range contribution to the dynamical matrix. Remember that because the ionic sites have inversion symmetry, all $R_{\alpha\beta}(\kappa\kappa'|\mathbf{q})$ are real.
- (iii) Use the Ewald summation method to evaluate $C_{\alpha\beta}(\kappa\kappa'|\mathbf{q})$ for $\mathbf{q} = [00\xi]$, i.e. the Δ -direction.
- (iv) Show that as $\xi \rightarrow 0$

$$C_{zz}(\kappa\kappa'|\mathbf{0}) = \frac{8\pi e^2}{3v_0}, \quad C_{xx}(\kappa\kappa'|\mathbf{0}) = C_{yy}(\kappa\kappa'|\mathbf{0}) = -\frac{4\pi e^2}{3v_0}.$$

- (v) Show that the corresponding optic modes are

$$\mu \omega_L^2 = \frac{e^2}{v_0} (A + 2B) + \frac{8\pi e^2}{3v_0}, \quad \mu \omega_T^2 = \frac{e^2}{v_0} (A + 2B) - \frac{4\pi e^2}{3v_0}.$$

- (vi) Use the expressions you obtained for $\overleftrightarrow{\mathbf{R}}$ and $\overleftrightarrow{\mathbf{C}}$ to obtain the phonon dispersion curves along the Δ -direction for NaCl, in the rigid ion model.

15.4 **Phonon dispersion curves in diamond:** Diamond belongs to the nonsymorphic space-group $Fd\bar{3}m$.

- (i) As we demonstrated in Appendix 1, the macroscopic electric field is associated with a dipole-moment array that arises from atomic displacements. We may express the polarization density as

$$\mathbf{P} = \sum_{l\kappa} \overleftrightarrow{\mathbf{A}}(l\kappa) \cdot \mathbf{u}(l\kappa)$$

where, as usual, $\mathbf{u}(l\kappa)$ is the displacement from equilibrium position $\mathbf{R}(l\kappa)$. Diamond has two atoms per primitive cell ($[000] + a/4[1,1,1]$). Use the property of invariance under arbitrary displacement, together with $S = (I|\boldsymbol{\tau})$, to show that diamond has no macroscopic polarization associated with its $\mathbf{q} = \mathbf{0}$ modes.

- (ii) The nearest-neighbor (nn) bond $[000] - a/4[1,1,1]$, second-nn bond $[000] - a/2[1,1,0]$ and third nn bond $[000] - a/4[-1,-1,-3]$ have bond-symmetry groups $3m$, mm , and m , respectively. Derive the corresponding symmetry-adapted force constant matrices.
- (iii) Use appropriate coset representatives to obtain force constant matrices belonging to the remaining orbit members of each bond.

- (iv) Construct the dynamical matrix in terms of the force constant matrices obtained above.
- (v) Show that the acoustic and optical modes at the Γ -point, i.e. $\mathbf{q} = \mathbf{0}$, have Γ_{15}^- and Γ_{25}^+ symmetries of O_h , the factor group of O_h^7 . Construct the symmetry-adapted vectors using the corresponding projection operators. (Note that in this case the symmetry-adapted vectors are actually the eigenvectors!)

Table 15.11. *Character table of $\mathbb{S}_\Delta$.*

	Δ_1	Δ_2	Δ'_2	Δ'_1	Δ_5
$(E \mathbf{0})$	1	1	1	1	1
$(U_x \mathbf{0})$	1	1	1	1	1
$(C_{4,x}, C_{4,x}^{-1} \boldsymbol{\tau})$	ζ	$-\zeta$	$-\zeta$	ζ	0
$(\sigma_y, \sigma_z \boldsymbol{\tau})$	ζ	ζ	$-\zeta$	$-\zeta$	0
$(\sigma_{yz}, \sigma_{\bar{y}z} \mathbf{0})$	1	-1	1	-1	0

$$\zeta = \exp[-iqa/4]$$

- (vi) The group of the wavevector along the Δ -direction ($\mathbf{q} = [q, 0, 0]$) is $\mathbb{S}_\Delta = 4mm \otimes \mathcal{T}$, and the corresponding character table is given in Table 15.11. Use Table 15.11 to obtain compatibility relations between Γ and Δ . Show that the eigenvalue problem reduces to two 1×1 and two 2×2 matrices, and determine the corresponding eigenvalues.
- (vii) Repeat the above steps for the Σ and Λ directions.
- (viii) Use the long-wavelength limit of the expression you obtained for the dynamical matrix, to derive the relations between the elastic constants and force constants of diamond. (Use the relations developed in Section 15.3.4.)

16

Experimental measurements and selection rules

16.1 Introduction

The last fifty years of the twentieth century witnessed the development of an array of sophisticated experimental techniques capable of providing precise measurements of a variety of microscopic properties of condensed matter systems, such as geometric and electronic structure, and dynamical modes: phonons, molecular vibrations and rotations, spin-dynamics and spin-waves, to name a few.

Among these techniques we mention neutron scattering, photoelectron emission, atom scattering, and optical techniques such as infra-red spectroscopy, X-ray, Raman, Brillouin and Rayleigh scattering spectroscopies. Moreover, many of them have been applied to study bulk and surface crystallographic structure.

The usefulness of many of these experimental techniques was found to depend on the usage of symmetry-based methods for the analysis of the ensuing data. These symmetry-based methods have become known as *selection rules*.

It is of great importance that the knowledge of the existence of selection rules governing a variety of condensed matter processes, and of the methods whereby such rules may be obtained, be widely disseminated so that the full utilization of group theory may be achieved.

Table 16.1. *Some important characteristics of different experimental probes.*

Probe	Electrons		Neutrons	Light atoms	Photons	
Energy	100 eV LEED	100 keV	10 meV	10–100 meV	10 keV Infra-red X-rays	
Wavelength (λ)	1 Å	~0.05 Å	1 Å	1–0.5 Å	1 μm–1 mm	1 Å
Extinction length (d_{ext})	5 Å	10^2 – 10^3 Å	10^5 Å	0 Å		10^4 Å
Absorption length (α)	10 Å	10^3 – 10^4 Å	10^8 Å		1 μm–1 mm	10^5 Å
Coherence length (ℓ)	100 Å	Å	Å	50–500 Å		10^4 Å

16.2 Selection rules

In all such experiments a beam of well-characterized particles, *the probe*, is directed into the system, whereupon the probe particles interact with the particles or quasi-particles of the system the experiment is studying. This interaction leads to *real* or *virtual* excitations of the relevant quasi-particles; subsequently, the experimental apparatus detects the emerging probe particles, or some other particles, which contain information regarding these excitations, be it changes in energies, spin-orientations, quasi-particle momenta, and so on. Two distinct types of studies arise depending on the detection technique used to examine the emerging probe particles: elastically scattered particles are used to provide structural information about the system, usually of a diffractive nature, while inelastically scattered particles provide information about the dynamical properties of the quasi-particles concerned, and are labeled *spectroscopies*.

An excitation process associated with some experimental probe can be represented by a quantum mechanical operator which we denote by $\mathcal{O}$, and usually involves a transition from an initial to a final state subject to energy conservation; it may be written as

$$\int dx^d \Psi_i \mathcal{O} \Psi_f \quad (16.1)$$

for a d -dimensional system. In Chapter 1 we argued that such an integral would vanish unless the integrand $\mathcal{J}$ is invariant under all operations belonging to $\mathcal{G}$, the group of the Hamiltonian, i.e. the integrand belongs to the invariant Irrep of the group. For simplicity, let us assume that Ψ_i , $\mathcal{O}$, and Ψ_f transform according to Irreps $^{(\mu)}\Gamma$, $^{(\sigma)}\Gamma$, and $^{(\nu)}\Gamma$ of $\mathcal{G}$, respectively. Then $\mathcal{J}$ transforms as the outer-product

$$^{(\mu)}\Gamma \otimes ^{(\sigma)}\Gamma \otimes ^{(\nu)}\Gamma.$$

Consequently, the integral does not vanish if $^{(1)}\Gamma$ appears in the Clebsch–Gordan series expansion, i.e. in the expansion

$$^{(\mu)}\Gamma \otimes ^{(\sigma)}\Gamma \otimes ^{(\nu)}\Gamma = \sum_{\rho} \langle \mu \otimes \sigma \otimes \nu | \rho \rangle ^{(\rho)}\Gamma,$$

$\langle \mu \otimes \sigma \otimes \nu | 1 \rangle \neq 0$; or, using (8.36),

$$\sum_{R \in \mathcal{G}} ^{(\mu)}\chi(R) ^{(\sigma)}\chi(R) ^{(\nu)}\chi(R) \neq 0. \quad (16.2)$$

16.2.1 Selection rules for space-groups

In the case of crystalline systems the general selection rule takes the form of an integral

$$\int d^d x \psi_{\mathbf{k}} \mathcal{O} \psi_{\mathbf{k}_s}^*, \quad (16.3)$$

where $\psi_{\mathbf{k}}$, $\mathcal{O}$, and $\psi_{\mathbf{k}_s}$ belong to the space-group Irreps $(^*\mathbf{k}, \mu)\Gamma$, $(^*\mathbf{k}'', \nu)\Gamma$, $(^*\mathbf{k}_s, \sigma)\Gamma$, respectively. The integral (16.3) vanishes when the Kronecker product

$$(^*\mathbf{k}, \mu)\Gamma \otimes (^*\mathbf{k}'', \nu)\Gamma \otimes (^*\mathbf{k}_s, \sigma)\Gamma^* \not\supseteq (^*\mathbf{0}, 1)\Gamma. \quad (16.4)$$

From (8.36) we obtain the frequency of the identity Irrep in the above Kronecker product, $\langle (^*\mathbf{k}, \mu) \otimes (^*\mathbf{k}'', \nu) \otimes (^*\mathbf{k}_s, \sigma)^* | (^*\mathbf{0}, 1) \rangle$, which we denote F , as

$$F = \frac{1}{s} \sum_{(R|\boldsymbol{\tau}+\mathbf{t})} (^*\mathbf{k}, \mu)\chi(R|\boldsymbol{\tau}+\mathbf{t}) (^*\mathbf{k}'', \nu)\chi(R|\boldsymbol{\tau}+\mathbf{t}) \times (^*\mathbf{k}_s, \sigma)\chi^*(R|\boldsymbol{\tau}+\mathbf{t}). \quad (16.5)$$

It is our task now to derive a useful expression for determining F .

The space-group character $(^*\mathbf{k}, \mu)\chi$

The character of the space-group Irrep $(^*\mathbf{k}, \mu)\chi$ can be expressed in terms of characters of the Irrep $(^{\mathbf{k}_1}, \mu)\chi$ of the space-subgroup $\mathbb{S}_{\mathbf{k}_1}$ of $\mathbf{k}_1 \in ^*\mathbf{k}$, from which it is induced.

We expand the space-group $\mathbb{S}$ in terms of left cosets of $\mathbb{S}_{\mathbf{k}_1}$ of the form

$$\mathbb{S} = \sum_{i=1}^{s/s_{\mathbf{k}_1}} (R_i|\boldsymbol{\rho}_i) \mathbb{S}_{\mathbf{k}_1}, \quad (16.6)$$

where $\boldsymbol{\rho}_i$ is the nonprimitive translation associated with the coset representatives. We define the space-subgroups conjugate to $\mathbb{S}_{\mathbf{k}_1}$ in $\mathbb{S}$ as

$$\mathbb{S}_{\mathbf{k}_i} = (R_i|\boldsymbol{\rho}_i)^{-1} \mathbb{S}_{\mathbf{k}_1} (R_i|\boldsymbol{\rho}_i), \quad (16.7)$$

with $(R_1|\boldsymbol{\rho}_1) = (E|\mathbf{0})$. We use the abbreviated notation

$$\mathbb{S}_{\mathbf{k}_i} \equiv (S_i|\boldsymbol{\tau}_i + \mathbf{t}_i) = (E|\mathbf{t}_i)(S_i|\boldsymbol{\tau}_i) \in \mathbb{S}_{\mathbf{k}_i}.$$

Since the $\mathbb{S}_{\mathbf{k}_i}$ are isomorphic to $\mathbb{S}_{\mathbf{k}_1}$, they share the same Irreps. Moreover, the isomorphism, defined by the map

$$\begin{aligned} \mathbb{S}_{\mathbf{k}_i} &= (R_i|\boldsymbol{\rho}_i)^{-1} \mathbb{S}_{\mathbf{k}_1} (R_i|\boldsymbol{\rho}_i) \\ &= (R_i|\boldsymbol{\rho}_i)^{-1} (E|\mathbf{t}_1)(S_1|\boldsymbol{\tau}_1)(R_i|\boldsymbol{\rho}_i) \\ &= (E|R_i^{-1}\mathbf{t}_1)(R_i^{-1}S_1R_i | R_i^{-1}(\boldsymbol{\tau}_1 + S_1\boldsymbol{\rho}_i - \boldsymbol{\rho}_i)) \\ &= (E|\mathbf{t}_i)(S_i|\boldsymbol{\tau}_i), \end{aligned} \quad (16.8)$$

implies that the matrix representative $^{(\mathbf{k}_1, \mu)}\Lambda(\mathcal{S}_{\mathbf{k}_1}) = ^{(\mathbf{k}_1)}\Delta(\mathbf{t})^{(\mu)}\Omega(S_1|\boldsymbol{\tau}_1)$ is mapped onto the matrix representative $^{(\mathbf{k}_i, \mu)}\Lambda(\mathcal{S}_{\mathbf{k}_i}) = ^{(\mathbf{k}_i)}\Delta(\mathbf{t})^{(\mu)}\Omega(S_i|\boldsymbol{\tau}_i)$, and we write

$$\begin{aligned} ^{(\mathbf{k}_i, \mu)}\Lambda(\mathcal{S}_{\mathbf{k}_i}) &= ^{(\mathbf{k}_i)}\Delta(\mathbf{t})^{(\mu)}\Omega(S_1|\boldsymbol{\tau}_1) \\ &= ^{(\mathbf{k}_i)}\Delta(\mathbf{t})^{(\mu)}\Omega\left((R_i|\boldsymbol{\rho}_i)(S_i|\boldsymbol{\tau}_i)(R_i|\boldsymbol{\rho}_i)^{-1}\right), \\ ^{(\mathbf{k}_i, \mu)}\chi(\mathcal{S}_{\mathbf{k}_i}) &= ^{(\mu)}\chi\left((R_i|\boldsymbol{\rho}_i)(S_i|\boldsymbol{\tau}_i)(R_i|\boldsymbol{\rho}_i)^{-1}\right)e^{-i\mathbf{k}_i \cdot \mathbf{t}}. \end{aligned} \quad (16.9)$$

According to (16.8) any element $(R|\boldsymbol{\tau} + \mathbf{t})$ of $\mathbb{S}$ must belong to one of the conjugate groups of $\mathbb{S}_{\mathbf{k}_1}$, and can be mapped onto an element of $\mathbb{S}_{\mathbf{k}_1}$ in the manner of (16.9), namely,

$$\mathbb{S}_{\mathbf{k}_1} = (R_i|\boldsymbol{\rho}_i)(R|\boldsymbol{\tau} + \mathbf{t})(R_i|\boldsymbol{\rho}_i)^{-1}, \quad (16.10)$$

by some coset representative $(R_i|\boldsymbol{\rho}_i)$. An Irrep $^{(\star\mathbf{k}, \mu)}\Gamma$ of $\mathbb{S}$ can be induced from an allowable Irrep $^{(\mathbf{k}_1, \mu)}\Lambda$ of $\mathbb{S}_{\mathbf{k}_1}$ via the *modified ground representation*, where the *blocks* of the matrix Irrep $^{(\star\mathbf{k}, \mu)}\Gamma(R|\boldsymbol{\tau} + \mathbf{t})$ are defined by

$$\left(^{(\star\mathbf{k}, \mu)}\Gamma(R|\boldsymbol{\tau} + \mathbf{t})\right)_{ij} = \begin{cases} ^{(\mu)}\Omega\left((R_i|\boldsymbol{\rho}_i)(R|\boldsymbol{\tau})(R_j|\boldsymbol{\rho}_j)^{-1}\right)e^{-i\mathbf{k}_i \cdot (\boldsymbol{\tau} + \mathbf{t})}, & \text{if } (R_i|\boldsymbol{\rho}_i)(R|\boldsymbol{\tau})(R_j|\boldsymbol{\rho}_j)^{-1} \in \mathbb{S}_{\mathbf{k}_1}, \\ 0, & \text{otherwise.} \end{cases} \quad (16.11)$$

We are now in a position to obtain an explicit expression for $^{(\star\mathbf{k}, \mu)}\chi(R|\boldsymbol{\tau} + \mathbf{t})$:

$$\begin{aligned} ^{(\star\mathbf{k}, \mu)}\chi(R|\boldsymbol{\tau} + \mathbf{t}) &= \sum_i \text{Tr}\left(^{(\star\mathbf{k}, \mu)}\Gamma(R|\boldsymbol{\tau} + \mathbf{t})\right)_{ii} \\ &= \sum_i ^{(\mu)}\chi\left((R_i|\boldsymbol{\rho}_i)(R|\boldsymbol{\tau})(R_i|\boldsymbol{\rho}_i)^{-1}\right)e^{-i\mathbf{k}_i \cdot (\boldsymbol{\tau} + \mathbf{t})} \boldsymbol{\Theta}_{ii}(\mathbf{k}), \end{aligned} \quad (16.12)$$

where

$$\boldsymbol{\Theta}_{ii}(\mathbf{k}) = \begin{cases} 1, & \text{if } (R_i|\boldsymbol{\rho}_i)(R|\boldsymbol{\tau} + \mathbf{t})(R_i|\boldsymbol{\rho}_i)^{-1} \in \mathbb{S}_{\mathbf{k}_1}, \\ 0, & \text{otherwise.} \end{cases}$$

Reduction of the frequency F

Next, we substitute expressions of the form (16.12) for every $^{(\star\mathbf{k}, \alpha)}\chi$ that appears on the r.h.s. of (16.5) for F , and we obtain

$$\begin{aligned} F &= \frac{1}{s} \sum_{(R|\boldsymbol{\tau} + \mathbf{t})} \sum_{ij\ell} \boldsymbol{\Theta}_{ii}(\mathbf{k}) \boldsymbol{\Theta}_{jj}(\mathbf{k}'') \boldsymbol{\Theta}_{\ell\ell}(\mathbf{k}') e^{-i(\mathbf{k}_i + \mathbf{k}_j'' - \mathbf{k}_\ell') \cdot (\boldsymbol{\tau} + \mathbf{t})} \\ &\quad \times ^{(\mu)}\chi\left((R_i|\boldsymbol{\rho}_i)(R|\boldsymbol{\tau})(R_i|\boldsymbol{\rho}_i)^{-1}\right) \\ &\quad \times ^{(\nu)}\chi\left((R_j|\boldsymbol{\rho}_j)(R|\boldsymbol{\tau})(R_j|\boldsymbol{\rho}_j)^{-1}\right) \\ &\quad \times ^{(\sigma)}\chi^*\left((R_\ell|\boldsymbol{\rho}_\ell)(R|\boldsymbol{\tau})(R_\ell|\boldsymbol{\rho}_\ell)^{-1}\right). \end{aligned} \quad (16.13)$$

We first perform the summation of the elements of $\mathbb{T}$, and obtain

$$\begin{aligned}
 F = \frac{1}{p} \sum_{(R|\tau)} \sum_{ij\ell} \delta(\mathbf{k}_i + \mathbf{k}_j'' - \mathbf{k}_\ell') \\
 \times {}^{(\mu)}\chi\left((R_i|\rho_i)(R|\tau)(R_i|\rho_i)^{-1}\right) \Theta_{ii}(\mathbf{k}) \\
 \times {}^{(\nu)}\chi\left((R_j|\rho_j)(R|\tau)(R_j|\rho_j)^{-1}\right) \Theta_{jj}(\mathbf{k}'') \\
 \times {}^{(\sigma)}\chi^*\left((R_\ell|\rho_\ell)(R|\tau)(R_\ell|\rho_\ell)^{-1}\right) \Theta_{\ell\ell}(\mathbf{k}').
 \end{aligned} \quad (16.14)$$

Notice that the summation in (16.14) is carried over the coset representatives of $\mathbb{S}/\mathbb{T}$, namely,

$$\mathbb{S} = \sum_{i=1}^{s/t=p} (R_i|\rho_i)\mathbb{T},$$

where p is the order of the point-group $\mathbb{P}$, isomorphic to $\mathbb{S}/\mathbb{T}$. The delta-function in (16.14) leads to the condition

$$\mathbf{k}_i + \mathbf{k}_j'' - \mathbf{k}_\ell' = \mathbf{0}. \quad (16.15)$$

If no such combination exists for $\mathbf{k}_i \in {}^*\mathbf{k}$, $\mathbf{k}_j'' \in {}^*\mathbf{k}''$, $\mathbf{k}_\ell' \in {}^*\mathbf{k}'$, then the integral (16.1) is zero.

If a combination that satisfies (16.15) exists, which we may label $(\mathbf{k}_1, \mathbf{k}_1'', \mathbf{k}_1')$, then we consider the constraints imposed by the theta-functions, namely,

$$R\mathbf{k}_1 \equiv \mathbf{k}_1, \quad R\mathbf{k}_1'' \equiv \mathbf{k}_1'', \quad R\mathbf{k}_1' \equiv \mathbf{k}_1'. \quad (16.16)$$

We denote the R s that satisfy (16.16) by $R_\cap$, such that

$$R_\cap \in (\mathbb{S}_{\mathbf{k}_1} \cap \mathbb{S}_{\mathbf{k}_1''} \cap \mathbb{S}_{\mathbf{k}_1'})/\mathbb{T} = \frac{\mathbb{S}_\cap}{\mathbb{T}}$$

where $\mathbb{S}_\cap/\mathbb{T}$ is of order r .

Zak pointed out [192] that when an $R_i \notin \mathbb{S}_\cap/\mathbb{T}$ operates on the set $(\mathbf{k}_1, \mathbf{k}_1'', \mathbf{k}_1')$, not only is the condition

$$R_i \mathbf{k}_1 + R_i \mathbf{k}_1'' - R_i \mathbf{k}_1' = \mathbf{0}$$

satisfied, but also the application of the conjugation operators

$$(R_i|\rho_i)(R_\cap|\tau_\cap)(R_i|\rho)^{-1} = (R_\cap|\tau_\cap) \quad (16.17)$$

to these vectors satisfy the relations

$$\begin{aligned}
 R_\cap(R_i\mathbf{k}_1) &= R_i R_\cap R_i^{-1}(R_i\mathbf{k}_1) = R_i\mathbf{k}_1, \\
 R_\cap(R_i\mathbf{k}_1'') &= R_i\mathbf{k}_1'', \\
 R_\cap(R_i\mathbf{k}_1') &= R_i\mathbf{k}_1'.
 \end{aligned}$$

Thus, we obtain p/r new conjugate subgroups

$$(R|\boldsymbol{\rho}) \frac{\mathbb{S}_{\cap}}{\mathbb{T}} (R|\boldsymbol{\rho})^{-1},$$

which contribute p/r equal sums to (16.14). Thus, we finally obtain the simplified expression

$$F = \frac{1}{r} \sum_{(R_{\cap}|\boldsymbol{\tau}_{\cap})} {}^{(\mu)}\chi(R_{\cap}|\boldsymbol{\tau}_{\cap}) {}^{(\nu)}\chi(R_{\cap}|\boldsymbol{\tau}_{\cap}) {}^{(\sigma)}\chi(R_{\cap}|\boldsymbol{\tau}_{\cap}). \quad (16.18)$$

The great simplification to the problem of evaluating the frequency F is clearly present in (16.18):

The summation is only over the group elements of $\mathbb{S}_{\cap}/\mathbb{T}$, which are the coset representatives of $\mathbb{S}/\mathbb{T}$ that are shared among the three subgroups

$$\mathbb{S}_{\mathbf{k}_1}/\mathbb{T}, \quad \mathbb{S}_{\mathbf{k}_1''}/\mathbb{T}, \quad \text{and} \quad \mathbb{S}_{\mathbf{k}_1'}/\mathbb{T}.$$

16.3 Differential scattering cross-sections in the Born approximation

Several of the experimental techniques discussed in this chapter involve the scattering of an incident beam of probe particles and its subsequent detection; this is the case for neutron, atom, electron, and photon scattering. In these cases the incoming and outgoing particles are described by plane-waves $e^{i\mathbf{k}\cdot\mathbf{r}}$. In this section we develop an expression for the angular (wavevector) and energy distribution of the outgoing particle flux.

16.3.1 Scattering states

In the absence of interaction between the probe particles and the target, the Hamiltonian of the composite system is given by

$$\mathcal{H}_0 = \mathcal{H}_p + \mathcal{H}_s, \quad (16.19)$$

where $\mathcal{H}_p$ is a free-particle Hamiltonian representing the probe particles,

$$\mathcal{H}_p = -\frac{\hbar^2}{2M} \nabla^2, \quad \mathcal{H}_p \psi_{\mathbf{k}}(\mathbf{r}) = \frac{\hbar^2 k^2}{2M} \psi_{\mathbf{k}}(\mathbf{r}),$$

where $\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}$, and $\mathcal{H}_s(\{\mathbf{x}_i\})$ is the target, or scatterer, Hamiltonian, where $\mathbf{x}_i$ is the position operator of its i th particle. $\mathcal{H}_s$ has well-defined eigenvalues and eigenvectors

$$\mathcal{H}_s |\phi_j\rangle = E_j |\phi_j\rangle.$$

The interaction is assumed to be of the form

$$\mathcal{V} = \sum_i v(\mathbf{r} - \mathbf{x}_i). \quad (16.20)$$

The total Hamiltonian is then $\mathcal{H} = \mathcal{H}_p + \mathcal{H}_s + \mathcal{H}_I$, and we write the corresponding Schrödinger equation as

$$\mathcal{H} \Psi = E \Psi. \quad (16.21)$$

Next, we expand Ψ in the form

$$\Psi = \sum_{j, \mathbf{k}} \psi_{\mathbf{k}}(\mathbf{r}) \phi_j \quad (16.22)$$

such that $\frac{\hbar^2 k^2}{2M} + E_j = E$. Substituting (16.22) in (16.21) we obtain

$$\frac{\hbar^2}{2M} \sum_{j, \mathbf{k}} \nabla_{\mathbf{r}}^2 |\psi_{\mathbf{k}}\rangle |\phi_j\rangle + E \sum_{j, \mathbf{k}} |\psi_{\mathbf{k}}\rangle |\phi_j\rangle - \sum_{j, \mathbf{k}} E_j |\psi_{\mathbf{k}}\rangle |\phi_j\rangle = \sum_{j, \mathbf{k}} \mathcal{V} |\psi_{\mathbf{k}}\rangle |\phi_j\rangle, \quad (16.23)$$

and taking the scalar product with ϕ_n we get

$$\frac{\hbar^2}{2M} \nabla_{\mathbf{r}}^2 |\psi_{\mathbf{k}}\rangle + [E - E_n] |\psi_{\mathbf{k}}\rangle = \langle \phi_n | \mathcal{V} | \psi_{\mathbf{k}} \rangle,$$

or

$$[\nabla_{\mathbf{r}}^2 + \mathcal{E}] |\psi_{\mathbf{k}}\rangle = \langle \phi_n | \mathcal{U} | \psi_{\mathbf{k}} \rangle, \quad (16.24)$$

where $\mathcal{E} = 2M(E - E_n)/\hbar^2$ and $\mathcal{U} = 2M\mathcal{V}/\hbar^2$.

To obtain a solution to this equation we use the Green function of the Helmholtz equation,

$$[\nabla^2 + E] G^{(\pm)}(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}'),$$

where, in the context of scattering, the superscript $\pm$ indicates outgoing and incoming solutions, respectively, namely

$$G^{(\pm)}(\mathbf{r}, \mathbf{r}') = -\frac{1}{4\pi} \frac{\exp[\pm ik|\mathbf{r} - \mathbf{r}'|]}{|\mathbf{r} - \mathbf{r}'|}.$$

The solutions for the outgoing and incoming scattering wavefunctions are written with the aid of the Lippmann-Schwinger equation as

$$\begin{aligned} \psi_{\mathbf{k}}^{(\pm)}(\mathbf{r}) &= \frac{e^{\pm i\mathbf{k} \cdot \mathbf{r}}}{(2\pi)^{3/2}} + \int d\mathbf{r}' G^{(\pm)}(\mathbf{r}, \mathbf{r}') \langle \phi_n | \mathcal{U}(\mathbf{r}') | \psi_{\mathbf{k}}^{(\pm)}(\mathbf{r}') \rangle \\ &= \frac{e^{\pm i\mathbf{k} \cdot \mathbf{r}}}{(2\pi)^{3/2}} - \frac{1}{4\pi} \int d\mathbf{r}' \frac{\exp[\pm ik_s|\mathbf{r} - \mathbf{r}'|]}{|\mathbf{r} - \mathbf{r}'|} \langle \phi_n | \mathcal{U}(\mathbf{r}') | \psi_{\mathbf{k}}^{(\pm)}(\mathbf{r}') \rangle, \end{aligned} \quad (16.25)$$

where $\hbar^2 k^2/2M = E$, while $\hbar^2 k_s^2/2M = E - E_n$. Notice that the scattering states carry the label $\mathbf{k}$, which is a good quantum number only in the asymptotic limit of a free particle.

We may interpret (16.25) with the aid of Figure 16.1. The scatterer region, i.e. that which gives rise to a nonvanishing contribution to the second term in the r.h.s. of (16.25), is limited to the volume of the scatterer sample being measured, which is located around the origin. The vector $\mathbf{r}$ is directed towards the observation point at which the wavefunction

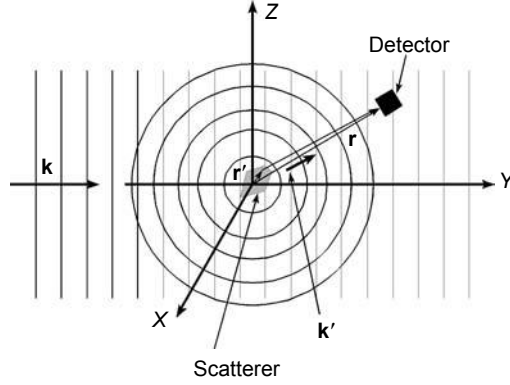


Fig. 16.1. Scattering geometry.

is being measured. The detector is usually placed far from the scatterer volume, and thus we are interested in studying the effect of the scatterer at a point far outside the sample volume. Because observations are always made by a detector placed very far away from the scatterer, we usually have

$$|\mathbf{r}| \gg |\mathbf{r}'|,$$

as depicted in Figure 16.1. We introduce

$$\begin{aligned} r &= |\mathbf{r}|, \\ r' &= |\mathbf{r}'|, \\ \alpha &= \angle(\mathbf{r}, \mathbf{r}'). \end{aligned}$$

For $r \gg r'$ we have

$$\begin{aligned} |\mathbf{r} - \mathbf{r}'| &= \sqrt{r^2 + r'^2 - 2rr' \cos \alpha} \\ &= r \left(1 - \frac{2r'}{r} \cos \alpha + \frac{r'^2}{r^2} \right) \\ &\simeq r - \hat{\mathbf{r}} \cdot \mathbf{r}', \end{aligned}$$

where

$$\hat{\mathbf{r}} \equiv \frac{\mathbf{r}}{r},$$

and we define

$$\mathbf{k}_s = k_s \hat{\mathbf{r}}.$$

The motivation for this definition is that $\mathbf{k}_s$ represents the propagation vector for waves reaching the observation point $\mathbf{r}$; this allows us to write

$$\exp[\pm i k_s |\mathbf{r} - \mathbf{r}'|] = \exp(\pm i k_s r) \exp[\pm i \mathbf{k}_s \cdot \mathbf{r}'] \quad (16.26)$$

for large r . It is legitimate to replace $1/|\mathbf{r} - \mathbf{r}'|$ by just $1/r$. So finally we obtain

$$\begin{aligned} \psi_{\mathbf{k}}^{(+)} &\xrightarrow{r \text{ large}} \frac{e^{\pm i\mathbf{k} \cdot \mathbf{r}}}{(2\pi)^{3/2}} - \frac{1}{4\pi} \frac{\exp(ik_s r)}{r} \int d\mathbf{r}' \exp[-i\mathbf{k}_s \cdot \mathbf{r}'] \langle \phi_n | \mathcal{U}(\mathbf{r}') | \psi_{\mathbf{k}}^{(+)}(\mathbf{r}') \rangle \\ &= \frac{1}{(2\pi)^{3/2}} \left[\exp[i\mathbf{k} \cdot \mathbf{r}] - \frac{(2\pi)^{3/2}}{4\pi} \frac{\exp(ik_s r)}{r} \langle \mathbf{k}_s \phi_n | \mathcal{U}(\mathbf{r}') | \psi_{\mathbf{k}}^{(+)}(\mathbf{r}') \rangle \right]. \end{aligned} \quad (16.27)$$

This form makes it very clear that we have the original plane-wave in propagation direction $\mathbf{k}$ plus an outgoing spherical wave with amplitude

$$\begin{aligned} & - \frac{1}{4\pi} (2\pi)^3 \int d\mathbf{r}' \frac{\exp[-i\mathbf{k}_s \cdot \mathbf{r}']}{(2\pi)^{3/2}} \langle \phi_n | \mathcal{U}(\mathbf{r}') | \psi_{\mathbf{k}}^{(+)} \rangle \\ &= - \frac{1}{4\pi} (2\pi)^3 \langle \mathbf{k}_s \phi_n | \mathcal{U} | \psi_{\mathbf{k}}^{(+)} \rangle. \end{aligned} \quad (16.28)$$

The Born series and the Born approximation

The Lippmann–Schwinger (LS) equation in the energy representation is given by

$$|\Psi^{(\pm)}(E)\rangle = |\Phi^{(\pm)}(E)\rangle + \frac{1}{E \pm i\epsilon - \mathcal{H}_0} V |\Psi^{(\pm)}(E)\rangle,$$

where $|\Phi^{(\pm)}(E)\rangle$ is the noninteracting, i.e. $V = 0$, solution

$$\mathcal{H}_0 |\Phi^{(\pm)}(E)\rangle = E |\Phi^{(\pm)}(E)\rangle.$$

It allows for the introduction of an iterative approximation technique, whose termination depends on the relative strength of the interaction V . The technique, known as the Born series, involves successive iterations of the LS equation, namely,

$$|\Psi^{(\pm)}(E)\rangle = \sum_{n=0}^{\infty} \left(\frac{1}{E \pm i\epsilon - \mathcal{H}_0} V \right)^n |\Phi^{(\pm)}(E)\rangle.$$

The usefulness of this series is that for small V or large E it may be truncated after only a few terms. In practice, one frequently keeps only the first term – *the first Born approximation* – given by

$$|\Psi^{(\pm)}(E)\rangle = |\Phi^{(\pm)}(E)\rangle + \frac{1}{E \pm i\epsilon - \mathcal{H}_0} V |\Phi^{(\pm)}(E)\rangle.$$

In order to apply this approximation to the expression (16.28), we derive the following expression for the scattering amplitude in the first Born approximation; after substituting $\Phi_{j,\mathbf{k}} = \phi_j \exp[i\mathbf{k} \cdot \mathbf{r}'] / (2\pi)^{3/2}$ for $|\psi_{\mathbf{k}}^{(\pm)}\rangle$,

$$\begin{aligned} \psi_{\mathbf{k}}^{(\pm)} &= \Phi_{j,\mathbf{k}} - \frac{1}{4\pi} \frac{\exp(ik_s r)}{r} \int d\mathbf{r}' \exp[i(\mathbf{k} - \mathbf{k}_s) \cdot \mathbf{r}'] \langle \phi_n | \mathcal{U}(\mathbf{r}', \{\mathbf{x}\}) | \phi_j \rangle \\ &= \Phi_{j,\mathbf{k}} - \frac{1}{4\pi} \frac{\exp(ik_s r)}{r} \int d\mathbf{r}' \exp[i\mathbf{Q} \cdot \mathbf{r}'] \langle \phi_n | \mathcal{U}(\mathbf{r}', \{\mathbf{x}\}) | \phi_j \rangle \\ &= \Phi_{j,\mathbf{k}} - \frac{1}{4\pi} \left\langle \phi_n \left| \sum_{\ell} e^{i\mathbf{Q} \cdot \mathbf{x}_{\ell}} \mathcal{U}(\mathbf{Q}, \{\mathbf{x}\}) \right| \phi_j \right\rangle \frac{\exp(ik_s r)}{r}, \end{aligned} \quad (16.29)$$

where $\mathbf{Q} = \mathbf{k} - \mathbf{k}_s$ is the momentum-transfer vector. Thus, in the FBA the scattering amplitude is proportional to the three-dimensional Fourier transform of the interaction potential with respect to the momentum-transfer wavevector.

16.3.2 Particle flux

We start by writing the Schrödinger equation

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] \psi = i\hbar \frac{\partial \psi}{\partial t}$$

and its complex conjugate, and obtain an expression for the continuity equation

$$\begin{aligned} \frac{\partial \rho}{\partial t} &= \frac{\partial}{\partial t} |\psi|^2 = -\frac{i\hbar}{2M} (\psi \nabla^2 \psi^* - \psi^* \nabla^2 \psi) \\ &= -\frac{i\hbar}{2M} \nabla \cdot (\psi \nabla \psi^* - \psi^* \nabla \psi). \end{aligned}$$

We then identify the flux as

$$\mathfrak{F} = -\frac{i\hbar}{2M} (\psi \nabla \psi^* - \psi^* \nabla \psi). \quad (16.30)$$

If we assume that the probe particles in the incident beam were prepared in a state $\psi_{\mathbf{k}_i}(\mathbf{r})$, we obtain an incident flux of

$$\mathfrak{F}_i = \frac{\hbar k_i}{2M}.$$

Using the scattering wavefunctions of (16.25) we obtain

$$\mathfrak{F}_n = \left(\frac{1}{4\pi r} \right)^2 \frac{\hbar k_s}{2M} |\mathcal{U}(\mathbf{Q})|^2 \left\langle \phi_n \left| \sum_j e^{i\mathbf{Q} \cdot \mathbf{x}_j} \right| \phi_i \right\rangle^2, \quad (16.31)$$

where $\mathfrak{F}_n$ is the flux arising when the final state of the scattering system is ϕ_n .

16.3.3 The differential scattering cross-section

In a scattering experiment the quantity actually measured is the number of particles scattered by a target into the element of solid angle between Ω and $\Omega + d\Omega$ within an energy window E_f and $E_f + dE_f$. Since energy conservation requires that

$$\frac{\hbar^2 \mathbf{k}^2}{2M} - \frac{\hbar^2 \mathbf{k}_s^2}{2M} = E_f - E_i = \hbar\omega,$$

where $\hbar\omega$ is the excitation energy, we use the alternative, and more convenient, label of the energy window $\omega \rightarrow \omega + d\omega$; and thus sum over all final states which have $E_f - E_i = \hbar\omega$ to obtain the scattered flux

$$\mathfrak{F}_s = \left(\frac{1}{4\pi r} \right)^2 \frac{\hbar k_s}{2M} \sum_f \left\langle \phi_f \left| \sum_j e^{i\mathbf{Q} \cdot \mathbf{x}_j} \mathcal{U}(\mathbf{Q}, \{\mathbf{x}\}) \right| \phi_i \right\rangle^2 \delta(\hbar\omega - E_f - E_i), \quad (16.32)$$

provided the scattering system was initially in the state ϕ_i . Since the scattering system is usually in thermal equilibrium with its surroundings, we should have a Boltzmann

probability distribution, P_i , for the states ϕ_i ; and we may sum over such initial states to obtain

$$\mathfrak{F}_s = \left(\frac{1}{4\pi r} \right)^2 \frac{\hbar k_s}{2M} \sum_{f,i} P_i \left| \left\langle \phi_f \left| \sum_j e^{i\mathbf{Q} \cdot \mathbf{x}_j} \mathcal{U}(\mathbf{Q}, \{\mathbf{x}\}) \right| \phi_i \right\rangle \right|^2 \delta(\hbar\omega - E_f - E_i). \quad (16.33)$$

The flux passing through an elemental solid angle $d\Omega$ subtended by an element of surface area ds can be expressed as

$$dN = |\mathfrak{F}_i| \frac{\partial \sigma(\hat{\mathbf{r}})}{\partial \Omega \partial \omega} d\Omega d\omega = \mathfrak{F}_s \cdot ds d\omega = |\mathfrak{F}_s| r^2 d\Omega d\omega, \quad (16.34)$$

where $\partial \sigma(\hat{\mathbf{r}})/\partial \Omega \partial \omega$ is known as the *differential scattering cross-section*, and $\hat{\mathbf{r}}$ is the direction of scattering.

Thus, we obtain an expression for the differential scattering cross-section (DSCS) of the form

$$\begin{aligned} \frac{\partial \sigma(\hat{\mathbf{r}})}{\partial \Omega \partial \omega} &= \left(\frac{1}{4\pi} \right)^2 \frac{k_s}{k} \sum_{f,i} P_i \\ &\times \left| \sum_j \left\langle \phi_f \left| e^{i\mathbf{Q} \cdot \mathbf{x}_j} \mathcal{U}(\mathbf{Q}, \{\mathbf{x}\}) \right| \phi_i \right\rangle \right|^2 \delta(\hbar\omega - E_f - E_i) \\ &= \left(\frac{1}{4\pi} \right)^2 \frac{k_s}{k} |\mathcal{U}(\mathbf{Q})|^2 \mathcal{S}(\mathbf{Q}, \omega), \end{aligned} \quad (16.35)$$

where $\mathcal{S}(\mathbf{Q}, \omega)$ is the *dynamical structure factor* of the scattering system,

$$\mathcal{S}(\mathbf{Q}, \omega) = \sum_{f,i} P_i \left| \sum_j \left\langle \phi_f \left| e^{i\mathbf{Q} \cdot \mathbf{x}_j} \right| \phi_i \right\rangle \right|^2 \delta(\hbar\omega - E_f - E_i). \quad (16.36)$$

It describes the distribution of momentum $\mathbf{Q}$ and energy $\hbar\omega$ transfer between the impinging beam and the target scatterer. The energy delta-function allows us to relax the summation over the indices i, f to cover all eigenstates.

The correlation function

It is convenient to introduce the Fourier transform of the dynamical structure factor, namely

$$\begin{aligned} \mathcal{C}(\mathbf{Q}, t) &= \int_{-\infty}^{\infty} d\omega e^{i\omega t} \mathcal{S}(\mathbf{Q}, \omega) \\ &= \sum_{f,i} P_i \left| \sum_j \left\langle \phi_f \left| e^{i\mathbf{Q} \cdot \mathbf{x}_j} \right| \phi_i \right\rangle \right|^2 e^{i(E_f - E_i)t/\hbar} \\ &= \sum_i P_i \sum_f \sum_{lm} \left\langle \phi_i \left| e^{-i\mathbf{Q} \cdot \mathbf{x}_l} \right| \phi_f \right\rangle e^{iE_f t/\hbar} \left\langle \phi_f \left| e^{i\mathbf{Q} \cdot \mathbf{x}_m} \right| \phi_i \right\rangle e^{-iE_i t/\hbar} \\ &= \sum_i P_i \sum_f \sum_{lm} \left\langle \phi_i \left| e^{-i\mathbf{Q} \cdot \mathbf{x}_l(0)} \right| \phi_f \right\rangle \left\langle \phi_f \left| e^{i\mathbf{Q} \cdot \mathbf{x}_m(t)} \right| \phi_i \right\rangle, \end{aligned} \quad (16.37)$$

where we treated the position vectors $\mathbf{x}_j$ as Heisenberg operators, such that

$$\begin{aligned} e^{iE_f t/\hbar} \left\langle \phi_f \left| e^{i\mathbf{Q} \cdot \mathbf{x}_m} \right| \phi_i \right\rangle e^{-iE_i t/\hbar} &= \left\langle \phi_f \left| e^{i\mathcal{H}t/\hbar} e^{i\mathbf{Q} \cdot \mathbf{x}_m(0)} e^{-i\mathcal{H}t/\hbar} \right| \phi_i \right\rangle \\ &= \left\langle \phi_f \left| e^{i\mathbf{Q} \cdot \mathbf{x}_m(t)} \right| \phi_i \right\rangle. \end{aligned}$$

The summation over f in (16.37) is just the identity operator and we get

$$\begin{aligned} \mathcal{C}(\mathbf{Q}, t) &= \sum_{lm} \sum_i P_i \left\langle \phi_i \left| e^{-i\mathbf{Q} \cdot \mathbf{x}_l(0)} e^{i\mathbf{Q} \cdot \mathbf{x}_m(t)} \right| \phi_i \right\rangle \\ &= \sum_{lm} \left\langle e^{-i\mathbf{Q} \cdot \mathbf{x}_l(0)} e^{i\mathbf{Q} \cdot \mathbf{x}_m(t)} \right\rangle_T, \end{aligned} \quad (16.38)$$

where $\langle \rangle_T$ is the thermal average. Expanding the position vectors $\mathbf{x}_j = \mathbf{R}_j + \mathbf{u}_j$, where $\mathbf{R}_j$ is the equilibrium position and $\mathbf{u}_j$ the displacement from equilibrium.

16.4 Light scattering spectroscopies

16.4.1 Interaction Hamiltonian

Starting with the nonrelativistic approximation to the Dirac equation with electromagnetic coupling we write the electron Hamiltonian [112]

$$\mathcal{H} \simeq \frac{1}{2m_e} (\boldsymbol{\sigma} \cdot \boldsymbol{\pi})(\boldsymbol{\sigma} \cdot \boldsymbol{\pi}) \quad (16.39)$$

where $\boldsymbol{\sigma}$ is the Pauli vector matrix, and $\boldsymbol{\pi} = \mathbf{p} + \frac{e}{c}\mathbf{A}$; and using the identity

$$(\boldsymbol{\sigma} \cdot \mathbf{a})(\boldsymbol{\sigma} \cdot \mathbf{b}) = \mathbf{a} \cdot \mathbf{b} + i\boldsymbol{\sigma} \cdot (\mathbf{a} \times \mathbf{b}),$$

we get

$$\begin{aligned} \mathcal{H} &\simeq \frac{1}{2m_e} \left[\boldsymbol{\sigma} \cdot \left(\mathbf{p} + \frac{e}{c}\mathbf{A} \right) \right]^2 \\ &= \frac{1}{2m_e} \left(\mathbf{p} + \frac{e}{c}\mathbf{A} \right)^2 + i\frac{e}{2m_e c} \boldsymbol{\sigma} \cdot [\mathbf{p} \times \mathbf{A} + \mathbf{A} \times \mathbf{p}]. \end{aligned}$$

Next, we use the identity

$$\mathbf{p} \times \mathbf{A} = -i\hbar \boldsymbol{\nabla} \times \mathbf{A} - \mathbf{A} \times \mathbf{p}$$

to obtain

$$\mathcal{H} = \frac{1}{2m_e} \mathbf{p}^2 + \frac{e}{m_e c} \mathbf{A} \cdot \mathbf{p} + \frac{e\hbar}{2m_e c} \boldsymbol{\sigma} \cdot \boldsymbol{\nabla} \times \mathbf{A} + \frac{e^2}{2m_e c^2} A^2. \quad (16.40)$$

The term $(e\hbar/2m_e c) \boldsymbol{\sigma} \cdot \boldsymbol{\nabla} \times \mathbf{A}$ represents the interaction of the spin magnetic moment with a magnetic field $\mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A}$; it will be considered only when dealing with magnetic systems. This Hamiltonian may be generalized for a noninteracting many-electron system in the form $\sum_j \mathcal{H}_j$, with

$$\mathcal{H}_j = \frac{\mathbf{p}_j^2}{2m_e} + \frac{e}{m_e c} \mathbf{A}(\mathbf{r}_j) \cdot \mathbf{p} + \frac{e\hbar}{2m_e c} \boldsymbol{\sigma} \cdot \boldsymbol{\nabla} \times \mathbf{A}(\mathbf{r}_j) + \frac{e^2}{2m_e c^2} A^2(\mathbf{r}_j),$$

where the index j identifies the j th electron in the system.

The vector potential $\mathbf{A}(\mathbf{r})$ can be written in second-quantized form as

$$\mathbf{A}(\mathbf{r}) = \sum_{\mathbf{k}} \left(\frac{2\pi\hbar c^2}{V\omega_{\mathbf{k}}} \right)^{1/2} \boldsymbol{\varepsilon}_{\mathbf{k}\lambda} \left(a_{\mathbf{k}\lambda} e^{i\mathbf{k}\cdot\mathbf{r}} + a_{\mathbf{k}\lambda}^\dagger e^{-i\mathbf{k}\cdot\mathbf{r}} \right), \quad (16.41)$$

where λ indexes radiation modes with wavevector $\mathbf{k}$, frequency $\omega_{\mathbf{k}\lambda}$, and polarization $\boldsymbol{\varepsilon}_{\mathbf{k}\lambda}$, and where the creation and annihilation operators satisfy

$$a_{\mathbf{k}}^\dagger |n_{\mathbf{k}\lambda}\rangle = \sqrt{n_{\mathbf{k}\lambda} + 1} |n_{\mathbf{k}\lambda} + 1\rangle, \quad (16.42)$$

$$a_{\mathbf{k}\lambda} |n_{\mathbf{k}\lambda}\rangle = \sqrt{n_{\mathbf{k}\lambda}} |n_{\mathbf{k}\lambda} - 1\rangle, \quad (16.43)$$

where $n_{\mathbf{k}\lambda}$ is the number of photons with wavevector $\mathbf{k}$, frequency $\omega_{\mathbf{k}\lambda}$, and polarization $\boldsymbol{\varepsilon}_{\mathbf{k}\lambda}$. The corresponding radiation Hamiltonian is expressed in second-quantized form as

$$\mathcal{H}_r = \sum_{\mathbf{k}\lambda} \hbar\omega_{\mathbf{k}\lambda} \left(a_{\mathbf{k}\lambda}^\dagger a_{\mathbf{k}\lambda} + \frac{1}{2} \right). \quad (16.44)$$

Matrix elements

In constructing the matrix elements of the interaction of photons with matter we use the following notation: The incident photon $\mathbf{k}_i\lambda_i$ is denoted by I , and the scattered photon $\mathbf{k}_s\lambda_s$ is denoted by S . For the sake of simplicity, we consider the interaction with a single electron j with position vector $\mathbf{r}_j$, and, eventually, we sum over all electrons. The initial and final states of the electron are denoted by $|i\rangle$ and $|f\rangle$, respectively.

Because the A^2 term is bilinear in the a operators, its matrix element has the form

$$\begin{aligned} \left\langle f, n_I - 1, n_S + 1 \left| \sum_j \mathbf{A}(\mathbf{r}_j) \cdot \mathbf{A}(\mathbf{r}_j) \right| i, n_I, n_S \right\rangle = \\ \frac{\hbar e^2}{2m_e V} \sqrt{\frac{4n_I(n_S + 1)}{\omega_I \omega_S}} \langle f | (\boldsymbol{\varepsilon}_I \cdot \boldsymbol{\varepsilon}_S) \exp[i\mathbf{Q} \cdot \mathbf{r}_j] | i \rangle, \end{aligned} \quad (16.45)$$

where $\mathbf{Q} = \mathbf{k}_I - \mathbf{k}_S$; it represents the annihilation of the incident photon $\mathbf{k}_I\lambda_I$ and the creation of the scattered $\mathbf{k}_S\lambda_S$ photon.

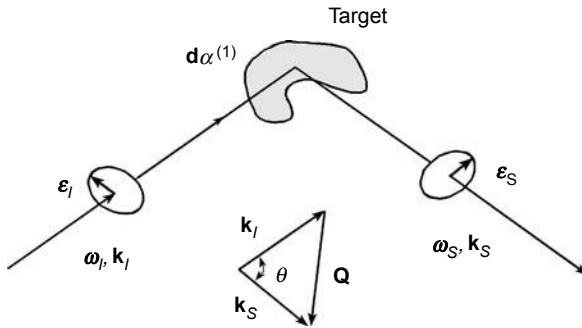


Fig. 16.2. Geometry of light scattering.

The $\mathbf{A} \cdot \mathbf{p}$ contribution contains only terms linear in the a operators, and its matrix elements have the form

$$\begin{aligned} \left\langle f, n_{\mathbf{k}} \pm 1 \left| \sum_j \mathbf{A}(\mathbf{r}_j) \cdot \mathbf{p}_j \right| i, n_{\mathbf{k}} \right\rangle &= \frac{e}{m_e} \sqrt{\frac{\hbar}{V\omega_{\mathbf{k}}}} \sqrt{(n_{\mathbf{k}} + 1/2 \pm 1/2)} \\ &\times \sum_j \langle f | e^{\pm i\mathbf{k} \cdot \mathbf{r}_j} \boldsymbol{\varepsilon}_{\mathbf{k}\lambda} \cdot \mathbf{p}_j | i \rangle, \end{aligned} \quad (16.46)$$

which involves the annihilation or creation of a single photon in first order. Consequently, it does not represent a scattering process. Such processes involve second-order contributions. In second order, there are two possible routes for the intermediate states:

$$\begin{aligned} |L\rangle &= |l, n_I - 1, n_S\rangle, & E_L &= E_l - \hbar\omega_I, \\ |L'\rangle &= |l', n_I, n_S + 1\rangle, & E_{L'} &= E_{l'} + \hbar\omega_S, \end{aligned}$$

and we get

$$\begin{aligned} \frac{\hbar e^2}{m_e^2 V} \sqrt{\frac{n_I(n_S + 1)}{\omega_I \omega_S}} \sum_l \left[\frac{\langle f | e^{-i\mathbf{k}_S \cdot \mathbf{r}_j} \boldsymbol{\varepsilon}_S \cdot \mathbf{p}_j | l \rangle \langle l | e^{i\mathbf{k}_I \cdot \mathbf{r}'_j} \boldsymbol{\varepsilon}_I \cdot \mathbf{p}_j | i \rangle}{E_i - E_l + \hbar\omega_I} \right. \\ \left. + \frac{\langle f | e^{i\mathbf{k}_I \cdot \mathbf{r}_j} \boldsymbol{\varepsilon}_I \cdot \mathbf{p}_j | l' \rangle \langle l' | e^{-i\mathbf{k}_S \cdot \mathbf{r}'_j} \boldsymbol{\varepsilon}_S \cdot \mathbf{p}_j | i \rangle}{E_i - E_{l'} - \hbar\omega_S} \right]. \end{aligned} \quad (16.47)$$

For condensed matter systems such as a crystal, whose size is large compared to the wavelength of the incident light, the dipole approximation cannot be applied. However, if we assume that the electronic wavefunctions are formed as Bloch sums over localized valence (Wannier) orbitals, we can associate a given electron with a certain atomic site $\mathbf{R} + \boldsymbol{\kappa}$, where $\mathbf{R}$ is a lattice vector and $\boldsymbol{\kappa}$ the position of the κ th atom in the primitive cell defined by $\mathbf{R}$. We write $\mathbf{r}_j = \mathbf{R} + \boldsymbol{\kappa} + \boldsymbol{\rho}_j$, where $\boldsymbol{\rho}_j$ is the position of the j th electron at site $\mathbf{R}\boldsymbol{\kappa}$. It is then permissible to make the dipole approximation as

$$e^{i\mathbf{k} \cdot \mathbf{r}_j} = e^{i\mathbf{k} \cdot (\mathbf{R} + \boldsymbol{\kappa})} e^{i\mathbf{k} \cdot \boldsymbol{\rho}_j} \simeq e^{i\mathbf{k} \cdot (\mathbf{R} + \boldsymbol{\kappa})},$$

and we write

$$\begin{aligned} \langle S | \mathcal{H}_{\text{int}} | I \rangle &= \frac{\hbar e^2}{m_e^2 V} \sqrt{\frac{n_I(n_S + 1)}{\omega_I \omega_S}} e^{i\mathbf{Q} \cdot (\mathbf{R} + \boldsymbol{\kappa})} \left((\boldsymbol{\varepsilon}_I \cdot \boldsymbol{\varepsilon}_S) \delta_{si} \right. \\ &\quad \left. + \frac{1}{m_e} \sum_l \boldsymbol{\varepsilon}_S \cdot \left[\frac{\mathbf{p}^{fl}(-\mathbf{k}_S) \mathbf{p}^{li}(\mathbf{k}_I)}{E_i - E_l + \hbar\omega_I} + \frac{\mathbf{p}^{f'l'}(\mathbf{k}_I) \mathbf{p}^{l'i}(-\mathbf{k}_S)}{E_i - E_{l'} - \hbar\omega_S} \right] \cdot \boldsymbol{\varepsilon}_I \right), \end{aligned} \quad (16.48)$$

where $\mathbf{p}^{lm}(\mathbf{k}) = \sum_{\mathbf{R}, \boldsymbol{\kappa}} \langle l | \mathbf{p} | m \rangle e^{i\mathbf{k} \cdot (\mathbf{R} + \boldsymbol{\kappa})}$.

Differential scattering cross-section

Using expression (16.48) for the scattering matrix element, and the density of scattering states

$$\frac{V}{8\pi^3 \hbar c^3} \omega_S^2 d\Omega,$$

and writing the DSCS as

$$\frac{\partial \sigma}{\partial \Omega} = \frac{\text{number of } \mathbf{k}_s \lambda_s \text{ photons scattered/sec sr}}{\text{number of } \mathbf{k}_i \lambda_i \text{ photons scattered/sec sr}} \quad (16.49)$$

we obtain

$$\begin{aligned} \frac{\partial \sigma}{\partial \Omega} &= \left(\frac{e^2}{mc^2} \right)^2 \frac{c}{V} \frac{\omega_S}{\omega_I} \frac{1}{n_I c/V} n_I (n_S + 1) \left| (\boldsymbol{\varepsilon}_I \cdot \boldsymbol{\varepsilon}_S) \delta_{fi} \right. \\ &\quad \left. + \frac{1}{m_e} \sum_l \boldsymbol{\varepsilon}_S \cdot \left[\frac{\mathbf{p}^{fl}(-\mathbf{k}_S) \mathbf{p}^{li}(\mathbf{k}_I)}{E_i - E_l + \hbar \omega_I} + \frac{\mathbf{p}^{fl'}(\mathbf{k}_I) \mathbf{p}^{l'i}(-\mathbf{k}_S)}{E_i - E_l - \hbar \omega_S} \right] \cdot \boldsymbol{\varepsilon}_I \right|^2 \\ &= r_0^2 \frac{\omega_S}{\omega_I} (n_S + 1) \left| (\boldsymbol{\varepsilon}_I \cdot \boldsymbol{\varepsilon}_S) \delta_{fi} \right. \\ &\quad \left. + \frac{1}{m_e} \sum_l \boldsymbol{\varepsilon}_S \cdot \left[\frac{\mathbf{p}^{fl}(-\mathbf{k}_S) \mathbf{p}^{li}(\mathbf{k}_I)}{E_i - E_l + \hbar \omega_I} + \frac{\mathbf{p}^{fl'}(\mathbf{k}_I) \mathbf{p}^{l'i}(-\mathbf{k}_S)}{E_i - E_l - \hbar \omega_S} \right] \cdot \boldsymbol{\varepsilon}_I \right|^2, \end{aligned} \quad (16.50)$$

where $r_0 = e^2/m_e c^2$ is the classical radius of the electron. This expression is one form of what is known as the Kramers–Heisenberg formula.

The dipole moment representation of the cross-section

An alternative form of (16.50) in terms of the electron position operators can be derived by making use of the identities

$$[\boldsymbol{\varepsilon} \cdot \mathbf{r}, \boldsymbol{\varepsilon}' \cdot \mathbf{p}] = i\hbar \boldsymbol{\varepsilon} \cdot \boldsymbol{\varepsilon}' \iff [r_j, p_k] = i\hbar \delta_{jk}, \quad (16.51)$$

$$\langle k | [\mathbf{r}, \mathcal{H}] | l \rangle = (E_l - E_k) \langle k | \mathbf{r} | l \rangle = i \frac{\hbar}{m_e} \langle k | \mathbf{p} | l \rangle, \quad (16.52)$$

to write

$$\begin{aligned} \langle f | [\boldsymbol{\varepsilon} \cdot \mathbf{r}, \boldsymbol{\varepsilon}' \cdot \mathbf{p}] | i \rangle &= i\hbar \boldsymbol{\varepsilon} \cdot \boldsymbol{\varepsilon}' \delta_{fi} \\ &= \sum_l [\langle f | \boldsymbol{\varepsilon} \cdot \mathbf{r} | l \rangle \langle l | \boldsymbol{\varepsilon}' \cdot \mathbf{p} | i \rangle - \langle f | \boldsymbol{\varepsilon}' \cdot \mathbf{p} | l \rangle \langle l | \boldsymbol{\varepsilon} \cdot \mathbf{r} | i \rangle] \\ &= i \frac{m_e}{\hbar} \sum_l [(E_l - E_i) \langle f | \boldsymbol{\varepsilon} \cdot \mathbf{r} | l \rangle \langle l | \boldsymbol{\varepsilon}' \cdot \mathbf{r} | i \rangle \\ &\quad - (E_f - E_l) \langle f | \boldsymbol{\varepsilon} \cdot \mathbf{r} | l \rangle \langle l | \boldsymbol{\varepsilon}' \cdot \mathbf{r} | i \rangle]. \end{aligned} \quad (16.53)$$

Next, we add

$$\begin{aligned} \hbar\omega_S \frac{m_e}{\hbar^2} \langle f | [\boldsymbol{\varepsilon} \cdot \mathbf{r}, \boldsymbol{\varepsilon}' \cdot \mathbf{r}] | i \rangle &= 0 \\ &= i\hbar\omega_S \frac{m_e}{\hbar} \sum_l [\langle f | \boldsymbol{\varepsilon} \cdot \mathbf{r} | l \rangle \langle l | \boldsymbol{\varepsilon}' \cdot \mathbf{r} | i \rangle - \langle f | \boldsymbol{\varepsilon}' \cdot \mathbf{r} | l \rangle \langle l | \boldsymbol{\varepsilon} \cdot \mathbf{r} | i \rangle] \end{aligned}$$

to the last line of (16.53), and obtain

$$\begin{aligned} \boldsymbol{\varepsilon} \cdot \boldsymbol{\varepsilon}' \delta_{fi} &= \frac{m_e}{\hbar^2} \sum_l [(E_l - E_i + \hbar\omega_S) \langle f | \boldsymbol{\varepsilon} \cdot \mathbf{r} | l \rangle \langle l | \boldsymbol{\varepsilon}' \cdot \mathbf{r} | i \rangle \\ &\quad - (E_f - E_l + \hbar\omega_S) \langle f | \boldsymbol{\varepsilon}' \cdot \mathbf{r} | l \rangle \langle l | \boldsymbol{\varepsilon} \cdot \mathbf{r} | i \rangle] . \end{aligned} \quad (16.54)$$

We can now express the DSCS in terms of the position operator $\mathbf{r}$, using (16.52) and (16.54), as

$$\begin{aligned} \frac{\partial\sigma}{\partial\Omega} &= r_0^2 m_e^2 \omega_I \omega_S^3 (n_S + 1) \\ &\quad \times \left| \sum_l \boldsymbol{\varepsilon}_S \cdot \left[\frac{\mathbf{r}^{fl}(-\mathbf{k}_S) \mathbf{r}^{li}(\mathbf{k}_I)}{E_i - E_l + \hbar\omega_I} + \frac{\mathbf{r}^{f'l'}(\mathbf{k}_I) \mathbf{r}^{l'i}(-\mathbf{k}_S)}{E_i - E_l - \hbar\omega_S} \right] \cdot \boldsymbol{\varepsilon}_I \right|^2 . \end{aligned} \quad (16.55)$$

The light scattering tensor

In the analysis of the scattering of light by quasi-particles in solids it is useful to recast the above expression for the scattering cross-section in the form of a scattering tensor which relates the Cartesian components of the scattered radiation field polarization vector to those of the incident field polarization vector. We define this tensor by rewriting (16.55) as

$$\frac{\partial\sigma}{\partial\Omega} = C \left| \boldsymbol{\varepsilon}_S \cdot \boldsymbol{\alpha}(-\mathbf{k}_S, \mathbf{k}_I) \cdot \boldsymbol{\varepsilon}_I \right|^2 . \quad (16.56)$$

Thus, the intensity of the scattered light polarized along the ν -direction for incident light in the μ -direction is proportional to $|\alpha_{\nu\mu}|^2$.

Effect of symmetry Clearly, from (16.55) we see that $\boldsymbol{\alpha}$ transforms like the outer-product $\mathbf{r} : \mathbf{r}$, i.e. its components $\alpha_{\nu\mu}$ transform as a second-rank tensor

$$\begin{aligned} \boldsymbol{\alpha}' &= {}^{(v)}\Gamma^\dagger(R) \boldsymbol{\alpha} {}^{(v)}\Gamma(R) \\ &= \sum_{\lambda\rho} {}^{(v)}\Gamma(R)_{\nu\lambda} {}^{(v)}\Gamma(R)_{\mu\rho} \alpha_{\lambda\rho} , \end{aligned} \quad (16.57)$$

where R is an element of $\mathcal{O}(3)$, and ${}^{(v)}\Gamma$ is the three-dimensional vector representation of R ; that is according to

$${}^{(v)}\Gamma \otimes {}^{(v)}\Gamma . \quad (16.58)$$

When the operators $\hat{S} = (\hat{R}|\mathbf{w})$ are symmetry elements belonging to a system's space-group $\mathbb{S}$, we require that $\boldsymbol{\alpha}' = \boldsymbol{\alpha}$ for that system. Moreover, for ω_j away from resonance, the scattering tensor is symmetric, $\alpha_{\nu\mu} = \alpha_{\mu\nu}$, so that (16.57) should be replaced by

$$\alpha_{\nu\mu} = \sum_{\lambda\rho} \left({}^{(\nu)}\Gamma(R)_{\nu\lambda} {}^{(\nu)}\Gamma(R)_{\mu\rho}^{(\nu)} + {}^{(\nu)}\Gamma(R)_{\mu\lambda} {}^{(\nu)}\Gamma(R)_{\nu\rho} \right) \alpha_{\lambda\rho}. \quad (16.59)$$

Inelastic scattering tensor

We define the inelastic scattering (polarizability) tensor as

$$\mathbf{d}\boldsymbol{\alpha} = \boldsymbol{\alpha} - \boldsymbol{\alpha}_0 = \sum_j \left[\frac{\partial \boldsymbol{\alpha}}{\partial q_j} dq_j + \sum_l \frac{\partial^2 \boldsymbol{\alpha}}{\partial q_j \partial q_l} dq_j dq_l + \cdots \right], \quad (16.60)$$

where $\mathbf{d}\boldsymbol{\alpha}(-\mathbf{k}_S, \mathbf{k}_I)$ has contributions from several excitation processes, each represented by a set of quasi-particle coordinates q_j . Depending upon the physical process under consideration, the tensor $\mathbf{d}\boldsymbol{\alpha}$ can be further specified in terms of the corresponding set q_j . For example, in an inelastic first-order (one-excitation) process, the intensity of scattering can be written as proportional to

$$C \left| \boldsymbol{\varepsilon}_S \cdot \mathbf{d}\boldsymbol{\alpha}^{(1)}(j\sigma) \cdot \boldsymbol{\varepsilon}_I \right|^2, \quad (16.61)$$

where the indices $j\sigma$ specify the symmetry of the excitation produced. $\mathbf{d}\boldsymbol{\alpha}^{(1)}$ is called the *first-order Raman* tensor. For a second-order (two-excitation) process the expression becomes

$$C \left| \boldsymbol{\varepsilon}_S \cdot \mathbf{d}\boldsymbol{\alpha}^{(2)}(j\sigma, j'\sigma') \cdot \boldsymbol{\varepsilon}_I \right|^2, \quad (16.62)$$

where, again, $\mathbf{d}\boldsymbol{\alpha}^{(2)}$ is the *second-order Raman* tensor. The excitations involved may be phonons, magnons, etc.

16.4.2 Phonons

When neither ω_I nor ω_S are at resonance, it is convenient to work in a generalized adiabatic framework. In the case of phonon Raman scattering, we introduce symmetry-adapted normal modes in the harmonic approximation, and write

$$\mathbf{u}(\omega_{\sigma j}|\mathbf{q}) = \mathcal{N} \hat{\mathbf{e}}(\sigma j) Q_j^{\sigma} e^{i(\mathbf{q}\cdot\mathbf{r}-\omega_{\sigma}t)},$$

where $\mathcal{N}$ is a normalization constant, $\hat{\mathbf{e}}(\sigma j)$ is the eigenvector transforming as the j th row of Irrep (σ) , and Q_j^{σ} the corresponding dynamical variable. The operator $\mathbf{d}\boldsymbol{\alpha}$ can be expanded in a Taylor series in the normal coordinates Q_j^{σ} as

$$\begin{aligned} \mathbf{d}\boldsymbol{\alpha} &= \sum_{\sigma j} \mathbf{d}\boldsymbol{\alpha}^{(1)}(\mathbf{R}^0; \sigma j) Q_j^{\sigma} \\ &+ \sum_{\sigma j, \sigma' j'} \mathbf{d}\boldsymbol{\alpha}^{(2)}(\sigma j; \sigma' j') Q_j^{\sigma} Q_{j'}^{\sigma'} + \cdots \end{aligned} \quad (16.63)$$

Clearly, terms linear in Q_j^{σ} produce one-phonon scattering, bilinear $Q_j^{\sigma} Q_{j'}^{\sigma'}$ produce two-phonon scattering, etc. The indices $j\sigma$ will be used to specify the symmetry of the phonon.

It should be noted that first-order scattering involving acoustic phonons is referred to as *Brillouin scattering*, in which case $\mathbf{d}\alpha^{(1)}$ corresponds to the photoelastic tensor. First-order scattering involving optical phonons falls in the domain of *Raman scattering*.

Symmetry properties of $\mathbf{d}\alpha^{(1)}(\sigma j)$ for phonons

When discussing the symmetry aspects of light scattering from phonons we consider two main consequences: first, we explore the selection rules, i.e. determine the active modes; and second, we identify the non-vanishing components of the corresponding inelastic light scattering tensor. From (16.58) and (16.63) we find that a mode σj may be observable by inelastic light scattering, i.e. is active, if

$$\left(\left[{}^{(\nu)}\Gamma \otimes {}^{(\nu)}\Gamma \right] \downarrow \mathbb{P} \right) \otimes {}^{(\sigma)}\Gamma \supset {}^{(1)}\Gamma,$$

or

$$\left[{}^{(\nu)}\Gamma \otimes {}^{(\nu)}\Gamma \right] \downarrow \mathbb{P} \supset {}^{(\sigma)}\Gamma, \quad (16.64)$$

i.e. the Irreps of the point-group $\mathbb{P}$ that appear in the subduction of the symmetrized outer-product of the 3D vector Rep are the active Raman or Brillouin modes. We recast this condition in the form

$$\sum_{R \in \mathbb{P}} \left[{}^{(\nu)}\chi^2(R) \right] {}^{(\sigma)}\chi(R) \neq 0. \quad (16.65)$$

Example 16.1

Point-group 4mm (C_{4v})

	E	C_4	C_2	σ	σ_d
$\left[{}^{(\nu)}\chi \otimes {}^{(\nu)}\chi \right] \downarrow 4mm$	6	0	2	2	2

${}^{(\nu)}\Gamma = \Gamma_1 \oplus \Gamma_5 \Rightarrow A_1 \oplus E$, and we have

$$\begin{aligned} {}^{(\nu)}\Gamma \otimes {}^{(\nu)}\Gamma &= 2\Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4 + 2\Gamma_5 \\ &= 2A_1 + A_2 + B_1 + B_2 + 2E, \\ \left[{}^{(\nu)}\Gamma \otimes {}^{(\nu)}\Gamma \right] &= 2\Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5 \\ &= 2A_1 + B_1 + B_2 + E. \end{aligned}$$

Thus, all symmetries except A_2 are Raman active in this case.

Example 16.2

Point-group $m\bar{3}m (O_h)$

$(^{(v)})\Gamma = \Gamma_4^- \Rightarrow T_{1u}$ and we have

$$(^{(v)})\Gamma \otimes (^{(v)})\Gamma = \Gamma_1^+ + \Gamma_3^+ + \Gamma_4^+ + \Gamma_5^+ = A_{1g} + E_g + T_{1g} + T_{2g};$$

only four out of the ten Irreps of O_h are allowed for light scattering. For systems possessing inversion symmetry, only even parity modes are active. Thus, in the case of systems with O_h symmetry, only Γ_i^+ Irreps are allowed; we then find that acoustic modes, which belong to Γ_4^- , are inactive. In the diamond structure, we find three active degenerate optic modes of Γ_5^+ symmetry, while systems with rocksalt or CsCl structure have optic modes with Γ_4^- symmetry and are inactive.

The inelastic light scattering tensor components corresponding to an active Irrep Γ of dimension d are determined with the aid of the following *Mathematica* program:

Program SymmTensor

```
i=0;
While[i<=d,i++;
  T0 = {{f11,f12,f13},{f21,f22,f23},{f31,f32,f33}};
  k=1;T1=T0;
  While[k < ng, k++,
    T1+ = Γ[k,i,i].Transpose[Rot[k]].T0.Rot[k];
  ];
  TX = Simplify[T1]; TX = Flatten[TX];
```

Replace the symmetrized, nonzero, tensor elements by Greek letters

```
abc = {α, β, γ, δ, ε, ζ, η, θ, λ};
TN = {};
Do[AppendTo[TN, i], {i, 1, 9}];
cnt = 0; nel = 0; mem = {}; ij = 1;
```

```

While[And[cnt < 9, nel < 9], nel++;
  Switch[FreeQ[mem,nel], True, xx=TX[[nel]];
    Switch[MatchQ[xx,0],
      True, ReplacePart[TN, 0, nel];
      cnt++; AppendTo[mem, nel],
      False, cnt += Count[TX, xx];
      TN = ReplacePart[TN, abc[[ij]],
        Position[TX, xx]];
      AppendTo[mem, Position[TX, xx]];
      ij++
    ]; Tensor[[i]] = Partition[TN,3];
Print[MatrixForm[Tensor[[i]]]]]
]

```

Since a second-rank tensor can be decomposed into a scalar, an axial, and a symmetric second-rank tensor, the Raman tensor has the tensor invariants [5]:

(i) the isotropic part,

$$\bar{\alpha}^2 = \frac{1}{9} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})^2,$$

(ii) the symmetric anisotropy,

$$\begin{aligned} \gamma_s^2 = & \frac{1}{2} [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2] \\ & + \frac{3}{4} [(\alpha_{xy} + \alpha_{yx})^2 + (\alpha_{yz} + \alpha_{zy})^2 + (\alpha_{zx} + \alpha_{xz})^2], \end{aligned}$$

and

(iii) the antisymmetric anisotropy,

$$\gamma_{as}^2 = \frac{3}{4} [(\alpha_{xy} - \alpha_{yx})^2 + (\alpha_{yz} - \alpha_{zy})^2 + (\alpha_{zx} - \alpha_{xz})^2],$$

where α_{ij} ($i, j = x, y, z$) are the elements of the Raman matrix.

To some extent, the symmetry of the Raman modes can be deduced by knowing the tensor invariants. For example, A_1 is the only representation with a nonvanishing $\bar{\alpha}^2$ invariant, while a dominant γ_s^2 contribution is typical for E_1 and E_2 symmetry. Note that E_1 modes can have $\gamma_{as}^2 \neq 0$. Antisymmetric scattering by phonons (E_1 and A_2 symmetry) is forbidden in nonresonant Raman scattering, but might evolve under resonances [113].

Table 16.2. Raman-active phonon symmetries and corresponding tensors^a.

System	Class	Raman tensors		
Monoclinic		$\begin{pmatrix} a & & \\ d & b & c \end{pmatrix}$	$\begin{pmatrix} e & \\ e & f \end{pmatrix}$	
	C_2	$A, \Gamma_1(y)$	$B, \Gamma_2(x, y)$	
	C_s	$A', \Gamma_1(x, z)$	$A', \Gamma_2(y)$	
	C_{2h}	A_g, Γ_1^+	B_g, Γ_2^+	
Orthorhombic		$\begin{pmatrix} a & & \\ & b & \\ & & c \end{pmatrix}$	$\begin{pmatrix} d \\ d \\ d \end{pmatrix}$	$\begin{pmatrix} e \\ e \\ f \end{pmatrix}$
	D_2	A, Γ_1	$B_1, \Gamma_3(z)$	$B_2, \Gamma_2(y)$
	C_{2v}	$A_1, \Gamma_1(z)$	A_2, Γ_3	$B_1, \Gamma_2(x)$
	D_{2h}	A_g, Γ_1^+	B_{1g}, Γ_3^+	B_{2g}, Γ_2^+
Trigonal		$\begin{pmatrix} a & c & \\ -c & a & b \end{pmatrix}$	$\begin{pmatrix} d & e & f \\ e & -d & h \\ g & i & \end{pmatrix}$	$\begin{pmatrix} e & -d & -h \\ -d & -e & f \\ -i & g & \end{pmatrix}$
	C_3	$A, \Gamma_1(z)$	$E, \Gamma_2(x)$	$E, \Gamma_3(y)$
	C_{3i}	A_g, Γ_1^+	E_g, Γ_2^+	E_g, Γ_3^+
		$\begin{pmatrix} a & & \\ & a & b \end{pmatrix}$	$\begin{pmatrix} c \\ -c \end{pmatrix}$	$\begin{pmatrix} d & \\ -f & -e \end{pmatrix}$
Tetragonal		$\begin{pmatrix} a & & \\ & a & \\ & & b \end{pmatrix}$	$\begin{pmatrix} a_2, \Gamma_1 \\ a_1, \Gamma_1(z) \\ a_{1g}, \Gamma_1^+ \end{pmatrix}$	$\begin{pmatrix} d & \\ f & e \end{pmatrix}$
	D_3	A_1, Γ_1	A_2, Γ_2	$E, \Gamma_3(y)$
	C_{3v}	$A_1, \Gamma_1(z)$	A_2, Γ_2	$E, \Gamma_3(-x)$
	$\bar{3}m$	A_{1g}, Γ_1^+	A_{2g}, Γ_2^+	E_g, Γ_3^+
		$\begin{pmatrix} a & c & \\ -c & & b \end{pmatrix}$	$\begin{pmatrix} d & \\ e & -d \end{pmatrix}$	$\begin{pmatrix} f & \\ h & i \end{pmatrix}$
				$\begin{pmatrix} -h & \\ f & g \end{pmatrix}$

$\frac{4}{\bar{4}}$	$\begin{matrix} C_4 \\ S_4 \end{matrix}$	$\begin{matrix} A_1\Gamma_1(z) \\ A_1\Gamma_1 \\ A_g\Gamma_1^+ \end{matrix}$	$\begin{matrix} B,\Gamma_2 \\ B,\Gamma_2(z) \\ E_g,\Gamma_2^+ \end{matrix}$	$\begin{matrix} E,\Gamma_3(x) \\ E,\Gamma_3(x) \\ E_g,\Gamma_3^+ \end{matrix}$	$\begin{matrix} E,\Gamma_4(y) \\ E,\Gamma_4(-y) \\ E_{-g}^{4+} \end{matrix}$
$\frac{4}{m}$	C_{4h}				
$4mm$	C_{4v}	$\begin{pmatrix} a & & \\ & a & \\ & & b \end{pmatrix}$	$\begin{pmatrix} & & c \\ & -c & \\ & & \end{pmatrix}$	$\begin{pmatrix} d & & \\ & -d & \end{pmatrix}$	$\begin{pmatrix} & & f \\ & e & \\ & & \end{pmatrix}$
422	$\begin{matrix} C_{4v} \\ D_4 \end{matrix}$	$\begin{matrix} A_1,\Gamma_1(z) \\ A_1,\Gamma_1 \\ A_1,\Gamma_1 \end{matrix}$	$\begin{matrix} A_2,\Gamma_2 \\ A_2,\Gamma_2 \\ A_2,\Gamma_2 \end{matrix}$	$\begin{matrix} B_1,\Gamma_3 \\ B_1,\Gamma_3 \\ B_1,\Gamma_3 \end{matrix}$	$\begin{matrix} B_2,\Gamma_4 \\ B_2,\Gamma_4 \\ B_2,\Gamma_4(z) \end{matrix}$
$42m$	D_{2d}	$\begin{matrix} A_1,\Gamma_1 \\ A_{1g},\Gamma_1^+ \end{matrix}$	$\begin{matrix} A_{2g},\Gamma_2^+ \\ A_{2g},\Gamma_2^+ \end{matrix}$	$\begin{matrix} B_{1g},\Gamma_3^+ \\ B_{1g},\Gamma_3^+ \end{matrix}$	$\begin{matrix} B_{2g},\Gamma_4^+ \\ B_{2g},\Gamma_4^+ \end{matrix}$
$4/mmm$	D_{4h}				
$\frac{6}{\bar{6}}$	$\begin{matrix} C_6 \\ C_{3h} \end{matrix}$	$\begin{pmatrix} a & c & \\ -c & a & \\ & & b \end{pmatrix}$	$\begin{pmatrix} & & d \\ & f & \\ e & g & \end{pmatrix}$	$\begin{pmatrix} & & -f \\ & -g & e \end{pmatrix}$	$\begin{pmatrix} & & h & -i \\ & h & -i & \\ & -i & -h & \end{pmatrix}$
$6/m$	$\begin{matrix} C_6 \\ C_{3h} \\ C_{6h} \end{matrix}$	$\begin{matrix} A_1\Gamma_1(z) \\ A_1,\Gamma_1 \\ A_g,\Gamma_1^+ \end{matrix}$	$\begin{matrix} E_1,\Gamma_5(x) \\ E',\Gamma_5^+ \\ E_{1g},\Gamma_5^+ \end{matrix}$	$\begin{matrix} E_1,\Gamma_6(y) \\ E'',\Gamma_6^+ \\ E_{1g},\Gamma_6^+ \end{matrix}$	$\begin{matrix} E_2,\Gamma_3 \\ E',\Gamma_3(y) \\ E_{2g},\Gamma_3^+ \end{matrix}$
622	D_6	$\begin{pmatrix} a & & \\ & a & \\ & & b \end{pmatrix}$	$\begin{pmatrix} & & c \\ & -c & \\ & & \end{pmatrix}$	$\begin{pmatrix} d & & \\ & e & \end{pmatrix}$	$\begin{pmatrix} & & f \\ & -d & \\ & & \end{pmatrix}$
$6mm$	C_{6v}	$\begin{matrix} A_1,\Gamma_1 \\ A_1,\Gamma_1(z) \end{matrix}$	$\begin{matrix} A_2,\Gamma_2 \\ A_2,\Gamma_2 \end{matrix}$	$\begin{matrix} E_1,\Gamma_5(x) \\ E_1,\Gamma_5(y) \end{matrix}$	$\begin{matrix} E_2,\Gamma_6 \\ E_2,\Gamma_6 \\ E_2,\Gamma_6 \end{matrix}$

Hexagonal

Table 16.2. *Cont.*

System	Class	Raman tensors					
$\bar{6}m2$	D_{3h}	A'_1, Γ_1	A'_2, Γ_2	E''_1, Γ_5	$E', \Gamma_6(x)$	$E'_2, \Gamma_6(y)$	
$6/mmm$	D_{6h}	A_{1g}, Γ_1^+	A_{2g}, Γ_2^+	E_{1g}, Γ_5^+	E_{2g}, Γ_6^+	E_{2g}, Γ_6^+	
Cubic		$\begin{pmatrix} a & & \\ & a & \\ & & a \end{pmatrix}$	$\begin{pmatrix} b & & \\ & b & \\ & & -2b \end{pmatrix}$	$\begin{pmatrix} -\sqrt{3}b & & \\ & \sqrt{3}b & \\ & & \sqrt{3}b \end{pmatrix}$	$\begin{pmatrix} c & & \\ & d & \\ & & c \end{pmatrix}$	$\begin{pmatrix} c & & \\ & d & \\ & & c \end{pmatrix}$	
	23	A, Γ_1	E, Γ_2	E, Γ_3	$T, \Gamma_4(x)$	$T, \Gamma_4(y)$	$T, \Gamma_4(z)$
	$m\bar{3}$	A_g, Γ_1^+	E_g, Γ_2^+	E_g, Γ_3^+	T_g, Γ_4^+	T_g, Γ_4^+	T_g, Γ_4^+
			$\begin{pmatrix} a & & \\ & a & \\ & & a \end{pmatrix}$	$\begin{pmatrix} b & & \\ & b & \\ & & -2b \end{pmatrix}$	$\begin{pmatrix} \sqrt{3} & -\sqrt{3}b & \\ & -\sqrt{3}b & \sqrt{3}b \end{pmatrix}$	$\begin{pmatrix} c & & \\ & -c & \\ & & -c \end{pmatrix}$	$\begin{pmatrix} c & & \\ & -c & \\ & & -c \end{pmatrix}$
432	O	A_1, Γ_1	E, Γ_3	E, Γ_3	T_1, Γ_4	T_1, Γ_4	T_1, Γ_4
$\bar{4}3m$	T_d	A_1, Γ_1	E, Γ_3	E, Γ_3	T_1, Γ_4	T_1, Γ_4	T_1, Γ_4
$m\bar{3}m$	O_h	A_{1g}, Γ_1^+	E_g, Γ_3^+	E_g, Γ_3^+	T_{1g}, Γ_4^+	T_{1g}, Γ_4^+	T_{1g}, Γ_4^+
		$\begin{pmatrix} d & & \\ & d & \\ & & d \end{pmatrix}$	$\begin{pmatrix} d & & \\ & d & \\ & & d \end{pmatrix}$				
432	O	T_2, Γ_4	T_2, Γ_4	T_2, Γ_5			
$\bar{4}3m$	T_d	T_2, Γ_5	T_2, Γ_5	T_2, Γ_5			
$m\bar{3}m$	O_h	T_{2g}, Γ_5^+	T_{2g}, Γ_5^+	T_{2g}, Γ_5^+			

^a From R. Loudon, *Advances in Physics*, **13**, 423–482.

16.5 Photoemission and dipole selection rules

Photoemission spectroscopy is an experimental technique that evolved out of the phenomenon of the photoelectric effect, which involves the emission of electrons from matter in response to light incident on it. Although photoemission encompasses several distinct techniques, they all involve the collection and subsequent analysis of photoemitted electrons [114, 115, 116, 117]. Here we discuss the technique of *angle-resolved photoemission spectroscopy* (ARPS), which is suitable for studying the energy and momentum distributions of photoemitted electrons. Application of conservation laws and symmetry aspects to the ARPS spectra allows detailed mapping of the electronic band structure of solids, both in the bulk and at the surface. Since its infancy in the late 1970s it has become apparent that a detailed understanding of the underlying selection rules is necessary for the interpretation of peak structures in the experimental ARPS spectra, as well as in the choice of the geometric experimental arrangement of source–sample–detector configuration that would allow the extraction of the relevant data.

The process of photoemission can be classified into two types: *surface photoemission*, which involves photoexcited surface-state electrons, and *bulk photoemission*, which involves photoexcited bulk-state electrons that subsequently travel to the surface before being emitted. Electron–electron and electron–phonon scattering limit the relevant photoexcitation region to an effective scattering length of the order of 10 Å. Because the momentum of a photon is much smaller than that of an electron with comparable energy, the photoexcitation process is considered as a direct transition between electronic states of defined symmetries. Therefore, dipole selection rules are important and have to be taken into consideration, especially when polarized radiation is used for the optical excitation, and when geometrical alignment of the photoemission detector (electron energy analyzer) is along a high-symmetry direction or plane.

We derive the selection rules of photoemission within the scattering formalism. We consider a semi-infinite geometry where the solid occupies the region $z < 0$, while the vacuum constitutes the region $z > 0$. We describe the motion of a single electron in the absence of the radiation field by the Hamiltonian $\mathcal{H}_0$

$$(\mathcal{H}_0 - E) \Phi_n(\mathbf{r}, \mathbf{k}, E) = 0, \quad (16.66)$$

where the eigenfunctions Φ are identified by the reduced wavevector $\mathbf{k}$, and the energy band index n . Because of the chosen geometry, translation symmetry is broken in the z -direction, the direction perpendicular to the surface, and k_z , the z -component of $\mathbf{k}$, is not a good quantum number. Nevertheless, since the detector is placed very far from the solid surface, it only detects free electron wavefunctions, and thus the z -component of the wavevector is included in labeling the scattering basis set.

We should clarify an important point regarding energy conservation. Inside the solid, the energy of a given state is referred to the zero of the inner-potential, sometimes designated the *muffin-tin zero*, which is negative with respect to the vacuum zero, to which the energy of a free electron is referred. The vacuum zero is E_v when referred to the inner-potential.

We then state energy conservation as follows:

$$\begin{aligned} E(\text{photoexcited state}) &= E(\text{initial state}) + \hbar\omega, \\ E(\text{photoemitted electron}) &\equiv E_{\text{out}} = E(\text{photoexcited state}) - E_v. \end{aligned} \quad (16.67)$$

The energy of a photoemitted electron is equal to the energy of its initial state plus the energy of the absorbed photon $\hbar\omega$, less E_v .

The Hamiltonian representing the interaction of the solid with the radiation field is given by a simplified form of (16.40), namely

$$\mathcal{H}' = \frac{ie\hbar}{mc} \mathbf{A}(\mathbf{r}; t) \cdot \nabla, \quad (16.68)$$

where we neglect both the magnetic and quadratic contributions to the photocurrent. To lowest order in $\mathcal{H}'$, we use the Born approximation to obtain the wavefunction of the electron emitted with a wavevector $\mathbf{k}_f$ and energy $E_f = E_i + \hbar\omega$,

$$\Psi(\mathbf{r}; \mathbf{k}_f, E_i + \hbar\omega) = \int_{\Omega} \mathcal{G}(\mathbf{r}, \mathbf{r}'; E_i + \hbar\omega) \mathcal{H}' \Phi(\mathbf{r}'; \mathbf{k}_i, E_i) d^3 r', \quad (16.69)$$

where $\hbar\omega$ is the photon energy, and $\mathcal{G}(\mathbf{r}, \mathbf{r}'; E_i + \hbar\omega)$ is the exact Green function for the unperturbed Hamiltonian $\mathcal{H}_0$, which can be represented in the eigenfunction form

$$\mathcal{G}(\mathbf{r}, \mathbf{r}'; E_i + \hbar\omega) = \sum_n \frac{\Phi_n(\mathbf{r}) \Phi_n(\mathbf{r}')}{E - E_n}. \quad (16.70)$$

However, for pedagogical reasons, we exploit the fact that the wavefunction at the detector is plane-wave-like, and express $\mathcal{G}$ in terms of the free electron Green function

$$\mathcal{G}_0 = -\frac{1}{2\pi} \frac{\exp[ik|\mathbf{r} - \mathbf{r}'|]}{|\mathbf{r} - \mathbf{r}'|}, \quad (16.71)$$

where $E = E_i + \hbar\omega = \hbar^2 k^2 / 2m_e$, with the aid of Dyson's equation, to obtain

$$\mathcal{G} = \mathcal{G}_0 (1 + \mathcal{T} \mathcal{G}_0), \quad (16.72)$$

where $\mathcal{T}$ is the operator describing emitter scattering. Since the photocurrent is measured some long distance from the emitter, we use the approximation (16.26) to write

$$\mathcal{G}_0 \sim -\frac{\exp(ikr)}{2\pi r} \exp[-i\mathbf{k} \cdot \mathbf{r}'], \quad \mathbf{k} = k\hat{\mathbf{r}}.$$

Substituting back in (16.69) we obtain

$$\begin{aligned} \Psi(\mathbf{r}; \mathbf{k}_f, E_i + \hbar\omega) \\ \xrightarrow{r \text{ large}} & -\frac{\exp(ik_f r)}{2\pi r} \int_{\mathcal{V}} \exp[-i\mathbf{k}_f \cdot \mathbf{r}'] (1 + \mathcal{T} \mathcal{G}_0) \mathcal{H}' \Phi(\mathbf{r}'; \mathbf{k}_i, E_i) d^3 r' \\ & = -\frac{\exp(ik_f r)}{2\pi r} \int_{\mathcal{V}} \Phi^*(\mathbf{r}'; \mathbf{k}_f, E_i + \hbar\omega) \mathcal{H}' \Phi(\mathbf{r}'; \mathbf{k}_i, E_i) d^3 r' \\ & = -\frac{\exp(ik_f r)}{2\pi r} M_{fi}. \end{aligned} \quad (16.73)$$

The initial states $\Phi(\mathbf{r}; \mathbf{k}_i, E_i)$ are confined to the volume of the solid $\mathcal{V}$; they decay exponentially into the vacuum. Moreover, occupied surface states also decay exponentially for

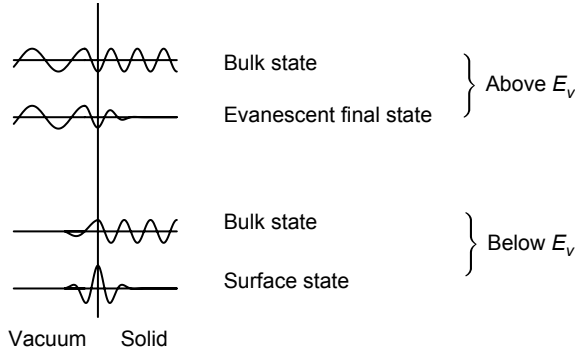


Fig. 16.3. Electronic wavefunctions in the surface region.

$z < 0$. Thus, for all practical purposes, the integral of (16.73) is to be carried over the region $z < 0$.

The final state

$$\Phi(\mathbf{r}'; \mathbf{k}_f, E_i + \hbar\omega) = (1 + \mathcal{G}_0^* \mathcal{T}^*) \exp[i\mathbf{k}_f \cdot \mathbf{r}'].$$

It can be envisaged through the following scenario: Imagine sending a plane-wave $\exp[i\mathbf{k}_f \cdot \mathbf{r}']$ toward the sample, where it is scattered by the sample, giving rise to outgoing diffraction waves; this scattering process is represented by the operator $\mathcal{G}_0^* \mathcal{T}^*$. This is just the well-known *low-energy electron diffraction*, LEED, state. Now, imagine that the time evolution of this state is reversed; we then obtain incoming scattered waves first, followed by an outgoing plane-wave directed toward the detector! This is just the time-reversed “LEED” state. This situation reflects the fact that the photoelectron is scattered prior to reaching the detector.

The final state $\Phi(\mathbf{r}'; \mathbf{k}_f, E_i + \hbar\omega)$ contains the outgoing plane-wave plus the scattered states. These incoming waves travel towards the surface both in the solid and in vacuum, and assure the continuity of the complete wavefunction and of its normal derivative; they are of two types:

- (i) Evanescent waves that are localized at the surface boundary, with energies lying in bulk energy gaps. These are solutions to the Schrödinger equation which are not allowed in the infinite crystal, but exist in the presence of a surface.
- (ii) Bulk Bloch-wave solutions to the Schrödinger equation.

The different types of electronic wavefunctions that may exist in the surface region are shown in Figure 16.3.

16.5.1 Wavevector selection rules

We denote the wavevectors of the outgoing plane-wave and the incoming waves by $\mathbf{k}_f^{\text{out}} = (\mathbf{K}_f^{\text{out}}, k_{\perp f}^{\text{out}})$ and $\mathbf{k}_f^{\text{in}} = (\mathbf{K}_f^{\text{in}}, k_{\perp f}^{\text{in}})$, respectively. $\mathbf{k}_f^{\text{out}}$ is the experimental quantity derived from angular resolution. We find that the periodic translation invariance parallel to the

surface leads to a conservation of $\mathbf{K}_f$ across the surface boundary to within a reciprocal lattice vector $\mathbf{G}_\parallel$. Thus, each of the above component-waves must satisfy the relations

$$\begin{aligned}\mathbf{K}_f^{\text{out}} &= \mathbf{K}_f^{\text{in}} + \mathbf{G}_\parallel, \\ k_{\perp f}^{\text{out}} &\neq k_{\perp f}^{\text{in}},\end{aligned}\tag{16.74}$$

where the second inequality reflects the conditions (16.67). Normal components $k_{\perp f}$ obey the relation

$$k_{\perp f} \equiv k_{\perp f}(\mathbf{K}_f, E),$$

with respect to their dispersion curves. Thus, a knowledge of $k_{\perp f}^{\text{out}}$ does not provide any information about $k_{\perp f}^{\text{in}}$. We need to have some information about the final-state dispersion inside the crystal. This can be obtained by different means:

- (i) Assumption of a free-electron-like dispersion, together with a prior knowledge of the Fermi energy and the work function.
- (ii) Use of calculated band structure for the final state.
- (iii) Applying the method of triangulation by carrying out the measurements on two different crystallographic faces.

16.5.2 Photoexcitation selection rules

To derive these selection rules [118, 119, 120, 121, 122], we use the fact that for $z < 0$ the eigenfunctions of $\mathcal{H}_0$ consist of linear combinations of Bloch waves of the form

$$\phi_n = \exp(i\mathbf{k}^{(n)} \cdot \mathbf{r}) u_n(\mathbf{r}; \mathbf{K}, E, k_{\perp}^{(n)}),\tag{16.75}$$

with u a periodic function of $\mathbf{r}$, to obtain an expression for M_{fi} in the form

$$\begin{aligned}M_{fi} &= \int_{z \leq 0} \exp \left[i \left(\mathbf{k}_i^{(m)} - \mathbf{k}_f^{(n)} \right) \cdot \mathbf{r} \right] u_f \mathbf{A} \cdot (\nabla + i\mathbf{k}_i) u_i d^3r \\ &= \int_{z \leq 0} \exp \left[i \left(\mathbf{k}_i^{(m)} - \mathbf{k}_f^{(n)} + \mathbf{q} \right) \cdot \mathbf{r} \right] u_f \mathbf{A}_0 \cdot (\nabla + i\mathbf{k}_i) u_i d^3r,\end{aligned}\tag{16.76}$$

where we set the vector potential

$$\mathbf{A}(\mathbf{r}) = \mathbf{A}_0 e^{i\mathbf{q} \cdot \mathbf{r}}, \quad \mathbf{q} = (\mathbf{Q}, q),$$

with $|\mathbf{q}| \ll \text{BZ dimension}$.

The integral in (16.76) can be expressed as a product of an integral over a primitive cell (mesh) and a lattice sum over the semi-infinite solid. We define a primitive lattice vector as $\mathbf{t} = \sum_{i=1}^3 m_i \hat{\mathbf{a}}_i$, and choose the basis vector $\mathbf{a}_3$ to be normal to the surface plane, such that

$$\begin{aligned}\mathbf{t} &= \mathbf{T} + m_3 \hat{\mathbf{a}}_3, \\ \mathbf{r} &= \mathbf{R} + z \mathbf{a}_3.\end{aligned}\tag{16.77}$$

We define $\mathbf{M}$ as the integral over the primitive cell Ω ,

$$\mathbf{M} = \int_{\Omega} \exp \left[i(\mathbf{k}_i - \mathbf{k}_f + \mathbf{Q}) \cdot \mathbf{r} \right] u_f^{(k)}(\mathbf{r}) (i\mathbf{k}_i + \nabla) u_i^{(k)}(\mathbf{r}) d^3r.\tag{16.78}$$

We can identify two contributions to (16.76):

(i) a contribution from surface states

$$\begin{aligned} M_s &= i\hbar \mathbf{A}_0 \cdot \mathbf{M} \frac{1}{N} \sum_{m_1, m_2=-\infty}^{\infty} \exp [i(\mathbf{K}_i - \mathbf{K}_f + \mathbf{Q}) \cdot \mathbf{T}] \\ &= i\hbar \mathbf{A}_0 \cdot \mathbf{M} \delta(\mathbf{K}_i - \mathbf{K}_f + \mathbf{Q}) \simeq i\hbar \mathbf{A}_0 \cdot \mathbf{M} \delta(\mathbf{K}_i - \mathbf{K}_f), \end{aligned} \quad (16.79)$$

and

(ii) a contribution from bulk states

$$\begin{aligned} M_B &= i\hbar \mathbf{A}_0 \cdot \mathbf{M} \sum_{m_1, m_2=-\infty}^{\infty} \exp [i(\mathbf{k}_i - \mathbf{k}_f + \mathbf{Q}) \cdot \mathbf{T}] \sum_{m_3=-1}^{-\infty} \exp [2\pi i \Delta k_{\perp} a_3 m_3] \\ &\simeq i\hbar \mathbf{A}_0 \cdot \mathbf{M} \delta(\mathbf{K}_i - \mathbf{K}_f) \sum_{m_3=-1}^{-\infty} \exp [2\pi i \Delta k_{\perp} a_3 m_3], \end{aligned} \quad (16.80)$$

where $\Delta k_{\perp} = k_{\perp i} - k_{\perp f} + q \simeq k_{\perp i} - k_{\perp f}$.

Before carrying out the semi-infinite sum over m_3 , we should consider the effect of two quantities on the outcome of the summation: the photon absorption coefficient α ; and the electronic extraction length λ_e , namely, the mean free path for elastic emission of photoexcited electrons. Defining $L^{-1} = \lambda_e^{-1} + \alpha$, we find that the probability of emitting an electron photoexcited at a distance $z < 0$ inside the solid is $\exp[z/L]$, and that we have to modify (16.78) and (16.80) as

$$\begin{aligned} M_B(L) &= -(2\pi)^2 i\hbar \mathbf{A}_0 \cdot \mathbf{M}(L) \delta(\mathbf{K}_i - \mathbf{K}_f) \exp [-(2\pi i \Delta k_{\perp} + L^{-1})a] \\ &\quad \times \sum_{m=0}^{\infty} \left(e^{-(2\pi i \Delta k_{\perp} + L^{-1})a} \right)^m \\ &= -i\hbar \mathbf{A}_0 \cdot \mathbf{M}(L) \delta(\mathbf{K}_i - \mathbf{K}_f) \left[e^{(2\pi i \Delta k_{\perp} + L^{-1})a} - 1 \right]^{-1}, \end{aligned} \quad (16.81)$$

$$\begin{aligned} \mathbf{M}(L) &= \int_{\Omega} \exp [i(\mathbf{k}_i - \mathbf{k}_f + \mathbf{Q}) \cdot \mathbf{r} + z L^{-1}] \\ &\quad \times u_f^{(b)}(\mathbf{r}) (i\mathbf{k}_i + \nabla) u_i^{(b)}(\mathbf{r}) d^3 r. \end{aligned} \quad (16.82)$$

Figure 16.4 shows a typical direct photoexcitation process between initial and final bands. Figure 16.5 shows the relative intensity for an effective extraction length of $L = 5a$, it has a half-maximum value of $\Delta k_{\perp} = 0.04$ of K_{BZ} , which is manifest as momentum broadening around $k_{\perp}$.

We are now left with the matrix element of (16.81) subject to the symmetry operations of the surface space-group. After applying the conserving delta-function $\delta(\mathbf{K}_i - \mathbf{K}_f)$ the exponential term is invariant under all operations of the surface space-group, and the integrand should then transform according to the Kronecker product

$${}^{(f)}\Gamma \otimes {}^{(v)}\Gamma \otimes {}^{(i)}\Gamma \quad (16.83)$$

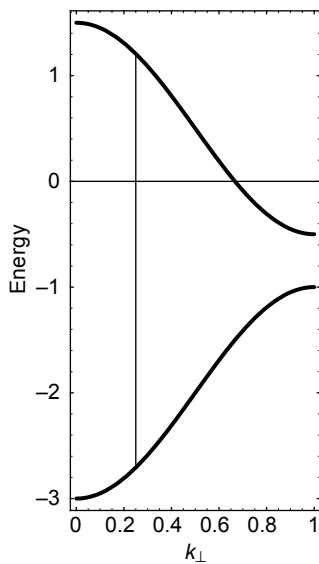
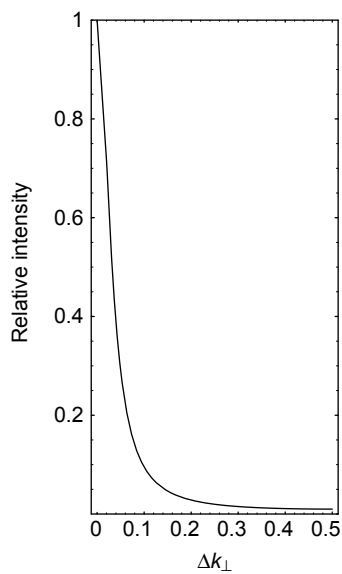


Fig. 16.4. Direct photoexcitation transition.

Fig. 16.5. Relative intensity as a function of $\Delta k_{\perp}$ for $L = 5a$.

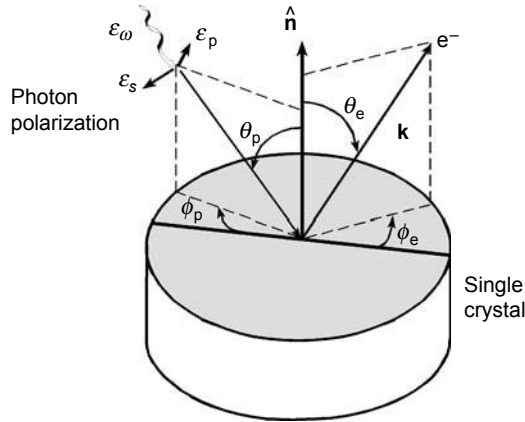


Fig. 16.6. Geometry of angle-resolved photoemission.

where $(i)\Gamma$ and $(f)\Gamma$ are Irreps of that group, while $(v)\Gamma$ is the 3D vector Rep. The key here is to identify the possible symmetry combinations of the final states, photon dipole operator, and initial states involved in the photoexcitation that contribute to a nonvanishing $\mathbf{M}$ in (16.82). The selection rules associated with $\mathbf{M}$ can be used to determine the symmetry of the states that are involved in direct transitions, both surface and bulk; and in cases of complicated spectra they can be used to reduce the number of lines, making an analysis more tractable. Moreover, in some cases, as we demonstrate below, the symmetry of the final state can be preset by the choice of the geometric arrangement of the source–sample–detector.

A typical geometry, showing the relative orientation of the radiation field, sample surface, and detector is given in Figure 16.6. Most important are θ_e and ϕ_e , the polar and azimuthal angles of electron emission relative to the sample normal and the crystallographic axes. Also shown are θ_p and ϕ_p , the polar and azimuthal angles of the incident light. The polarization of the incident light has s- and p-components, perpendicular and parallel to the plane of incidence¹, respectively. In general, the directions of the photon polarization and electron emission can be controlled.

- (i) **The photon dipole operator** Synchrotron sources provide the convenience of linearly polarized radiation, which allows different alignment geometries of the light polarization with respect to the crystallographic axes of the sample. Two geometries, Figure 16.7, have been extensively used when the plane of incidence intersects a surface high-symmetry direction: (a) s-polarization, with the $\mathbf{A}$ -vector normal to the high-symmetry direction (principal-axis of the crystalline surface); (b) p-polarization, with the $\mathbf{A}$ -vector in the plane of incidence.
- (ii) **The final state** The electron detector (electron energy analyzer) employed in angle-resolved photoemission experiments has an angle-resolving aperture that

¹ The plane of incidence is formed by the direction of photon propagation and the normal to the surface.

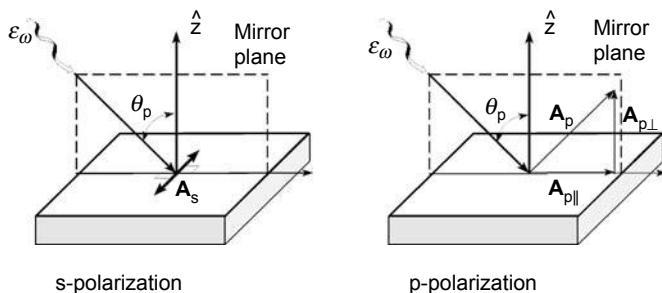


Fig. 16.7. Geometry of s- and p-polarizations.

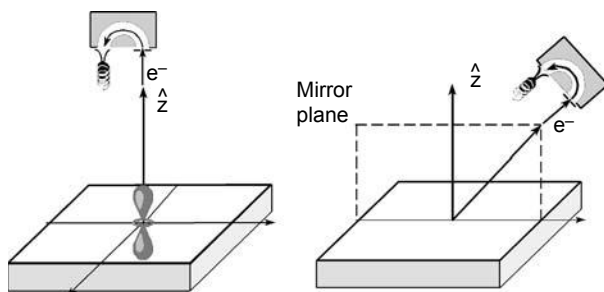


Fig. 16.8. Sample-detector geometry in angle-resolved photoemission experiments.

defines the direction of photoemitted electrons collected by the detector. In such experiments, the analyzer aperture is positioned either normal to the surface, normal emission, or coinciding with a mirror symmetry plane, as shown in Figure 16.8.

In order for the final state of the photoexcitation to be detectable, it should have a nonvanishing amplitude along the line joining the origin at the surface to the detector aperture. This can be achieved in normal emission if the final state belongs to the identity Irrep of the point-group that leaves the surface normal invariant, Figure 16.8. When the detector is located in a mirror plane, the final state wavefunction must be totally symmetric with respect to the symmetry operations associated with the mirror plane, Figure 16.8.

Example 16.3

Symmetry of final states in normal emission from cubic systems

The symmetry of a final photoexcitation state will depend on the surface orientation of the cubic crystal. As shown in the case of an f.c.c. lattice in Figure 16.9, for (001)-oriented surface, normal emission is along the [001], Δ -direction, and the symmetry of the final state has to be Δ_1 . Similarly, we find that the detectable final state, in normal emission, for a (110)-surface (Σ -direction) is Σ_1 , and for a (111)-surface Λ_1 .

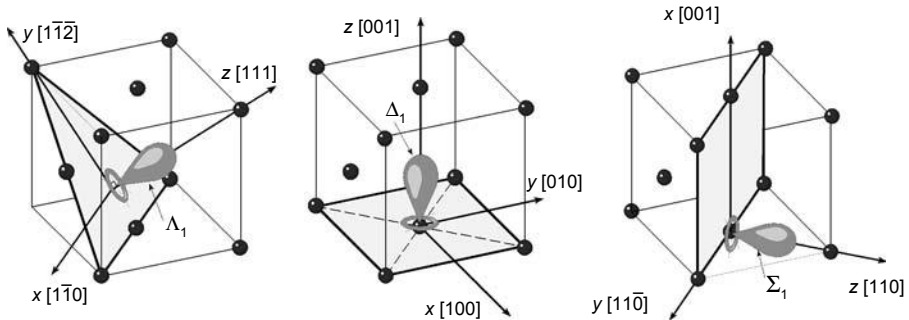


Fig. 16.9. Low-index surfaces of the f.c.c. lattice, showing the orientation of the Cartesian axes x , y , z with respect to the crystallographic directions.

Example 16.4

Selection rules for cubic systems in normal emission

	Irrep	Orbit type	Pol.	Irrep	Orbit type	Pol.	Irrep	Orbit type	Pol.
Final state	Δ_1	s, p_z, d_{z^2}		Σ_1	s, p_z, d_{z^2}		Λ_1	s, p_z, d_{z^2}	
Initial state	Δ_1	s, p_z, d_{z^2}	p	Σ_1	s, p_z, d_{z^2}	p	Λ_1	s, p_z, d_{z^2}	p
	Δ_2	$d_{x^2-y^2}$	forb.	Σ_2	d_{xy}	forb.	Λ_3	p_x, d_{xz}	$s(\mathbf{A} \parallel y)$
	Δ'_2	d_{xy}	forb.	Σ_3	p_x, d_{xz}	$s(\mathbf{A} \parallel x)$	Λ_3	p_y, d_{yz}	$s(\mathbf{A} \parallel y)$
	Δ_5	p_x, d_{xz}	$s(\mathbf{A} \parallel x)$	Σ_4	p_y, d_{yz}	$s(\mathbf{A} \parallel y)$	Λ_2	$d_{x^2-y^2}$	forb.
	Δ_5	p_y, d_{yz}	$s(\mathbf{A} \parallel y)$						
	Δ'_1		forb.						

The incorporation of spin complicates the labeling scheme for the symmetries of the wavefunctions, but actually adds little to the analysis of dipole selection rules. The reason behind this is that the dipole operator $\mathbf{A} \cdot \mathbf{p}$ acts only on the spatial components of the wavefunctions and not on the spin components. Since the total wavefunction is the product of a spatial function and a spinor, one simply needs to determine the spatial symmetry of the wavefunctions in dealing with polarization selection rules. The spin-orbit interaction mixes states, but does not destroy the underlying polarization selection rules on the spatial wavefunction.

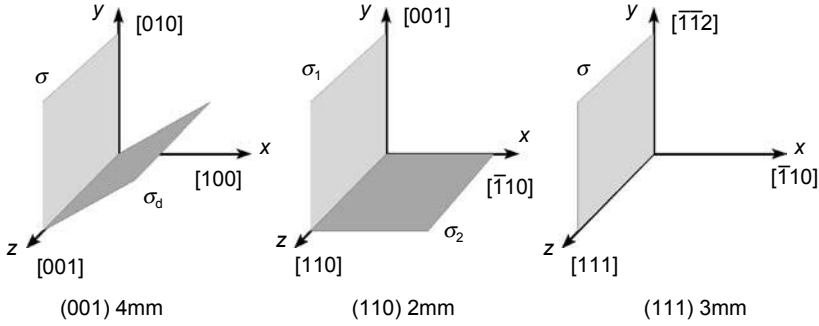


Fig. 16.10. Selection rules for cubic systems for normal emission.

16.6 Neutron and atom scattering spectroscopies

Neutron and light neutral atomic beams at thermal energies provide the rather exceptional compatibility with the energy and momentum ranges that characterize bulk and surface dynamical excitations in condensed matter systems. As such, neutron and atom probes present unique and complementary techniques for mapping the dispersion curves of dynamical excitations (such as phonons and magnons) throughout the bulk and surface Brillouin zones, respectively.

16.6.1 Neutron scattering spectroscopy

Neutrons interact with condensed matter systems in two ways:

- (i) They interact with the constituent nuclei with a typical interaction range of about 10^{-5} Å. Since slow-neutrons have a wavelength much greater than this interaction range, neutron–nucleus scattering can be considered to be s-wave scattering, and can be characterized by a *scattering length* parameter b .
- (ii) They also interact magnetically with the target's electrons. These interactions can be differentiated into a coupling with the spin-moment and with the orbital-moment of an electron.

Nuclear scattering and phonons

The determination of crystal phonon frequencies through experiments of coherent inelastic neutron scattering (INS) is now a rather standard technique in solid state physics. It is derived from the scattering of neutrons from the nuclei of the constituent atoms [123, 124, 125].

In the present analysis we adopt the conventional Fermi pseudopotential, which has the form

$$v(\mathbf{r} - \mathbf{x}_j) = \frac{2\pi b_j \hbar^2}{M} \delta(\mathbf{r} - \mathbf{x}_j), \quad (16.84)$$

where b_j is the neutron–nucleus scattering length corresponding to species j ; b_j is obtained from experimental measurements using the expression of the total scattering cross-section

$$\sigma_j = 4\pi b_j^2,$$

associated with s-wave scattering. For the sake of pedagogy, we consider the case of a monatomic system, so that there is only one b .

Substitution of (16.84) in (16.38) gives

$$\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} = b^2 \left(\frac{k_f}{k} \right) \sum_{lm} \int dt e^{-i\omega t} \left\langle e^{-i\mathbf{Q} \cdot \mathbf{x}_l(0)} e^{i\mathbf{Q} \cdot \mathbf{x}_m(t)} \right\rangle_T. \quad (16.85)$$

Writing $\mathbf{x}_l = \mathbf{R}_l + \mathbf{u}_l$, where we use the notation of Chapter 15, we obtain

$$\left\langle e^{-i\mathbf{Q} \cdot \mathbf{x}_l(0)} e^{i\mathbf{Q} \cdot \mathbf{x}_m(t)} \right\rangle_T = e^{-i\mathbf{Q} \cdot (\mathbf{R}_l - \mathbf{R}_m)} \left\langle e^{-i\mathbf{Q} \cdot \mathbf{u}_l(0)} e^{i\mathbf{Q} \cdot \mathbf{u}_m(t)} \right\rangle_T. \quad (16.86)$$

Next, we use the Baker–Hausdorff relation

$$e^A e^B = e^{A+B} e^{[A,B]/2}$$

and write

$$\left\langle e^{-i\mathbf{Q} \cdot \mathbf{u}_l(0)} e^{i\mathbf{Q} \cdot \mathbf{u}_m(t)} \right\rangle_T = \left\langle e^{-i\mathbf{Q} \cdot (\mathbf{u}_m(t) - \mathbf{u}_l(0))} \right\rangle_T e^{[\mathbf{Q} \cdot \mathbf{u}_m(t), \mathbf{Q} \cdot \mathbf{u}_l(0)]/2}, \quad (16.87)$$

where, as will be shown, the commutator is just a c-number.

In order to proceed further we use the expansion of $\mathbf{u}_l$ in terms of the symmetrized normal mode field operators given in Chapter 15, namely,

$$\begin{aligned} \mathbf{u}_l(t) = \sum_{\mathbf{q}, \mu} \sqrt{\frac{\hbar}{2NM\omega_\mu(\mathbf{q})}} \hat{\mathbf{e}}_\mu(\mathbf{q}) \\ \times \left[e^{i(\mathbf{q} \cdot \mathbf{R}_l - \omega_\mu(\mathbf{q})t)} a_\mu(\mathbf{q}) + e^{-i(\mathbf{q} \cdot \mathbf{R}_l - \omega_\mu(\mathbf{q})t)} a_\mu^\dagger(\mathbf{q}) \right], \end{aligned} \quad (16.88)$$

where $\hat{\mathbf{e}}$ is the polarization-vector of the $\mu\mathbf{q}$ mode, and the creation/annihilation operators satisfy

$$[a_\mu(\mathbf{q}), a_\nu^\dagger(\mathbf{q}')] = \delta_{\mu,\nu} \delta_{\mathbf{q},\mathbf{q}'}, \quad (16.89)$$

so that the thermal average

$$\langle a_\mu^\dagger(\mathbf{q}) a_\nu(\mathbf{q}') \rangle_T = \delta_{\mu,\nu} \delta_{\mathbf{q},\mathbf{q}'} \langle n_\mu(\mathbf{q}) \rangle_T = \frac{1}{\exp[\hbar\omega_\mu(\mathbf{q})/k_B T] - 1}.$$

With the aid of (16.88) and (16.89), we find that commutators appearing in (16.87) are just the c-numbers

$$\begin{aligned} [\mathbf{u}_m(t), \mathbf{u}_l(0)] &= \frac{2i\hbar}{2NM\omega_\mu(\mathbf{q})} \sum_{\mu\mathbf{q}} \frac{|\mathbf{Q} \cdot \hat{\mathbf{e}}_\mu(\mathbf{q})|^2}{2\omega_\mu(\mathbf{q})} \sin \theta_{lm}(\mathbf{q}, t) \\ \theta_{lm}(\mathbf{q}, t) &= \mathbf{q} \cdot (\mathbf{R}_l - \mathbf{R}_m) + \omega_\mu(\mathbf{q})t. \end{aligned} \quad (16.90)$$

In order to evaluate the thermal average in (16.87), we use the identity for Bose operators

$$\langle e^{\hat{A}} \rangle_T = \exp \left[\frac{1}{2} \langle \hat{A}^2 \rangle_T \right],$$

to write

$$\left\langle e^{-i\mathbf{Q} \cdot (\mathbf{u}_m(t) - \mathbf{u}_l(0))} \right\rangle_T = \exp \left[- \left\langle \frac{\{ \mathbf{Q} \cdot (\mathbf{u}_m(t) - \mathbf{u}_l(0)) \}^2}{2} \right\rangle_T \right]. \quad (16.91)$$

A proof of this identity can be outlined as follows:

Writing A as some linear operator of the field operators

$$A = x a + y a^\dagger,$$

and using the Baker–Hausdorff relation to write

$$\begin{aligned} \langle \exp[A] \rangle_T &= \langle \exp[x a] \exp[y a^\dagger] \rangle_T \exp[xy/2], \\ \langle \exp[x a] \exp[y a^\dagger] \rangle_T &= \frac{1}{Z} \sum_{n=0}^{\infty} e^{-\beta E_n} \langle n | \exp[x a] \exp[y a^\dagger] | n \rangle, \\ Z &= \exp[-\beta \hbar \omega / 2] \sum_{n=0}^{\infty} \exp[-n\beta \hbar \omega] = \frac{\exp(-\beta \hbar \omega / 2)}{1 - \exp(-\beta \hbar \omega)}. \end{aligned}$$

Expressing $|n\rangle$ in terms of $a^\dagger$ as

$$|n\rangle = \left(\frac{1}{n!} \right)^{1/2} a^{\dagger n} |0\rangle$$

we obtain

$$\exp[y a^\dagger] |n\rangle = \sum_{m=0}^{\infty} \left(\frac{(n+m)!}{n!} \right)^{1/2} \frac{y^m}{m!} |n+m\rangle,$$

which leads to

$$\begin{aligned} \langle n | \exp[x a] \exp[y a^\dagger] | n \rangle &= \sum_{lm} ((n+l)! + (n+m)!)^{1/2} \frac{x^l y^m}{l! m! n!} \langle n+l | n+m \rangle \\ &= \sum_{m=0}^{\infty} \frac{(n+m)!}{n! (m!)^2} (xy)^m. \end{aligned}$$

Next, we use this result, together with the identity

$$\sum_{n=0}^{\infty} \frac{(n+m)!}{n! m!} z^n = \frac{1}{(1-z)^{m+1}},$$

to obtain

$$\begin{aligned}\langle \exp[x a] \exp[y a^\dagger] \rangle_T &= \frac{1}{Z} Z \sum_{m=0}^{\infty} \frac{1}{m!} \left(\frac{xy}{1 - \exp(-\beta \hbar \omega)} \right)^m \\ &= \exp \left[\frac{xy}{1 - \exp(-\beta \hbar \omega)} \right] = \exp [xy (\langle a^\dagger a \rangle_T + 1)],\end{aligned}$$

which gives

$$\langle \exp[A] \rangle_T = \exp \left[xy (\langle a^\dagger a \rangle_T + 1/2) \right] = \exp \left[\frac{1}{2} \langle A^2 \rangle_T \right].$$

Again, using (16.88) we obtain

$$\begin{aligned}\mathbf{Q} \cdot (\mathbf{u}_m(t) - \mathbf{u}_l(0)) &= \sqrt{\frac{\hbar}{NM}} \sum_{\mathbf{q}\mu} \frac{\mathbf{Q} \cdot \hat{\epsilon}_\mu(\mathbf{q})}{\sqrt{2\omega_\mu(\mathbf{q})}} [f_{ml}^\mu(\mathbf{q}, t) a_\mu(\mathbf{q}) + f_{ml}^{\mu*}(\mathbf{q}, t) a_\mu^\dagger(\mathbf{q})] \\ f_{ml}^\mu(\mathbf{q}, t) &= e^{i(\mathbf{q} \cdot \mathbf{R}_m - \omega_\mu(\mathbf{q})t)} - e^{i\mathbf{q} \cdot \mathbf{R}_l} \\ f_{ml}^\mu f_{ml}^{\mu*} &= 2 (1 - \cos \theta_{lm})\end{aligned}\tag{16.92}$$

so that

$$\begin{aligned}[\mathbf{Q} \cdot (\mathbf{u}_m(t) - \mathbf{u}_l(0))]^2 &= \frac{\hbar}{NM} \sum_{\mathbf{q}\mu} \frac{|\mathbf{Q} \cdot \hat{\epsilon}_\mu(\mathbf{q})|^2}{2\omega_\mu(\mathbf{q})} f_{ml}^\mu f_{ml}^{\mu*} [a_\mu(\mathbf{q}) a_\mu^\dagger(\mathbf{q}) + a_\mu^\dagger(\mathbf{q}) a_\mu(\mathbf{q})] \\ &= 2w(\mathbf{Q}) - 2g_{lm}(\mathbf{Q}),\end{aligned}\tag{16.93}$$

where

$$\begin{aligned}w(\mathbf{Q}) &= \frac{\hbar}{NM} \sum_{\mathbf{q}\mu} \frac{|\mathbf{Q} \cdot \hat{\epsilon}_\mu(\mathbf{q})|^2}{2\omega_\mu(\mathbf{q})} (2n_\mu(\mathbf{q}) + 1), \\ g_{lm}(\mathbf{Q}) &= \frac{\hbar}{NM} \sum_{\mathbf{q}\mu} \frac{|\mathbf{Q} \cdot \hat{\epsilon}_\mu(\mathbf{q})|^2}{2\omega_\mu(\mathbf{q})} (2n_\mu(\mathbf{q}) + 1) \cos \theta_{lm}.\end{aligned}\tag{16.94}$$

Substituting (16.93), (16.91), and (16.90) in (16.87) we obtain

$$\left\langle e^{-i\mathbf{Q} \cdot \mathbf{u}_l(0)} e^{i\mathbf{Q} \cdot \mathbf{u}_m(t)} \right\rangle_T = e^{-2W(\mathbf{Q})} e^{G_{lm}(\mathbf{Q}, t)},\tag{16.95}$$

where

$$\begin{aligned}
 W(\mathbf{Q}) &= \frac{\hbar}{NM} \sum_{\mathbf{q}\mu} \frac{|\mathbf{Q} \cdot \hat{\epsilon}_\mu(\mathbf{q})|^2}{2\omega_\mu(\mathbf{q})} (2\langle n_\mu(\mathbf{q}) \rangle_T + 1) \\
 &= \langle (\mathbf{Q} \cdot \mathbf{u}_l(0))^2 \rangle_T, \\
 G_{lm}(\mathbf{Q}) &= \frac{\hbar}{NM} \sum_{\mathbf{q}\mu} \frac{|\mathbf{Q} \cdot \hat{\epsilon}_\mu(\mathbf{q})|^2}{\omega_\mu(\mathbf{q})} \left[(2\langle n_\mu(\mathbf{q}) \rangle + 1) \cos \theta_{lm} + i \sin \theta_{lm} \right] \\
 &= \frac{\hbar}{NM} \sum_{\mathbf{q}\mu} \frac{|\mathbf{Q} \cdot \hat{\epsilon}_\mu(\mathbf{q})|^2}{\omega_\mu(\mathbf{q})} \left[(\langle n_\mu(\mathbf{q}) \rangle + 1) e^{i\theta_{lm}} + \langle n_\mu(\mathbf{q}) \rangle e^{-i\theta_{lm}} \right]. \quad (16.96)
 \end{aligned}$$

The second term in (16.95) contains all multiphonon scattering events; we can limit our analysis to single-phonon scattering events by considering only up to linear terms in its expansion, namely,

$$e^{G_{lm}(\mathbf{Q}, t)} \simeq 1 + G_{lm}(\mathbf{Q}, t).$$

Substituting back in (16.94) and combining it with (16.87) and (16.78) we obtain

$$\begin{aligned}
 \left\langle e^{-i\mathbf{Q} \cdot \mathbf{x}_l(0)} e^{i\mathbf{Q} \cdot \mathbf{x}_m(t)} \right\rangle_T &= \\
 e^{-2W(\mathbf{Q})} \left[e^{-i\mathbf{Q} \cdot (\mathbf{R}_l - \mathbf{R}_m)} + \frac{\hbar}{NM} \sum_{\mathbf{q}\mu} \frac{|\mathbf{Q} \cdot \hat{\epsilon}_\mu(\mathbf{q})|^2}{\omega_\mu(\mathbf{q})} \right. \\
 \times \left. \left((\langle n_\mu(\mathbf{q}) \rangle + 1) e^{i(\mathbf{Q} + \mathbf{q}) \cdot (\mathbf{R}_l - \mathbf{R}_m) + i\omega_\mu(\mathbf{q})t} + \langle n_\mu(\mathbf{q}) \rangle e^{i(\mathbf{Q} - \mathbf{q}) \cdot (\mathbf{R}_l - \mathbf{R}_m) - i\omega_\mu(\mathbf{q})t} \right) \right]. \quad (16.97)
 \end{aligned}$$

We finally obtain an expression for the differential scattering cross-section by substituting (16.97) in (16.86), and remembering that

$$\sum_{lm} e^{-i\mathbf{K} \cdot (\mathbf{R}_l - \mathbf{R}_m)} = N \frac{(2\pi)^3}{v_0} \sum_{\mathbf{G}} \delta(\mathbf{K} - \mathbf{G}),$$

where v_0 is the primitive cell volume,

$$\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} = \mathfrak{D}(\mathbf{Q}) + \mathfrak{J}(\mathbf{Q}), \quad (16.98)$$

where

- (i) $\mathfrak{D}(\mathbf{Q})$ is the elastic diffraction term corresponding to zero energy exchange; it is given by

$$\mathfrak{D}(\mathbf{Q}) = \frac{(2\pi)^3 N b^2}{v_0} \left(\frac{k_f}{k} \right) e^{-2W(\mathbf{Q})} \sum_{\mathbf{G}} \delta(\mathbf{Q} - \mathbf{G}).$$

- (ii) The second term $\mathfrak{J}(\mathbf{Q})$ represents scattering events involving single-phonon exchange. It consists of:

(a) the single-phonon-emission term,

$$\frac{(2\pi)^3 \hbar}{v_0} \left(\frac{k_f}{k} \right) \sum_{\mu, \mathbf{q}} [\langle n_\mu(\mathbf{q}) \rangle + 1] \frac{\delta(\omega - \omega_\mu(\mathbf{q}))}{2\omega_\mu(\mathbf{q})} \times \delta(\mathbf{Q} + \mathbf{q} - \mathbf{G}) |F_\mu(\mathbf{Q})|^2, \quad (16.99)$$

with energy and momentum conservation relations

$$\mathbf{Q} = \mathbf{G} - \mathbf{q}, \quad \frac{\hbar^2 k^2}{2M} - \frac{\hbar^2 k_f^2}{2M} = \hbar\omega_\mu(\mathbf{q}).$$

(b) the single-phonon-absorption term,

$$\frac{(2\pi)^3 \hbar}{v_0} \left(\frac{k_f}{k} \right) \sum_{\mu, \mathbf{q}} \langle n_\mu(\mathbf{q}) \rangle \frac{\delta(\omega + \omega_\mu(\mathbf{q}))}{2\omega_\mu(\mathbf{q})} \times \delta(\mathbf{Q} - \mathbf{q} - \mathbf{G}) |F_\mu(\mathbf{Q})|^2, \quad (16.100)$$

with energy and momentum conservation relations

$$\mathbf{Q} = \mathbf{G} + \mathbf{q}, \quad \frac{\hbar^2 k_f^2}{2M} - \frac{\hbar^2 k^2}{2M} = \hbar\omega_\mu(\mathbf{q}).$$

The structure factor $F_\mu(\mathbf{Q})$ is given by

$$F_\mu(\mathbf{Q}) = \frac{b}{\sqrt{M}} e^{-W(\mathbf{Q})} \mathbf{Q} \cdot \hat{\epsilon}_\mu(\mathbf{q}) = \mathbf{a}(\mathbf{Q}) \cdot \hat{\epsilon}_\mu(\mathbf{q}); \quad (16.101)$$

it contains all the symmetry information regarding the scattering process.

In practice, it is possible to obtain a mapping of the phonon-dispersion curves for the system of interest by repeating the measurements at many $\mathbf{Q}$ s.

It is quite straightforward to generalize the above results to the case of a multi-atomic primitive cell with different species. For elastic diffractive scattering we obtain

$$\mathfrak{D}(\mathbf{Q}) = \frac{(2\pi)^3 N}{v_0} \left(\frac{k_f}{k} \right) \sum_{\mathbf{G}} \delta(\mathbf{Q} - \mathbf{G}) \sum_s |\mathbf{a}_s(\mathbf{Q})|^2 \sum_{r \in s} e^{i\mathbf{G} \cdot \boldsymbol{\kappa}_r}. \quad (16.102)$$

where the index s labels the species in the atomic basis in the primitive unit cell, $r \in s$, $\boldsymbol{\kappa}_{rs}$ the corresponding vector in the primitive cell, and

$$\mathbf{a}_s(\mathbf{Q}) = \frac{b_s}{\sqrt{M_s}} e^{-W_s(\mathbf{G})} \mathbf{Q}$$

is the exponent of the corresponding Debye–Waller factor.

For inelastic scattering, this is simply done by extending $F_\mu(\mathbf{Q})$ at a particular scattering vector $\mathbf{Q}$, where $\mathbf{Q} \pm \mathbf{q} = \mathbf{G}$, to a sum over the atomic basis, namely,

$$F_\mu(\mathbf{Q}) = \sum_s \sum_{r \in s} \mathbf{a}_s(\mathbf{Q}) \cdot \hat{\epsilon}(r|\mathbf{q}\mu) e^{i(\mathbf{Q}+\mathbf{q}) \cdot \boldsymbol{\kappa}_r}. \quad (16.103)$$

The structural zone

Notice that the terms $e^{i(\mathbf{Q}+\mathbf{q})\cdot\boldsymbol{\kappa}} = e^{i\mathbf{G}\cdot\boldsymbol{\kappa}}$ are periodic in reciprocal space when the $\boldsymbol{\kappa}$ s are rational fractions of the primitive vectors; in this case, we identify the *structural zone* of periodicity as containing several Brillouin zones. If one or more of the fractions are irrational, then the structural zone is infinite in the corresponding directions.

Symmetry selection rules in inelastic neutron scattering

As usual, the symmetry information in inelastic neutron scattering (INS) can be classified with respect to the action of the operations $S = (R|\mathbf{w})$ belonging to the space-group of the wavevector $\mathbf{q}$, $\mathbb{G}_{\mathbf{q}}$ [126, 127, 128, 129, 130, 131]. We proceed in two steps:

- (i) Under the action of S , the polarization vectors $\hat{\mathbf{e}}(r|\mathbf{q}\mu)$ transform according to one of the small Irreps $^{(\tau,\mathbf{q})}\Lambda$ of $\mathbb{G}_{\mathbf{q}}$. In order to allow for the possibility of Irreps of dimensions > 1 and for the multiple appearance of some Irreps, the index μ is understood to stand for τ, j, l , the Irrep index, row index, and Irrep recurrence index, respectively. Thus, we write

$$\hat{S}\hat{\mathbf{e}}(r|\mathbf{q}(\tau, j)) = \sum_{i=1}^{d_\tau} {}^{(\tau,\mathbf{q})}\Lambda(S)_{ij} \hat{\mathbf{e}}(r|\mathbf{q}(\tau, i)), \quad (16.104)$$

where d_τ is the dimension of Irrep $^{(\tau,\mathbf{q})}\Lambda$, so that d_τ degenerate modes transform according to $^{(\tau,\mathbf{q})}\Lambda$.

Alternatively, we may regard $\hat{S}$ as transforming the mode of polarization vector $\hat{\mathbf{e}}(r|\mathbf{q}(\tau, j))$ into a new one with polarization vector $\hat{S}\hat{\mathbf{e}}(r|\mathbf{q}(\tau, j))$, which is given by

$$\hat{S}\hat{\mathbf{e}}(r|\mathbf{q}(\tau, j)) = \hat{R}\hat{\mathbf{e}}(t|\mathbf{q}(\tau, j)) \exp(-i\hat{R}\mathbf{q}\cdot\mathbf{w}) \exp[i(\mathbf{R}\mathbf{q}-\mathbf{q})\cdot\boldsymbol{\kappa}_r], \quad (16.105)$$

where atom t is the symmetry equivalent to r by S .

- (ii) The transformation of the quantity

$$F_\mu(\mathbf{Q}) = \sum_s \mathbf{a}_s(\mathbf{Q}) \cdot \sum_r \hat{\mathbf{e}}(r|\mathbf{q}(\tau, j)) e^{i(\mathbf{Q}+\mathbf{q})\cdot\boldsymbol{\kappa}_r}, \quad (16.106)$$

which contains all the symmetry information of the scattering process relevant to the j th phonon branch. This transformation can be obtained by combining (16.104) and (16.105) and substituting in (16.106) we obtain

$$\begin{aligned} F_i(\hat{R}\mathbf{Q}) &= \sum_{\kappa} a_{\kappa}(\hat{R}\mathbf{Q}) \cdot \hat{\mathbf{e}}_{\kappa}(\mathbf{q}|\tau, i) e^{i(\hat{R}\mathbf{Q}+\mathbf{q})\cdot\boldsymbol{\kappa}} e^{-W_{\kappa}(\hat{R}\mathbf{Q})} \\ &= \sum_{j=1}^{d_\tau} {}^{(\tau,\mathbf{q})}\Lambda^*(S)_{ij} \sum_{\kappa} a_{\kappa}(\hat{R}\mathbf{Q}) \cdot \hat{S}\hat{\mathbf{e}}_{\kappa}(\mathbf{q}|\tau, j) e^{i(\hat{R}\mathbf{Q}+\mathbf{q})\cdot\boldsymbol{\kappa}} e^{-W_{\kappa}(\hat{R}\mathbf{Q})} \end{aligned}$$

$$\begin{aligned}
&= \sum_{j=1}^{d_\tau} {}^{(\tau, \mathbf{q})} \Lambda^*(S)_{ij} \sum_{\kappa} a_{\kappa}(\hat{R}\mathbf{Q}) \cdot \hat{R} \hat{\mathbf{e}}_{\rho}(\mathbf{q}|\tau, j) e^{-i\hat{R}\mathbf{q} \cdot \mathbf{w}} e^{i(\hat{R}\mathbf{q} - \mathbf{q}) \cdot \boldsymbol{\kappa}} \\
&\quad \times e^{i(\hat{R}\mathbf{Q} + \mathbf{q}) \cdot \boldsymbol{\kappa}} e^{-W_{\kappa}(\hat{R}\mathbf{Q})} \\
&= \sum_{j=1}^{d_\tau} {}^{(\tau, \mathbf{q})} \Lambda^*(S)_{ij} \sum_{\kappa} a_{\kappa} \hat{R} [\mathbf{Q} \cdot \hat{\mathbf{e}}_{\rho}(\mathbf{q}|\tau, j)] e^{-i\hat{R}\mathbf{q} \cdot \mathbf{w}} e^{i\hat{R}(\mathbf{Q} + \mathbf{q}) \cdot \boldsymbol{\kappa}} \\
&\quad \times e^{-W_{\kappa}(\hat{R}\mathbf{Q})}.
\end{aligned}$$

Taking into account the rotational symmetry between the Debye–Waller terms, it is straightforward to show that the dynamical structure factor given by (16.106), and corresponding to these d_τ degenerate modes, satisfies

$$F_i(R\mathbf{Q}) = \sum_{j=1}^{d_\tau} {}^{(\tau, \mathbf{q})} \Lambda((R|\mathbf{w}))_{ij}^* \exp(R\mathbf{Q} \cdot \mathbf{w}) F_j(\mathbf{Q}). \quad (16.107)$$

For a general $\mathbf{Q}$, this equation implies the trivial result that

$$\sum_{j=1}^{d_\tau} |F_j(\mathbf{Q})|^2 = \sum_{j=1}^{d_\tau} |F_j(R\mathbf{Q})|^2,$$

i.e. the scattered intensities are equivalent for scattering vectors rotated by R .

Mode-extinction and restricted point-groups Since for a given phonon wavevector $\mathbf{q}$ we can define different $\mathbf{Q}$ s according to the relation

$$\mathbf{Q} = \mathbf{G} - \mathbf{q},$$

we need to confine our discussion, when dealing with a particular $\mathbf{Q}$, to symmetry operations that transform $\mathbf{Q}$ into itself, and not into $\mathbf{Q} + \mathbf{G}'$, since the latter defines a different $\mathbf{Q}$, namely, $\mathbf{Q}' = \mathbf{G} + \mathbf{G}' - \mathbf{q}$. Hence, we introduce the *restricted* point-group of $\mathbf{Q}$, $P_{\mathbf{Q}}^{(s)}$, whose elements satisfy the condition

$$\hat{R}\mathbf{Q} \begin{cases} = \mathbf{Q}, \\ \neq \mathbf{Q} + \mathbf{G} \end{cases} \quad R \in \mathcal{G}_{\mathbf{Q}}, R \in P_{\mathbf{Q}}^{(s)}$$

so that $P_{\mathbf{Q}}^{(s)} \subset \mathcal{G}_{\mathbf{Q}}$. Under the operations of $P_{\mathbf{Q}}^{(s)}$, (16.107) reduces to

$$\begin{aligned}
F_i(\mathbf{Q}) &= \sum_{j=1}^{d_\tau} {}^{(\tau, \mathbf{q})} \Lambda((R|\mathbf{w}))_{ij}^* \exp(\mathbf{Q} \cdot \mathbf{w}) F_j(\mathbf{Q}) \\
&= \sum_{j=1}^{d_\tau} {}^{(\tau, \mathbf{q})} \Delta(R)_{ij} F_j(\mathbf{Q}), \quad (16.108)
\end{aligned}$$

or

$$\mathbf{F}(\mathbf{Q}) = {}^{(\tau, \mathbf{Q})} \Delta(R) \mathbf{F}(\mathbf{Q}), \quad (16.109)$$

where ${}^{(\tau, \mathbf{Q})} \Delta$ is a representation of $P_{\mathbf{Q}}^{(s)}$. Equation (16.109) can only be satisfied if ${}^{(\tau, \mathbf{Q})} \Delta$ contains the identity Irrep, i.e.

$$\sum_{R \in P_{\mathbf{Q}}^{(s)}} {}^{(\tau, \mathbf{q})} \chi^*(R|\mathbf{w}) \exp[i\mathbf{Q} \cdot \mathbf{w}] \neq 0, \quad (16.110)$$

where ${}^{(\tau, \mathbf{q})} \chi$ is the character of $(R|\mathbf{w})$ in the small Irrep ${}^{(\tau, \mathbf{q})} \Lambda$.

Thus, we can state that:

All phonon modes of wavevector $\mathbf{q}$ and symmetry given by the small Irrep ${}^{(\tau, \mathbf{q})} \Lambda$ will be INS inactive at a scattering wavevector $\mathbf{Q}$ ($\mathbf{Q} + \mathbf{q} = \mathbf{G}$) if (16.110) is not satisfied.

Examining the relation $\mathbf{Q} = \mathbf{G} - \mathbf{q}$ reveals that, for $R \in \mathcal{G}_{\mathbf{q}}$

$$R\mathbf{Q} = R\mathbf{G} - R\mathbf{q} = R\mathbf{G} - \mathbf{G}_R - \mathbf{q}, \quad (16.111)$$

where $R\mathbf{q} = \mathbf{G}_R + \mathbf{q}$. Hence, $R\mathbf{Q} = \mathbf{Q}$ requires that

$$R\mathbf{G} - \mathbf{G}_R = \mathbf{G}. \quad (16.112)$$

This gives rise to two cases:

(i) The wavevector $\mathbf{q}$ lies inside the Brillouin zone, then

$$R\mathbf{q} = \mathbf{q}, \quad \mathbf{G}_R = \mathbf{0}, \quad \forall R \in \mathcal{G}_{\mathbf{q}} = P_{\mathbf{q}}^{(s)}$$

$$R\mathbf{G} = \mathbf{G}, \quad R \in P_{\mathbf{G}}^{(s)}.$$

Then $P_{\mathbf{Q}}^{(s)} = P_{\mathbf{G}}^{(s)} \cap \mathcal{G}_{\mathbf{q}}$: the intersection of the point-group $\mathcal{G}_{\mathbf{q}}$ and the restricted point-group of the reciprocal lattice vector $\mathbf{G} = \mathbf{Q} + \mathbf{q}$. The character ${}^{(\tau, \mathbf{q})} \chi((R|\mathbf{w}))$ can be expressed, in this case, as ${}^{(\tau, \mathbf{q})} \chi(R) \exp(-i\mathbf{q} \cdot \mathbf{w})$, where ${}^{(\tau, \mathbf{q})} \chi(R)$ is the character of an Irrep τ of the point-group $\mathcal{G}_{\mathbf{q}}$. Therefore, (16.110) reduces to

$$\sum_{R \in P_{\mathbf{Q}}^{(s)}} {}^{(\tau, \mathbf{q})} \chi(R)^* \exp(i\mathbf{G} \cdot \mathbf{w}) \neq 0, \quad (16.113)$$

which is just a simple check on the presence of the identity Irrep in the Kronecker product of the two irreps, τ and $\exp(i\mathbf{G} \cdot \mathbf{w})$, of $\mathcal{G}_{\mathbf{q}}$ and $P_{\mathbf{G}}^{(s)}$, respectively, when reduced to their common subgroup $P_{\mathbf{Q}}^{(s)}$.

For symmorphic space-groups,

$$\exp(i\mathbf{G} \cdot \mathbf{w}) = \exp(i\mathbf{G} \cdot \mathbf{t}) = 1, \quad \forall \mathbf{G},$$

and the selection rule becomes a simple check of whether the representation subduced in $P_{\mathbf{Q}}^{(s)}$ by the Irrep τ contains the identity representation or not.

For nonsymmorphic groups, the resulting extinctions are also valid for $\mathbf{G}$ s that satisfy $\exp(i\mathbf{G} \cdot \mathbf{w}) = 1$, i.e. for all elements $(R|\mathbf{t})$ with R belonging to the point-group $P_{\mathbf{Q}}^{(s)}$. The reciprocal lattice vectors corresponding to nonextinct Bragg diffraction reflections fulfill this condition. Hence, it can be generally stated that:

The selection rules for phonons of a nonsymmorphic space-group coincide with those of the corresponding symmorphic group if the Brillouin zone of the measurement is centered in a non-forbidden Bragg reflection.

Conversely, in Brillouin zones centered on extinct Bragg reflections, new phonon extinction rules exist that depend on the nonprimitive translational part of the symmetry operations.

- (ii) Wavevector $\mathbf{q}$ lies on the Brillouin zone boundary, in which case $\mathbf{G}_R$ may be nonzero for some operations of $\mathcal{G}_{\mathbf{q}}$, and thus $P_{\mathbf{Q}}^{(s)}$ may contain operations that do not belong to $P_{\mathbf{G}}^{(s)}$. Equation (16.113) can still be applied if we replace the characters $\tau_{\chi}(R)$ by a multiplier Irrep of $\mathcal{G}_{\mathbf{q}}$; or, alternatively, avoid the use of multiplier irreps and use directly (16.110), the small irreps of $\mathcal{G}_{\mathbf{q}}$.

Examples In order to elucidate the ideas and techniques presented above, we discuss several examples that represent an exhaustive spectrum of space-group types encountered in INS experiments [131]. In each case, we confine our discussion to selection rules for modes at the Γ -point ($\mathbf{q} = \mathbf{0}$), the Σ - or Δ -lines ($\mathbf{q} = (\alpha, 0, 0)$), and the X -point ($\mathbf{q} = (1/2, 0, 0)$) for some space-groups. Since extinction constraints are the result of symmetry, we only consider $\mathbf{G}$ vectors with nontrivial symmetry groups. Thus the selection rules entries are limited to Brillouin zone centers $\mathbf{G}$, where some extinction exists for phonons observed at $\mathbf{Q} = \mathbf{G} - \mathbf{q}$. We only list in each case the irreps of the phonons which are *active*.

Examples 16.5

Space-group $Pmm2$ ($\mathcal{C}_{2v}^1$, #25)

(a) Γ -point ($\mathbf{Q} = \mathbf{G}$)

	E	C_{2z}	m_x	m_y
$^{(1)}\Gamma$	1	1	1	1
$^{(2)}\Gamma$	1	1	-1	-1
$^{(3)}\Gamma$	1	-1	-1	1
$^{(4)}\Gamma$	1	-1	1	-1

We consider here the Brillouin zone vectors, $\mathbf{G} = \mathbf{Q}$, with nontrivial symmetry:

$$\begin{aligned} (0, 0, l) P_{\mathbf{Q}}^{(s)} = mm2 &\Rightarrow \begin{cases} {}^{(1)}\Gamma & \sum \chi = 4 \\ {}^{(2)}\Gamma, {}^{(3)}\Gamma, {}^{(4)}\Gamma & \sum \chi = 0 \end{cases} \\ (h, 0, l) P_{\mathbf{Q}}^{(s)} = m11 &\Rightarrow \begin{cases} {}^{(1)}\Gamma, {}^{(3)}\Gamma & \sum \chi = 2 \\ {}^{(2)}\Gamma, {}^{(4)}\Gamma & \sum \chi = 0 \end{cases} \\ (0, k, l) P_{\mathbf{Q}}^{(s)} = 1m1 &\Rightarrow \begin{cases} {}^{(1)}\Gamma, {}^{(4)}\Gamma & \sum \chi = 2 \\ {}^{(2)}\Gamma, {}^{(3)}\Gamma & \sum \chi = 0 \end{cases} \end{aligned}$$

We note that ${}^{(2)}\Gamma$ is silent except at a general Brillouin zone; this suggests that we can identify the symmetry of all measured Γ phonons by making measurements at three different Brillouin zones.

(b) Σ -line ($\mathbf{Q} = \mathbf{G} - (q_x, 0, 0)$)

$\mathcal{G}_{\Sigma} = 1m1 = (E, m_y)$, with two Irreps ${}^{(1)}\Sigma$ and ${}^{(2)}\Sigma$.

$$P_{\mathbf{Q}}^{(s)} = P_{\mathbf{G}}^{(s)} \cap \mathcal{G}_{\Sigma},$$

yielding

$$\begin{aligned} (h, 0, l), \quad P_{\mathbf{G}}^{(s)} = \mathcal{G}_{\Sigma}, \quad P_{\mathbf{Q}}^{(s)} = 1m1 &\Rightarrow {}^{(2)}\Sigma \text{ extinct} \\ (0, k, l), \quad P_{\mathbf{G}}^{(s)} = m11, \quad P_{\mathbf{Q}}^{(s)} = 1 &\Rightarrow \text{no extinction} \end{aligned}$$

(c) X -point ($\mathbf{Q} = \mathbf{G} - (l/2, 0, 0)$)

$\mathcal{G}_{\mathbf{q}} = mm2$, with four Irreps ${}^{(i)}X = {}^{(i)}\Gamma$, $i = 1, \dots, 4$. This case is redundant, it does not yield any new scattering vector $\mathbf{Q}$ symmetries different from those obtained for the Σ -line. We are thus left with a single selection rule:

$$(h, 0, l), \quad P_{\mathbf{Q}}^{(s)} = 1m1; \Rightarrow {}^{(1)}X, {}^{(3)}X, \text{ active},$$

which is obviously the result of continuity, where these two X Irreps are compatible with the only active Irrep along the Σ -line.

Example 16.6

Space-group $Pnn2$ ($\mathcal{C}_{2v}^{10}$, #34)

(a) Γ -point

$$\mathcal{G}_{\Gamma} = (E|000), (C_{2z}|000), (m_x|1/2, 1/2, 1/2), (m_y|1/2, 1/2, 1/2).$$

The Irreps are the same as given above. However, because this is a nonsym-morphic group, $\exp(i\mathbf{G} \cdot \mathbf{t})$ is not trivial. Yet it is straightforward to obtain the

corresponding values of $\exp(i\mathbf{G} \cdot \mathbf{t})$ for different types of $\mathbf{G}$ and to apply (16.113):

$$(0, 0, l) \quad l \neq 0, l \text{ even } {}^{(1)}\Gamma; l \text{ odd } {}^{(2)}\Gamma, \text{ active}$$

$$(h, 0, l) \quad h \neq 0, h + l \text{ even } {}^{(1)}\Gamma, {}^{(3)}\Gamma; h + l \text{ odd } {}^{(2)}\Gamma, {}^{(4)}\Gamma, \text{ active}$$

$$(0, k, l) \quad h \neq 0, k + l \text{ even } {}^{(1)}\Gamma, {}^{(4)}\Gamma; k + l \text{ odd } {}^{(2)}\Gamma, {}^{(3)}\Gamma, \text{ active}$$

We obtain selection rules similar to those for $Pmm2$ listed above for Brillouin zones centered at nonextinct Bragg reflections (even parities).

- (b) Σ -line: The only new selection rule appears at Brillouin zones corresponding to extinct Bragg reflections:

$$(h, 0, l) \quad h \neq 0, h + l \text{ even } {}^{(1)}\Sigma; h + l \text{ odd } {}^{(2)}\Sigma, \text{ active}$$

- (c) X -point: No selection can be derived for this point.

Example 16.7

Space-group $Pnma(\mathcal{D}_{2h}^{16}, \#62)$

This space-group is associated with a simple orthorhombic lattice structure. It comprises

$$(E \mid 000), \left(C_{2x} \left| \frac{a}{2} \frac{b}{2} \frac{c}{2} \right.\right), \left(\sigma_x \left| \frac{a}{2} \frac{b}{2} \frac{c}{2} \right.\right), (I \mid 000), \\ \left(C_{2z} \left| \frac{a}{2} 0 \frac{c}{2} \right.\right), \left(C_{2y} \left| 0 \frac{b}{2} 0 \right.\right), \left(\sigma_y \left| 0 \frac{b}{2} 0 \right.\right), \left(\sigma_z \left| \frac{a}{2} 0 \frac{c}{2} \right.\right).$$

The crystal structure is referred to as *aragonite*, and is typified by a form of CaCO_3 .

The set of possible symmetry types of vectors $\mathbf{G}$ for the Brillouin zone is now larger:

$$(0, 0, l) [mm2], (h, 0, 0) [2mm], (0, k, 0) [m2m], \\ (0, k, l) [m11], (h, 0, l) [1m1], \text{ and } (h, k, 0) [11m].$$

The Σ -line has $2mm$ symmetry and the X -point has again the full symmetry mmm . Let us consider first the resulting selection rules for the Γ -point and Σ -line, where the active modes are listed.

- (a) Γ -point

The Irreps of the point-group $\mathcal{D}_{2h}$ are given in Table 16.3.

$$(0, 0, l) \quad l \neq 0, l \text{ even} \quad {}^{(1)}\Gamma^+, {}^{(4)}\Gamma^- \\ \quad \quad \quad l \text{ odd} \quad {}^{(2)}\Gamma^+, {}^{(3)}\Gamma^- \\ (0, k, 0) \quad k \neq 0, k \text{ even} \quad {}^{(1)}\Gamma^+, {}^{(3)}\Gamma^- \\ \quad \quad \quad k \text{ odd} \quad {}^{(2)}\Gamma^+, {}^{(4)}\Gamma^-$$

Table 16.3. Irreps of $\mathcal{D}_{2h}$.

	E	C_{2x}	C_{2y}	C_{2z}	I	σ_x	σ_y	σ_z
$(1)\Gamma^+$	1	1	1	1	1	1	1	1
$(2)\Gamma^+$	1	1	-1	-1	1	1	-1	-1
$(3)\Gamma^+$	1	-1	1	-1	1	-1	1	-1
$(4)\Gamma^+$	1	-1	-1	1	1	-1	-1	1
$(1)\Gamma^-$	1	1	1	1	-1	-1	-1	-1
$(2)\Gamma^-$	1	1	-1	-1	-1	-1	1	1
$(3)\Gamma^-$	1	-1	1	-1	-1	1	-1	1
$(4)\Gamma^-$	1	-1	-1	1	-1	1	1	-1

$$\begin{aligned}
 (h, 0, 0) \quad h \neq 0, h \text{ even} & \quad (1)\Gamma^+, (2)\Gamma^- \\
 & \quad h \text{ odd} \quad (2)\Gamma^+, (1)\Gamma^- \\
 (h, 0, l) \quad h, l \neq 0, h + l \text{ even} & \quad (1)\Gamma^+, (3)\Gamma^+, (2)\Gamma^-, (4)\Gamma^- \\
 & \quad h + l \text{ odd} \quad (2)\Gamma^+, (4)\Gamma^+, (1)\Gamma^-, (3)\Gamma^- \\
 (0, k, l) \quad k, l \neq 0, & \quad (1)\Gamma^+, (2)\Gamma^+, (3)\Gamma^-, (4)\Gamma^- \\
 (h, k, 0) \quad h, k \neq 0, h \text{ even} & \quad (1)\Gamma^+, (4)\Gamma^+, (2)\Gamma^-, (3)\Gamma^- \\
 & \quad h \text{ odd} \quad (2)\Gamma^+, (3)\Gamma^+, (1)\Gamma^-, (4)\Gamma^-
 \end{aligned}$$

(b) Σ -line

$$\begin{aligned}
 (h, 0, 0) \quad h \text{ even} & \quad (1)\Sigma, h \text{ odd} \quad (3)\Sigma \\
 (h, 0, l) \quad l \neq 0, & \quad (1)\Sigma, (3)\Sigma \\
 (h, k, 0) \quad k \neq 0, h \text{ even} & \quad (1)\Sigma, (4)\Sigma, h \text{ odd} \quad (2)\Sigma, (3)\Sigma
 \end{aligned}$$

Because $Pnma$ is a nonsymmorphic space-group it has specific extinction rules at Brillouin zones whose centers are extinct Bragg reflections that are the result of nonsymmorphic operations, namely odd parities. The remaining rules are common with the space-group $Pmmm$.

All symmetry labels can be determined by performing a combination of measurements at the Γ -point and Σ -line, in different types of BZs, and then applying the method of mode symmetry identification.

(c) X -point: There are only two two-dimensional Irreps to be considered. The corresponding selection rules can be derived from the compatibility relations with the Σ -line.

$$(1)X = (1)\Sigma + (3)\Sigma \text{ and } (2)X = (2)\Sigma + (4)\Sigma: (h, 0, l) l \neq 0 - (1)X.$$

Example 16.8

Space-group $Pn\bar{3}m$ (O_h^4 , #224)

This space-group is associated with a simple cubic lattice. It comprises the outer-product of the simple cubic translation group with $\mathcal{T}_d \oplus (I | \frac{a}{2} \frac{a}{2} \frac{a}{2}) \mathcal{T}_d$, where the elements of $\mathcal{T}_d$ were discussed in Chapter 2.

Cuprite, Cu_2O , has this crystal structure, where the Cu atoms occupy the positions

$$\begin{aligned}\kappa_1 &= (a/4)(-1, 1, 1), & \kappa_2 &= (a/4)(1, -1, 1), \\ \kappa_3 &= (a/4)(1, 1, -1), & \kappa_4 &= (a/4)(-1, -1, -1),\end{aligned}$$

and the O atoms have

$$\kappa_5 = (a/4)(0, 0, 0), \quad \kappa_6 = (a/4)(1, 1, 1).$$

The structure reciprocal lattice vectors are $(\pm 2, \pm 2, 0)$, and so the structure zone corresponds to an f.c.c. Wigner–Seitz cell, 16 times the volume of the cubic Brillouin zone. A given phonon can therefore be observed at 16 inequivalent points in the structure zone. Total diffractive extinction (missing spots) occurs at:

Point	Copper				Oxygen	
	$e^{i\mathbf{G} \cdot \kappa_1}$	$e^{i\mathbf{G} \cdot \kappa_2}$	$e^{i\mathbf{G} \cdot \kappa_3}$	$e^{i\mathbf{G} \cdot \kappa_4}$	$e^{i\mathbf{G} \cdot \kappa_5}$	$e^{i\mathbf{G} \cdot \kappa_6}$
$\frac{2\pi}{a}(\pm 1, 0, 0)$	$\mp i$	$\pm i$	$\pm i$	$\mp i$	1	-1
$\frac{2\pi}{a}(0, \pm 1, 0)$	$\pm i$	$\mp i$	$\pm i$	$\mp i$	1	-1
$\frac{2\pi}{a}(0, 0, \pm 1)$	$\pm i$	$\pm i$	$\mp i$	$\mp i$	1	-1

The INS selection rules are:

- (a) Γ -point (O_h): The point-group O_h has 10 Irreps: $(1)\Gamma^\pm$, $(2)\Gamma^\pm$ 1-dimensional, $(3)\Gamma^\pm$ (Γ_{12}) 2-dimensional, $(3)\Gamma^\mp$ (Γ_{25}) and $(4)\Gamma^\mp$ (Γ_{15}) 3-dimensional.

$$(h, 0, 0) \quad h \neq 0, h \text{ even} \quad (1)\Gamma^+, (3)\Gamma^+, (4)\Gamma^-, h \text{ odd} \quad (2)\Gamma^-, (3)\Gamma^-$$

$$(h, h, h) \quad h \neq 0, \quad (1)\Gamma^+, (5)\Gamma^+, (2)\Gamma^-, (4)\Gamma^-$$

$$(0, k, k) \quad k \neq 0, \quad (1)\Gamma^+, (3)\Gamma^+, (5)\Gamma^+, (4)\Gamma^-, (5)\Gamma^-$$

$$(0, k, l) \quad k, l \neq 0, k + l \text{ even} \quad (1)\Gamma^+, (2)\Gamma^+, (3)\Gamma^+, (4)\Gamma^+, (5)\Gamma^+, (4)\Gamma^-, (5)\Gamma^-$$

$$k+l \text{ odd } {}^{(4)}\Gamma^+, {}^{(5)}\Gamma^+, {}^{(1)}\Gamma^-, {}^{(2)}\Gamma^-, {}^{(3)}\Gamma^-, {}^{(4)}\Gamma^-, {}^{(5)}\Gamma^-$$

$$(h, k, k) \quad h, k \neq 0, \quad {}^{(1)}\Gamma^+, {}^{(3)}\Gamma^+, {}^{(4)}\Gamma^+, {}^{(5)}\Gamma^+, {}^{(2)}\Gamma^+, {}^{(3)}\Gamma^-, {}^{(4)}\Gamma^-, {}^{(5)}\Gamma^-$$

Only the selection rules for a single representative Brillouin zone within each set of symmetry equivalent ones is listed; so that $(0, k, k)$ represents the set $(0, k, \pm k)$, $(h, \pm h, 0)$, and $(h, 0, \pm h)$, which have equivalent extinction rules with identical allowed Irreps.

(b) Δ -line ($\mathbf{q} = (\alpha, 0, 0)$)

$$(h, 0, 0) \quad h \neq 0, \quad h \text{ even } {}^{(1)}\Delta$$

$$h \text{ odd } {}^{(3)}\Delta$$

$$(h, 0, l), (h, k, 0) \quad l(k) \neq 0, \quad h+l(k) \text{ even } {}^{(1)}\Delta, {}^{(2)}\Delta, {}^{(5)}\Delta$$

$$h+l(k) \text{ odd } {}^{(3)}\Delta, {}^{(4)}\Delta, {}^{(5)}\Delta$$

$$(h, k, k), (h, k, -k) \quad k \neq 0, \quad {}^{(1)}\Delta, {}^{(3)}\Delta, {}^{(5)}\Delta$$

(c) X -point

$$(h, 0, 0) \quad {}^{(1)}X$$

$$(h, k, k), (h, k, -k) \quad k \neq 0, \quad {}^{(1)}X, {}^{(3)}X, {}^{(4)}X$$

Neutron magnetic scattering

This scattering process involves interactions between the magnetic moments of incident neutrons and electron magnetic moments [132]. The electron magnetic moment has contributions from its spin and momentum operators.

Interaction Hamiltonian To elucidate the form of these contributions, we consider the motion of an electron in the magnetic field of a neutron, represented by the neutron magnetic dipole vector potential $\mathbf{A}(\mathbf{r}_{eN})$,

$$\mathbf{A}(\mathbf{r}_{eN}) = \frac{\boldsymbol{\mu}_N \times \mathbf{r}_{eN}}{r_{eN}^3},$$

$$\mathbf{A}(\mathbf{Q}) = \int d\mathbf{r} e^{i\mathbf{Q} \cdot \mathbf{r}_{eN}} \mathbf{A}(\mathbf{r}_{eN}) = -\frac{4\pi i}{Q^2} (\boldsymbol{\mu}_N \times \mathbf{Q}), \quad (16.114)$$

with $\mathbf{r}_{eN} = \mathbf{r} - \mathbf{r}_N$, where $\mathbf{r}$ and $\mathbf{r}_N$ are the electron and neutron positions. Starting with (16.40), and keeping only linear terms in $\mathbf{A}$, we obtain the interaction potential

$$v(\mathbf{r}_{eN}) = \frac{e}{m_e c} \mathbf{A} \cdot \mathbf{p} + \frac{e\hbar}{2m_e c} \boldsymbol{\sigma} \cdot \nabla \times \mathbf{A}$$

$$= \frac{e}{m_e c} \left[\mathbf{A} \cdot \mathbf{p} + \mathbf{s} \cdot \nabla \times \mathbf{A} \right]$$

$$= \frac{e}{m_e c} \left[\mathbf{A} \cdot \mathbf{p} + (\mathbf{s} \cdot \nabla) (\boldsymbol{\mu}_N \cdot \nabla) \frac{1}{r_{eN}} + 4\pi \mathbf{s} \cdot \boldsymbol{\mu}_N \right], \quad (16.115)$$

where we set $\hbar\sigma = 2s$, and we used the identity

$$\begin{aligned}\nabla \times \frac{\boldsymbol{\mu}_N \times (\mathbf{r}_{eN})}{r_{eN}^3} &= -\nabla \times \boldsymbol{\mu}_N \times \nabla \left(\frac{1}{r_{eN}} \right) \\ &= (\boldsymbol{\mu}_N \cdot \nabla) \nabla \left(\frac{1}{r_{eN}} \right) - \boldsymbol{\mu}_N \nabla^2 \left(\frac{1}{r_{eN}} \right) \\ &= \nabla \left(\boldsymbol{\mu}_N \cdot \nabla \frac{1}{r_{eN}} \right) + 4\pi \boldsymbol{\mu}_N \delta(\mathbf{r}_{eN}).\end{aligned}$$

Taking the Fourier transform of v with respect to $\mathbf{r}_N$, we obtain

$$\begin{aligned}v(\mathbf{r}, \mathbf{Q}) &= \frac{e}{m_e c} e^{i\mathbf{Q} \cdot \mathbf{r}} \int d\mathbf{r}_{eN} e^{-i\mathbf{Q} \cdot \mathbf{r}_{eN}} \left[(\mathbf{A} \cdot \mathbf{p}) \right. \\ &\quad \left. + (\mathbf{s} \cdot \nabla) (\boldsymbol{\mu}_N \cdot \nabla) \frac{1}{r_{eN}} + 4\pi \mathbf{s} \cdot \boldsymbol{\mu}_N \right] \\ &= \frac{4\pi e}{m_e c} e^{i\mathbf{Q} \cdot \mathbf{r}} \left[i \frac{\boldsymbol{\mu}_N \times \mathbf{Q}}{Q^2} \cdot \mathbf{p} + \frac{(\mathbf{s} \cdot \mathbf{Q})(\boldsymbol{\mu}_N \cdot \mathbf{Q})}{Q^2} - \mathbf{s} \cdot \boldsymbol{\mu}_N \right] \\ &= \frac{4\pi e}{m_e c Q^2} e^{i\mathbf{Q} \cdot \mathbf{r}} \left[i (\boldsymbol{\mu}_N \times \mathbf{Q}) \cdot \mathbf{p} + \mathbf{s} \cdot (\mathbf{Q} \times \boldsymbol{\mu}_N \times \mathbf{Q}) \right] \\ &= \frac{4\pi e}{m_e c Q^2} e^{i\mathbf{Q} \cdot \mathbf{r}} \boldsymbol{\mu}_N \cdot \left[i(\mathbf{Q} \times \mathbf{p}) + \mathbf{Q} \times (\mathbf{s} \times \mathbf{Q}) \right].\end{aligned}\quad (16.116)$$

For pedagogical reasons, we drop the first term involving the linear momentum operator, and concentrate instead on the term containing the spin magnetic moment; we then write

$$v(\mathbf{r}, \mathbf{Q}) = \frac{4\pi}{Q^2} e^{i\mathbf{Q} \cdot \mathbf{r}} \boldsymbol{\mu}_N \cdot [\mathbf{Q} \times (\boldsymbol{\mu}_s \times \mathbf{Q})]. \quad (16.117)$$

The orbital angular momentum is found to be quenched by the crystal-field interactions in condensed matter magnetic systems where the crystal-field ground-state is nondegenerate. However, when this state is degenerate, the degeneracy is removed by spin-orbit interactions; in which case we replace the spin magnetic moment by that of the total angular momentum operator $\mathbf{J} = \mathbf{L} + 2\mathbf{S}$, and we may modify (16.117) to include this moment, and write

$$v(\mathbf{r}, \mathbf{Q}) = \frac{4\pi}{Q^2} e^{i\mathbf{Q} \cdot \mathbf{r}} \boldsymbol{\mu}_N \cdot [\mathbf{Q} \times (\boldsymbol{\mu} \times \mathbf{Q})], \quad (16.118)$$

where $\boldsymbol{\mu}$ is the magnetic moment due to either $\mathbf{S}$ or $\mathbf{J}$.

Neutron magnetic interactions in condensed matter systems We are now ready to construct the interaction Hamiltonian between a neutron and a condensed matter target containing magnetic electrons, by superimposing the contributions of all magnetic electrons in the form

$$\begin{aligned}V_m(\mathbf{r}) &= \sum_j v(\mathbf{r} - \mathbf{R}_j, \mathbf{Q}) \\ &= 4\pi \sum_j \delta(\mathbf{r} - \mathbf{R}_j) e^{i\mathbf{Q} \cdot \mathbf{R}_j} \boldsymbol{\mu}_N \cdot [\hat{\mathbf{Q}} \times (\boldsymbol{\mu}_j \times \hat{\mathbf{Q}})],\end{aligned}$$

where $\hat{\mathbf{Q}} = \mathbf{Q}/Q$, and $\mathbf{R}_j$ is the position vector of the j th electron. We evaluate the scattering matrix element in the FBA between neutron states $|\mathbf{k}, s_N\rangle$ and $|\mathbf{k}_s, s'_N\rangle$, and target states $|i\rangle$ and $|f\rangle$. Again, for pedagogical reasons we further limit our discussion to systems with localized magnetic electrons. We expand the target states in the form

$$\begin{aligned} |i\rangle &= |\Phi(\mathbf{r})\rangle |n_i\rangle, \\ |f\rangle &= |\Phi(\mathbf{r})\rangle |n_f\rangle, \end{aligned} \quad (16.119)$$

where $|\Phi(\mathbf{r})\rangle$ is the spatial wavefunction of the magnetic electrons expressed as a Bloch $|\Phi(\mathbf{r})\rangle = \sum_l |\phi(\mathbf{r} - \mathbf{x}_l)\rangle$, with $\mathbf{R}_j = \mathbf{r} + \mathbf{x}_j$, $\mathbf{x}_j$ being the position of the j th atom; $|n\rangle$ is the spin function.

$$\begin{aligned} \langle s'_N \mathbf{k}_s f | V_m(\mathbf{r}) | s_N \mathbf{k} i \rangle &= 4\pi \langle s'_N | \boldsymbol{\mu}_N | s_N \rangle \\ &\quad \cdot \left\langle f \left| \sum_j e^{i\mathbf{Q} \cdot \mathbf{R}_j} [\hat{\mathbf{Q}} \times (\boldsymbol{\mu}_j \times \hat{\mathbf{Q}})] \right| i \right\rangle \\ &= 4\pi \langle \phi(\mathbf{r}) | e^{i\mathbf{Q} \cdot \mathbf{r}} | \phi(\mathbf{r}) \rangle \\ &\quad \times \langle s'_N | \boldsymbol{\mu}_N | s_N \rangle \cdot \left\langle f \left| \sum_j e^{i\mathbf{Q} \cdot \mathbf{x}_j} [\hat{\mathbf{Q}} \times (\boldsymbol{\mu}_j \times \hat{\mathbf{Q}})] \right| i \right\rangle \\ &= 4\pi \mathcal{F}(\mathbf{Q}) \langle s'_N | \boldsymbol{\mu}_N | s_N \rangle \cdot \langle n_f | \hat{\mathbf{Q}} \times \boldsymbol{\mu}(\mathbf{Q}) \times \hat{\mathbf{Q}} | n_i \rangle, \end{aligned} \quad (16.120)$$

where

$$\boldsymbol{\mu}(\mathbf{Q}) = \sum_j e^{i\mathbf{Q} \cdot \mathbf{x}_j} \boldsymbol{\mu}_j,$$

and $\mathcal{F}(\mathbf{Q})$ is the form factor of the electronic wavefunction. We assume here that the spatial wavefunction remains unchanged by the scattering process. Equation (16.120) allows us to write the DSCS as

$$\begin{aligned} \frac{\partial^2 \sigma}{\partial \Omega \partial \omega} &= \frac{4\pi k_f}{k} |\mathcal{F}(\mathbf{Q})|^2 \sum_{s_N, s'_N} \langle s_N | \rho_N | s_N \rangle \sum_{if} P_i \\ &\quad \times \int dt e^{i\omega t} \langle s_N | \boldsymbol{\mu}_N | s'_N \rangle \cdot \langle n_i | \hat{\mathbf{Q}} \times \boldsymbol{\mu}(-\mathbf{Q}) \times \hat{\mathbf{Q}} | n_f \rangle \\ &\quad \times \langle s'_N | \boldsymbol{\mu}_N | s_N \rangle \cdot \langle n_f | \hat{\mathbf{Q}} \times \boldsymbol{\mu}(\mathbf{Q}, t) \times \hat{\mathbf{Q}} | n_i \rangle, \end{aligned} \quad (16.121)$$

where P_i is the thermal probability of the initial state $|n_i\rangle$, ρ_N is the density matrix describing the neutron beam polarization, and

$$\hbar\omega = E_f - E_i = \frac{\hbar^2}{2M} (k_f^2 - k^2).$$

The sum over s'_N can be written as

$$\begin{aligned} &\sum_{s_N, s'_N} \langle s_N | \rho_N | s_N \rangle \langle s_N | \boldsymbol{\mu}_N^\alpha | s'_N \rangle \langle s'_N | \boldsymbol{\mu}_N^\beta | s_N \rangle \\ &= \sum_{s_N} \langle s_N | \rho_N | s_N \rangle \langle s_N | \boldsymbol{\mu}_N^\alpha \boldsymbol{\mu}_N^\beta | s_N \rangle = \mu_N^2 \delta_{\alpha\beta}, \end{aligned}$$

so that (16.121) becomes

$$\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} = 4\pi \mu_N^2 \frac{k_f}{k} |\mathcal{F}(\mathbf{Q})|^2 \times \int dt e^{i\omega t} \left\langle \left[\hat{\mathbf{Q}} \times \boldsymbol{\mu}(-\mathbf{Q}) \times \hat{\mathbf{Q}} \right] \cdot \left[\hat{\mathbf{Q}} \times \boldsymbol{\mu}(\mathbf{Q}, t) \times \hat{\mathbf{Q}} \right] \right\rangle_T, \quad (16.122)$$

which then, with the aid of the identity

$$(\hat{\mathbf{n}} \times \mathbf{a} \times \hat{\mathbf{n}}) \cdot (\hat{\mathbf{n}} \times \mathbf{b} \times \hat{\mathbf{n}}) = \mathbf{a} \cdot \mathbf{b} - (\mathbf{a} \cdot \hat{\mathbf{n}})(\mathbf{b} \cdot \hat{\mathbf{n}}),$$

can be reduced to

$$\begin{aligned} \frac{\partial^2 \sigma}{\partial \Omega \partial \omega} &= 4\pi \mu_N^2 \frac{k_f}{k} |\mathcal{F}(\mathbf{Q})|^2 \int_{-\infty}^{\infty} dt e^{i\omega t} \\ &\times \left\langle \boldsymbol{\mu}(-\mathbf{Q}) \cdot \boldsymbol{\mu}(\mathbf{Q}, t) - (\boldsymbol{\mu}(-\mathbf{Q}) \cdot \hat{\mathbf{Q}})(\boldsymbol{\mu}(\mathbf{Q}, t) \cdot \hat{\mathbf{Q}}) \right\rangle_T \\ &= 4\pi \mu_N^2 \frac{k_f}{k} |\mathcal{F}(\mathbf{Q})|^2 \sum_{\alpha\beta} (\delta_{\alpha\beta} - \hat{\mathbf{Q}}_\alpha \hat{\mathbf{Q}}_\beta) \int_{-\infty}^{\infty} dt e^{i\omega t} \mathbf{S}_{\alpha\beta}(\mathbf{Q}, t), \end{aligned} \quad (16.123)$$

where

$$\mathbf{S}_{\alpha\beta}(\mathbf{Q}, t) = \langle \mu_\alpha(-\mathbf{Q}) \mu_\beta(\mathbf{Q}, t) \rangle_T,$$

and we can finally write

$$\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} = 4\pi \mu_N^2 \frac{k_f}{k} |\mathcal{F}(\mathbf{Q})|^2 \mathcal{A}(\mathbf{Q}) \delta(\hbar\omega \pm \Delta E), \quad (16.124)$$

with

$$\mathcal{A}(\mathbf{Q}) = \sum_{\alpha\beta} (\delta_{\alpha\beta} - \hat{\mathbf{Q}}_\alpha \hat{\mathbf{Q}}_\beta) \mathbf{S}_{\alpha\beta}(\mathbf{Q}, \omega). \quad (16.125)$$

Selection rules for neutron magnetic scattering It is now obvious from (16.124) that all information relevant to the symmetry selection rules that govern neutron magnetic scattering is contained in $\mathcal{A}(\mathbf{Q})$. In order to extricate such information we start by expressing $\mathbf{S}_{\alpha\beta}(\mathbf{Q}, t)$ in terms of the spin operators of the magnetic electrons, and we obtain

$$\begin{aligned} \mathbf{S}_{\alpha\beta}(\mathbf{Q}, t) &= \langle \mu_\alpha(-\mathbf{Q}) \mu_\beta(\mathbf{Q}, t) \rangle_T = \sum_{jl} \left\langle e^{-i\mathbf{Q} \cdot \mathbf{x}_j} \mu_j^\alpha e^{i\mathbf{Q} \cdot \mathbf{x}_l(t)} \mu_l^\beta(t) \right\rangle_T \\ &= \sum_{jl} \left\langle e^{i\mathbf{Q} \cdot (\mathbf{u}_l(t) - \mathbf{u}_j)} \right\rangle_T \left\langle e^{-i\mathbf{Q} \cdot (\mathbf{R}_j - \mathbf{R}_l)} \mu_j^\alpha \mu_l^\beta(t) \right\rangle_T \\ &\simeq e^{-2W(\mathbf{Q})} \sum_{jl} e^{-i\mathbf{Q} \cdot (\mathbf{R}_j - \mathbf{R}_l)} \left\langle \mu_j^\alpha \mu_l^\beta(t) \right\rangle_T \end{aligned}$$

$$\begin{aligned}
&= \left(\frac{e\hbar}{m_e c} \right)^2 e^{-2W(\mathbf{Q})} \sum_{jl} e^{-i\mathbf{Q} \cdot (\mathbf{R}_j - \mathbf{R}_l)} \langle S_j^\alpha S_l^\beta(t) \rangle_T \\
&= \left(\frac{e\hbar}{m_e c} \right)^2 e^{-2W(\mathbf{Q})} \langle S_{-\mathbf{Q}}^\alpha S_{\mathbf{Q}}^\beta(t) \rangle_T.
\end{aligned} \tag{16.126}$$

We first consider the case of a ferromagnet, and we choose the z -direction as the quantization axis. We then find that $S_{\text{tot}}^z = \sum_l S_l^z$ is conserved, and hence commutes with the Hamiltonian

$$[S_{\text{tot}}^z, \mathcal{H}] = 0,$$

and with the ladder operators

$$S_l^\pm = S_l^x \pm iS_l^y.$$

We find that

$$\langle S_j^+ S_l^+(t) \rangle_T = \langle S_j^- S_l^-(t) \rangle_T = 0,$$

which in turn leads to

$$\langle S_{-\mathbf{Q}}^x S_{\mathbf{Q}}^y(t) + S_{-\mathbf{Q}}^y S_{\mathbf{Q}}^x(t) \rangle_T = 0.$$

We also find that

$$\begin{aligned}
\langle S_{-\mathbf{Q}}^x S_{\mathbf{Q}}^z(t) \rangle_T &= \langle S_{-\mathbf{Q}}^y S_{\mathbf{Q}}^z(t) \rangle_T = 0, \\
\langle S_{-\mathbf{Q}}^x S_{\mathbf{Q}}^x(t) \rangle_T &= \langle S_{-\mathbf{Q}}^y S_{\mathbf{Q}}^y(t) \rangle_T,
\end{aligned}$$

because the x - and y -axes are equivalent. Thus, $\mathcal{A}(\mathbf{Q})$ reduces to

$$\begin{aligned}
\mathcal{A}(\mathbf{Q}) &= \left(\frac{e\hbar}{m_e c} \right)^2 e^{-2W(\mathbf{Q})} \int_{-\infty}^{\infty} dt e^{i\omega t} \left[(1 - \hat{\mathbf{Q}}_z^2) \langle S_{-\mathbf{Q}}^z S_{\mathbf{Q}}^z(t) \rangle_T \right. \\
&\quad \left. + (1 + \hat{\mathbf{Q}}_z^2) \langle S_{-\mathbf{Q}}^x S_{\mathbf{Q}}^x(t) \rangle_T \right].
\end{aligned} \tag{16.127}$$

Using the relation

$$S^x = \frac{1}{2} (S^+ + S^-),$$

and designating the direction of magnetization by the unit vector $\hat{\boldsymbol{\sigma}}$, we obtain the alternative expression

$$\begin{aligned}
\mathcal{A}(\mathbf{Q}) &= \left(\frac{e\hbar}{m_e c} \right)^2 e^{-2W(\mathbf{Q})} \left[(1 - (\mathbf{Q} \cdot \hat{\boldsymbol{\sigma}})^2) \int_{-\infty}^{\infty} dt e^{i\omega t} \langle S_{-\mathbf{Q}}^z S_{\mathbf{Q}}^z(t) \rangle_T \right. \\
&\quad \left. + \frac{1}{4} (1 + (\mathbf{Q} \cdot \hat{\boldsymbol{\sigma}})^2) \int_{-\infty}^{\infty} dt e^{i\omega t} \left(\langle S_{-\mathbf{Q}}^+ S_{\mathbf{Q}}^-(t) \rangle_T + \langle S_{-\mathbf{Q}}^- S_{\mathbf{Q}}^+(t) \rangle_T \right) \right].
\end{aligned} \tag{16.128}$$

We now employ expression (16.128) to discuss the symmetry aspects of both elastic and inelastic neutron scattering.

Elastic scattering The first term in (16.128) leads to elastic scattering. We demonstrate this by writing

$$\int_{-\infty}^{\infty} d\omega \mathbf{S}_{zz}(\mathbf{Q}, \omega) = \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} d\omega e^{i\omega t} \langle S_{-\mathbf{Q}}^z S_{\mathbf{Q}}^z(t) \rangle_T = \langle S_{-\mathbf{Q}}^z S_{\mathbf{Q}}^z \rangle_T.$$

This leads to Bragg diffraction in the form

$$\frac{\partial \sigma}{\partial \Omega} = 4\pi \mu_N^2 \frac{k_f}{k} \langle S \rangle_T^2 \sum_{\mathbf{G}} |\mathcal{F}(\mathbf{Q})|^2 (1 - (\mathbf{Q} \cdot \hat{\boldsymbol{\sigma}})^2) \delta(\mathbf{Q} - \mathbf{G}). \quad (16.129)$$

It is now easy to extend this expression to cases where there exist several spin directions associated with different sublattices, and we write

$$\frac{\partial \sigma}{\partial \Omega} = 4\pi \mu_N^2 \frac{k_f}{k} \langle S \rangle_T^2 \sum_{l, \mathbf{G}} |\mathcal{F}_l(\mathbf{Q})|^2 (1 - (\mathbf{Q} \cdot \hat{\boldsymbol{\sigma}}_l)^2) \delta(\mathbf{Q} - \mathbf{G} - \mathbf{q}_l). \quad (16.130)$$

Inelastic scattering The contributions to neutron inelastic scattering come from the second term in (16.115). We write, using the Holstein–Primakoff transformation,

$$S_l^+ = \sqrt{\frac{2S}{N}} \sum_{\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{R}_l} b_{\mathbf{q}},$$

$$S_l^- = \sqrt{\frac{2S}{N}} \sum_{\mathbf{q}} e^{-i\mathbf{q} \cdot \mathbf{R}_l} b_{\mathbf{q}}^\dagger,$$

to obtain

$$\begin{aligned} \langle S_{-\mathbf{Q}}^+ S_{\mathbf{Q}}^-(t) \rangle_T &= \sum_{jl} e^{-i\mathbf{Q} \cdot (\mathbf{R}_j - \mathbf{R}_l)} \langle S_j^+ S_l^-(t) \rangle_T \\ &= \frac{2S}{N} \sum_{\substack{jl \\ \mathbf{q}\mathbf{q}'}} e^{-i(\mathbf{Q}-\mathbf{q}) \cdot \mathbf{R}_j} e^{i(\mathbf{Q}-\mathbf{q}') \cdot \mathbf{R}_l} \langle b_{\mathbf{q}} b_{\mathbf{q}'}^\dagger \rangle_T \\ &= \frac{2S}{N} \sum_{jl\mathbf{q}} e^{-i(\mathbf{Q}-\mathbf{q}) \cdot (\mathbf{R}_j - \mathbf{R}_l)} \delta_{\mathbf{q}\mathbf{q}'} (n(\mathbf{q}) + 1), \\ \langle S_{-\mathbf{Q}}^- S_{\mathbf{Q}}^+(t) \rangle_T &= \frac{2S}{N} \sum_{jl\mathbf{q}} e^{-i(\mathbf{Q}-\mathbf{q}) \cdot (\mathbf{R}_j - \mathbf{R}_l)} \delta_{\mathbf{q}\mathbf{q}'} n(\mathbf{q}), \end{aligned} \quad (16.131)$$

$$\mathcal{A}(\mathbf{Q}) = \frac{2S}{N} \left(1 + \frac{Q_3^2}{Q^2} \right) \sum_{\mathbf{q}} \left[\left(n(\mathbf{q}) + \frac{1}{2} \pm \frac{1}{2} \right) \sum_{jl} e^{i(\mathbf{Q} \pm \mathbf{q}) \cdot (\mathbf{R}_j - \mathbf{R}_l)} \right]. \quad (16.132)$$

We find that the only restriction is that

$$\sum_{\substack{jl \\ \mathbf{q}=\mathbf{Q} \pm \mathbf{G}}} e^{i(\mathbf{Q} \pm \mathbf{q}) \cdot (\mathbf{R}_j - \mathbf{R}_l)} \neq 0.$$

16.6.2 Atom scattering spectroscopy

The scattering of nonpenetrating particles has become one of the most valuable probes for studying the structure and dynamics of surfaces, both geometric and magnetic [108, 133, 134, 135, 136, 137, 138, 139]. In order to exclude multiphonon events, and thus avoid the possibility of classical scattering, neutral, inert, light atoms at thermal energies are employed. Helium atoms at thermal energies are the most attractive, since their de Broglie wavelength at such energies varies in the range 0.5–1.0 Å, which is comparable to the characteristics of thermal neutron beams. Moreover, incident neutral atoms, at such energies, do not penetrate the top surface layer, rather, they scatter at distances of about 2–3 Å above the plane of surface ions. Consequently, atom beam probes are exclusively surface sensitive. The structure and dynamics of the surface lattice are studied by the scattering of a monochromatized beam of helium atoms in their electronic ground-state (He^0); while the surface magnetic properties are discerned by the scattering of metastable He atoms in the $2S^3$ triplet state (He^* , with lifetime $\sim 10^4$ seconds).

The formalism for this type of scattering has been developed along two different approaches: a semi-classical approach based on the eikonal formalism, and a quantum mechanical one, based on the *distorted-wave* Born approximation (DWBA).

The scattering potential

The atom/surface scattering potential is dominated by electronic interactions for both He^0 and He^* . Both species have a long-range attractive van der Waals contribution, but differ in their short-range overlap component.

Ground-state He^0 The electrons of a He^0 atom are bound by ~ 25 eV, and the resulting interaction is mainly attributed to the exclusion hole in the surface electron density. It is found to be linearly dependent on the surface electron density. Consequently, the interaction potential assumes the overall periodicity of this density, which, in turn, reflects the geometric periodicity of the surface.

We then express the potential experienced by a light neutral atom at position $\mathbf{r} = (z, \mathbf{R})$, where z is its distance above the surface, and $\mathbf{R}$ its position parallel to the surface, as

$$V(\mathbf{r}) = \sum_l v_\kappa(\mathbf{r} - \mathbf{x}_{l\kappa}),$$

where $\mathbf{x}_{l\kappa} = \mathbf{r}_{l\kappa}^0 + \mathbf{u}_{l\kappa}$ (here we use $\mathbf{r}_{l\kappa}^0 = (z_{l\kappa}^0, R_{l\kappa}^0)$ to denote the equilibrium position), and $\mathbf{u}_{l\kappa}$ is a small instantaneous displacement of surface atom l from $\mathbf{r}_{l\kappa}^0$. Expanding this potential about the equilibrium configuration of the surface atoms, and keeping only linear terms in the displacement, we obtain

$$\begin{aligned} V(\mathbf{r}) &= \sum_{l\kappa} \left[v(\mathbf{r} - \mathbf{r}_{l\kappa}^0) + \mathbf{F}_{l\kappa} \cdot \mathbf{u}_{l\kappa} \right] \\ &= U(\mathbf{r}) + v_{\text{ph}}(\mathbf{r}), \end{aligned} \quad (16.133)$$

$$\mathbf{F}_{l\kappa} = \nabla_{\mathbf{x}_{l\kappa}} v(\mathbf{r} - \mathbf{x}_{l\kappa}) \Big|_{\mathbf{x}_{l\kappa} = \mathbf{r}_{l\kappa}^0}, \quad (16.134)$$

where U is a static potential giving rise to elastic diffractive scattering, and v_{ph} is the potential due to surface vibrations.

Triplet-state He^* He^* scattering from surfaces has three distinct differences from the above scenario:

- (i) The He 2s electron is bound only by about 4.7 eV, which is comparable to the binding energies of the surface valence electrons. The interaction with the surface electrons becomes more complicated, but the ensuing potential is still expected to reflect the periodicity of the surface.
- (ii) When the He^* probe is limited to studies of insulating magnetic surfaces, such that the 2s level overlaps with the surface insulating gap, it can only decay, $\text{He}^* \rightarrow \text{He}^0$, through an Auger channel. This decay channel leads to a violation of the unitarity of the scattering process of the He^* beam, and can be represented by the introduction of an imaginary component of $U(\mathbf{r})$, namely $U_I(\mathbf{r})$.

However, the Auger decay process satisfies a spin-dependent selection rule that can be represented by a term proportional to $\langle \mathbf{S}_{\text{He}} \rangle \cdot \langle \mathbf{S}_l \rangle$, where $\mathbf{S}_{\text{He}}$ and $\mathbf{S}_l$ are the spin operators of a He^* atom and a surface site l , respectively. $U(\mathcal{R})$ is a complex potential whose real part is the adiabatic potential.

- (iii) An exchange interaction term of the form

$$v_m = \sum_m J(|\mathcal{R} - \mathbf{R}_m|) \mathbf{S}_{\text{He}} \cdot \mathbf{S}_m, \quad (16.135)$$

where $\mathbf{S}_m$ is the spin operator at the magnetic site $\mathbf{R}_m$. The exchange interaction $J(|\mathcal{R} - \mathbf{R}_m|)$ is a function of the He^* center-of-mass (COM) position $\mathcal{R}$, and thus acts as an effective potential in the motion of the He^* 's COM, thus allowing energy exchange between the surface electron-spin system and the COM of a He^* atom.

We then write the total potential, in this case, as

$$V = U + \mathbf{v}_{\text{ph}} + v_m. \quad (16.136)$$

Scattering states

Since $\mathbf{v}_{\text{ph}}, v_m \ll U$, we use the two-potential approximation of Gell-Mann and Goldberger [140] and construct the scattering states using U only.

Moreover, because of the planar nature of the surface, we take the Fourier transform of the potential parallel to the surface, and we write

$$U(\mathbf{r}) = \sum_{\mathbf{G}} U_{\mathbf{G}}(z) e^{i\mathbf{G} \cdot \mathbf{R}}. \quad (16.137)$$

For the sake of simplicity, since we are only interested in studying the inelastic scattering channel associated with spin-spin interactions, we retain only the reciprocal lattice vector $\bar{G} = 0$ component of $U(\mathcal{R})$, thus neglecting the diffractive scattering channels that arise from the periodic spatial dependence of both the real and imaginary parts of U .

The distorted-wave Born approximation (DWBA) Now, instead of the plane-wave character of the scattering states used in the usual Born approximation, they are here constructed from wavefunctions of the form

$$\phi^{(\pm)} \approx \left(\frac{1}{L} \right)^{3/2} \chi^{(\pm)}(k_z; z) \exp(i\mathbf{K} \cdot \mathbf{R}), \quad (16.138)$$

i.e. products of a plane-wave for the particle motion parallel to the surface, and a normal wavefunction $\chi^{(\pm)}(k_z; z)$, where L is a quantization length. The wavefunctions $\chi^{(\pm)}(k_z; z)$ obey the equation

$$\left(\frac{\hbar^2}{2M} \frac{\partial^2}{\partial z^2} + \frac{\hbar^2 k_z^2}{2M} - U(z) \right) \chi^{(\pm)}(k_z; z) = 0, \quad (16.139)$$

where (+) denotes outgoing and (−) incoming waves.

Phonon scattering

We write the composite initial and final wavefunctions for the one-phonon exchange in the form

$$\begin{aligned} |\Phi_i\rangle &= |\phi^{(+)}(\mathbf{r})\rangle |n(\mathbf{q}_{\parallel}, j)\rangle, \\ |\Phi_f\rangle &= |\phi^{(-)}(\mathbf{r})\rangle |n(\mathbf{q}_{\parallel}, j) \pm 1\rangle, \end{aligned} \quad (16.140)$$

which yields the DWBA matrix element

$$T_{fi} = \sum_{l\kappa} \int d^3r \Phi_f^* \mathbf{F}_{l\kappa} \Phi_i \cdot \langle n(\mathbf{q}_{\parallel}, j) \pm 1 | \mathbf{u}_{l\kappa} | n(\mathbf{q}_{\parallel}, j) \rangle. \quad (16.141)$$

We can simplify this expression as follows: First, we expand

$$\begin{aligned} \mathbf{u}_{l\kappa} &= \sum_{\mathbf{q}_{\parallel}, j} A(\mathbf{q}_{\parallel}, j) \hat{\mathbf{e}}_{\kappa}(\mathbf{q}_{\parallel}, j) \left(e^{i\mathbf{q}_{\parallel} \cdot \mathbf{R}_{l\kappa}} a(\mathbf{q}_{\parallel}, j) + e^{-i\mathbf{q}_{\parallel} \cdot \mathbf{R}_{l\kappa}} a^{\dagger}(\mathbf{q}_{\parallel}, j) \right), \\ A(\mathbf{q}_{\parallel}, j) &= \sqrt{\frac{\hbar}{2MN\omega_{\mathbf{q}_{\parallel}}(j)}}, \end{aligned}$$

and obtain

$$\begin{aligned} \langle n(\mathbf{q}_{\parallel}, j) \pm 1 | \mathbf{u}_{l\kappa} | n(\mathbf{q}_{\parallel}, j) \rangle &= \sqrt{n(\mathbf{q}_{\parallel}, j) + \frac{1}{2} \pm \frac{1}{2}} \\ &\times A(\mathbf{q}_{\parallel}, j) \hat{\mathbf{e}}_{\kappa}(\mathbf{q}_{\parallel}, j) e^{\mp i\mathbf{q}_{\parallel} \cdot \mathbf{R}_{l\kappa}}. \end{aligned} \quad (16.142)$$

Second, we evaluate the integral

$$\begin{aligned} \int d^3r \Phi_f^* \mathbf{F}_{l\kappa} \Phi_i &= \int d^3r \chi^{(-)*}(k_{zf}; z) e^{i\mathbf{K}_f \cdot \mathbf{R}} \mathbf{F}_{l\kappa} \chi^{(+)}(k_{zi}; z) e^{-i\mathbf{K}_i \cdot \mathbf{R}} \\ &= - \int dz \chi^{(-)*}(k_{zf}; z) \\ &\quad \times \int d\mathbf{R} e^{-i(\mathbf{K}_i - \mathbf{K}_f) \cdot \mathbf{R}} \left(\partial/\partial z, \nabla_{\mathbf{R}} \right) v(\mathbf{r} - \mathbf{R}_{l\kappa}) \chi^{(+)}(k_{zi}; z) \\ &= e^{-i\mathbf{Q} \cdot \mathbf{R}_{l\kappa}} \int dz \chi^{(-)*}(k_{zf}; z) \left(i\mathbf{Q}, \partial/\partial z \right) v(\mathbf{Q}, z) \chi^{(+)}(k_{zi}; z) \\ &= e^{-i\mathbf{Q} \cdot \mathbf{R}_{l\kappa}} \int dz \chi^{(-)*}(k_{zf}; z) \mathbf{F}_{\kappa}(\mathbf{Q}, z) \chi^{(+)}(k_{zi}; z) \\ &= e^{-i\mathbf{Q} \cdot (\mathbf{R}_l + \kappa)} \mathbf{F}_{\kappa}(\mathbf{k}_f, \mathbf{k}_i), \end{aligned}$$

where normalization constants were absorbed in the functions χ . We arrive at the following expression for T_{fi}

$$\begin{aligned}
 T_{fi} &= \sum_{l, \mathbf{q}_{\parallel}} e^{-i(\mathbf{Q} \pm \mathbf{q}_{\parallel}) \cdot \mathbf{R}_l} \sum_{\kappa, j} e^{-i(\mathbf{Q} \pm \mathbf{q}_{\parallel}) \cdot \boldsymbol{\kappa}} \sqrt{n(\mathbf{q}_{\parallel}, j) + \frac{1}{2} \pm \frac{1}{2}} \\
 &\quad \times A(\mathbf{q}_{\parallel}, j) \hat{\mathbf{e}}_{\kappa}(\mathbf{q}_{\parallel}, j) \cdot \mathbf{F}_{\kappa}(\mathbf{k}_f, \mathbf{k}_i) \\
 &= \sum_{\kappa, \mathbf{G}, j} \delta(\mathbf{Q} \pm \mathbf{q}_{\parallel} - \mathbf{G}) \sqrt{n(\mathbf{q}_{\parallel}, j) + \frac{1}{2} \pm \frac{1}{2}} \\
 &\quad \times A(\mathbf{q}_{\parallel}, j) e^{-i\mathbf{G} \cdot \boldsymbol{\kappa}} \hat{\mathbf{e}}_{\kappa}(\mathbf{q}_{\parallel}, j) \cdot \mathbf{F}_{\kappa}(\mathbf{k}_f, \mathbf{k}_i). \tag{16.143}
 \end{aligned}$$

The differential reflection coefficient

The differential reflection coefficient is expressed in terms of the transition matrix T as [133]

$$\begin{aligned}
 \frac{\partial^2 \mathcal{R}(\mathbf{k}_f, \mathbf{k}_i)}{\partial E_f \partial \Omega_f} &= \left(\frac{L}{2\pi} \right)^3 \frac{2\pi M |\mathbf{k}_f|}{\hbar^3 j_i} \sum_{\{\mathbf{n}_f\}} \sum_{\{\mathbf{n}_i\}} \rho(\{\mathbf{n}_i\}) |T_{fi}|^2 \delta(E_f - E_i) \\
 &= \left(\frac{L}{2\pi} \right)^3 \frac{2\pi M |\mathbf{k}_f|}{\hbar^3 j_i} \sum_{\mathbf{q}_{\parallel}, \mathbf{G}, j} \frac{n(\mathbf{q}_{\parallel}, j) + 1/2 \pm 1/2}{\omega_{\mathbf{q}_{\parallel}}(j)} \delta(\mathbf{Q} \pm \mathbf{q}_{\parallel} - \mathbf{G}) \\
 &\quad \times \delta(\mathcal{E}_f - \mathcal{E}_i - \hbar \omega_{\mathbf{q}_{\parallel}}(j)) \left| \sum_{\kappa} e^{\mp i \mathbf{q}_{\parallel} \cdot \boldsymbol{\kappa}} \hat{\mathbf{e}}_{\kappa}(\mathbf{q}_{\parallel}, j) \cdot \mathbf{F}_{\kappa}(\mathbf{k}_f, \mathbf{k}_i) \right|^2, \tag{16.144}
 \end{aligned}$$

where $E_i = \mathcal{E}_i + \hbar^2 k_i^2 / 2M$ and $E_f = \mathcal{E}_f + \hbar^2 k_f^2 / 2M$, are the initial and final energies of the combined system, respectively, with $\mathcal{E}$ the energy associated with the surface phonon system; $j_i = \hbar k_{iz} / ML$ is the incident flux; and $\rho(\{\mathbf{n}_i\})$ is the distribution of initial phonon states, given in terms of the surface phonon occupation numbers $\{\mathbf{n}_i\}$.

The ensuing potential can then be written in the form

$$U(z) = U_0 e^{-i\delta} \exp[-\alpha z],$$

where the complex character of U is contained in the phase angle δ . Thus, in the case of He^0 scattering, $\delta = 0$. The solutions for a real exponential potential, $U_0 \exp[-\alpha z]$, have been derived by Jackson and Mott [141] in terms of modified Bessel functions of the second kind, K_{ip} , with imaginary order ip , whose integral representation is given by

$$K_{ip}(y) = \int_0^\infty \exp[-y \cosh(u)] \cos(pu) du. \tag{16.145}$$

The eigenvalues and normalized eigenfunctions in this case are

$$\varepsilon_p = \left[\frac{(\hbar \alpha)^2}{8M} \right] p^2, \quad k_z = \alpha p / 2, \tag{16.146}$$

$$\chi(p; z) = \mathcal{N}_p^{1/2} K_{ip}(y), \tag{16.147}$$

where

$$y = \left[\frac{(8MU_0)^{1/2}}{\alpha\hbar} \right] \exp(-\alpha z/2) \quad (16.148)$$

and

$$\mathcal{N}_p = \left[\frac{4p \sinh(\pi p)}{\pi} \right]. \quad (16.149)$$

We extend the solution to the present case of an exponential potential with a complex amplitude by writing y as

$$\begin{aligned} y &= \left[\frac{(8MU_0)^{1/2} e^{-i\delta/2}}{\alpha\hbar} \right] \exp(-\alpha z/2) \\ &= \kappa e^{-i\delta/2} \exp(-\alpha z/2). \end{aligned} \quad (16.150)$$

It is clear from (16.145) that in the limit $z \rightarrow -\infty$, ($y \rightarrow \infty$), $K_{ip} \rightarrow 0$; and the asymptotic form for $z \rightarrow \infty$, ($y \rightarrow 0$) is

$$K_{ip}(y \rightarrow 0) \simeq \rightarrow e^{k\delta/\alpha} \left(\frac{\pi}{4p \sinh(p\pi)} \right)^{1/2} \left[e^{-[ikz+\eta_p]} + e^{-(2k\delta/\alpha)} e^{[ikz+\eta_p]} \right], \quad (16.151)$$

where

$$\eta_p = p \ln \left(\frac{2}{\kappa} \right) + \arg \Gamma(ip) \quad (16.152)$$

where the last term in (16.151) is a Γ -function with an imaginary argument ip . The right-hand side of (16.150) comprises incoming and outgoing plane-waves, with a reflection coefficient amplitude of $\exp[-2k\delta/\alpha]$. Thus, we choose the normalization of the wave function χ

$$\mathcal{N}_p = \left[\frac{4p \sinh(\pi p)}{\pi} \right] e^{-(2k\delta/\alpha)} \quad (16.153)$$

so that the incoming amplitude at $z = \infty$ is unity. We then identify the square of the coefficient of the outgoing wave $\exp[-4k\delta/\alpha]$ with the ratio of the reflected intensity (I_s) to the incident beam intensity (I_0). We can then make an estimate, based on experimental results, that the phase angle of the complex potential $\delta \simeq \pi/10$.

Because of the complex character of the scattering potential, evaluation of the transition matrix elements that enter the expression of the differential reflection coefficient requires the time-reversed solutions [142]

$$\left(\frac{\hbar^2}{2M} \frac{\partial^2}{\partial z^2} + \frac{\hbar^2 k_z^2}{2M} - U^* \right) \chi^{(T\pm)}(k_z; z) = 0, \quad (16.154)$$

which are simply $K_{-ip}(y^*)$.

The differential reflection coefficient can be expressed in terms of the transition matrix T as

$$\frac{\partial^2 \Re(\mathbf{k}_f, \mathbf{k}_i)}{\partial E_f \partial \Omega_f} = \left(\frac{L}{2\pi} \right)^3 \frac{2\pi M |\mathbf{k}_f|}{\hbar^3 j_i} \sum_{\{n_f\}} \sum_{\{n_i\}} \rho(\{n_i\}) |T_{fi}|^2 \delta(E_f - E_i), \quad (16.155)$$

where $E_i = \mathcal{E}_i + \hbar^2 k_i^2 / 2M$ and $E_f = \mathcal{E}_f + \hbar^2 k_f^2 / 2M$, are the initial and final energies of the combined system, respectively, with $\mathcal{E}$ the energy associated with the surface electron-spin system; $j_i = \hbar k_{iz} / ML$ is the incident flux, and $\rho(\{n_i\})$ is the distribution of initial spin-wave states, given in terms of the surface magnon occupation numbers $\{n_i\}$. In the DWBA the transition matrix element T_{fi} is taken between the initial and final states $\Psi_i = \langle \phi_i^{(+)} | \langle \sigma_i, s_i |$ and $\Psi_f = \langle \phi_f^{(T-)} | \langle \sigma_f, s_f |$, of the unperturbed system, where σ and s denote the spin states of the He^* and the surface magnetic electrons, respectively, and $\langle \phi_f^{(T-)} |$ is the time-reversed solution. The expression for T_{fi} is then given in terms of the eigenstates of (16.139) and their time-reversed partners (16.154) as [142]

$$\begin{aligned} T_{fi} = & \frac{1}{L} (\chi^{(T-)}(k_{fz}; z), U \chi^{(+)}(k_{iz}; z)) \delta(\mathbf{K}_f - \mathbf{K}_i) \\ & + \frac{1}{L^3} \sum_m \int d\mathbf{R} \exp[i(\mathbf{K}_f - \mathbf{K}_i) \cdot \mathbf{R}] (\chi^{(T-)}(k_{fz}; z), J(\mathcal{R} - \mathbf{R}_m) \chi_i^{(+)}(k_{iz}; z)) \\ & \times \langle \sigma_i, s_i | \boldsymbol{\Sigma} \cdot \mathbf{S}_m | s_f, \sigma_f \rangle, \end{aligned} \quad (16.156)$$

The first term in (16.156) represents elastic specular reflection due to the potential U ; since it is of no interest here it will be discarded, leaving the magnetic transition matrix element T_{fi}^{M} . As shown in Appendix A of reference [138], the inelastic magnetic scattering contribution to the transition matrix T_{fi}^{MI} is given by

$$\begin{aligned} T_{fi}^{\text{MI}} = & \frac{1}{L} \mathcal{J}(k_{fz}; k_{iz}) (NS/2)^{1/2} \frac{\mathcal{A}_0}{L^2} \langle \sigma_i, s_i | (\Sigma^+ \hat{\mathbf{a}}^\dagger_{-\mathbf{Q}} + \Sigma^- \hat{\mathbf{a}}_{\mathbf{Q}}) | s_f, \sigma_f \rangle \\ \mathcal{J}(k_{fz}; k_{iz}) = & \int_{-\infty}^{\infty} \chi^{(T-)}(p; z) J(z) \chi^+(p'; z) dz, \end{aligned} \quad (16.157)$$

where $\mathbf{Q} = \mathbf{K}_f - \mathbf{K}_i + \mathbf{G}$, $\hat{\mathbf{a}}_{\mathbf{Q}}^\dagger, \hat{\mathbf{a}}_{\mathbf{Q}}$ are surface spin-wave creation and annihilation operators, respectively. $\mathcal{A}_0$ is the area of a surface unit cell, and $N = L^2 / \mathcal{A}_0$. Substituting for T_{fi} in (16.155) we obtain

$$\begin{aligned} \frac{d^2 \mathcal{R}(\mathbf{k}_f, \mathbf{k}_i)}{dE_f d\Omega_f} = & \left(\frac{M}{2\pi\hbar^2} \right)^2 \frac{S \mathcal{A}_0 |\mathcal{J}(k_{fz}; k_{iz})|^2}{2} \frac{|\mathbf{k}_f|}{k_{iz}} \sum_{\{n_i\}} \rho(\{n_i\}) \delta[E_f - E_i] \\ & \times \langle \sigma_i, s_i | [\Sigma^+ \Sigma^- \hat{\mathbf{a}}^\dagger_{-\mathbf{Q}} \hat{\mathbf{a}}_{-\mathbf{Q}} + \Sigma^- \Sigma^+ \hat{\mathbf{a}}_{\mathbf{Q}} \hat{\mathbf{a}}_{\mathbf{Q}}^\dagger] | s_i, \sigma_i \rangle. \end{aligned} \quad (16.158)$$

The Debye–Waller factor in the eikonal approximation The differential reflection coefficient is written in terms of the transition operator $\hat{T}$ as [136, 137, 143]

$$\frac{\partial^2 \mathcal{R}}{\partial E \partial \Omega} = \frac{L^4 M^2}{8\pi^3 \hbar^5} \frac{v}{v_{iz}} \int_{-\infty}^{\infty} dt e^{-i \frac{E t}{\hbar}} \langle \hat{T}_{\mathbf{P} \leftarrow \mathbf{P}_i}^\dagger(0) \hat{T}_{\mathbf{P} \leftarrow \mathbf{P}_i}(t) \rangle. \quad (16.159)$$

The transition operator $\hat{T}$ is obtained using the scattering wavefunction expressed in the eikonal approximation. This approximation is justifiable because the velocity of the He^* atoms is large compared to the velocity of the surface atoms, and in view of the small mass of the He^* atom, its influence on the motion of the surface can be neglected. In this approximation the transition matrix element becomes

$$\hat{T}_{\mathbf{P} \leftarrow \mathbf{P}_i} = -\frac{i\hbar^2 |k_{iz}|}{ML^3} \int d\mathbf{R} e^{i[\mathbf{Q} \cdot \mathbf{R} + q_z \zeta(\mathbf{R})]} e^{-\frac{\sigma}{q_z} [1 - (1/3) \xi(\mathbf{R}) \langle \hat{S}_z(\mathbf{R}) \rangle]}, \quad (16.160)$$

where $\alpha = MV_0 z_0 / \hbar^2$, $\mathbf{Q} = \mathbf{K} - \mathbf{K}_i$, $q_z = k_z - k_{iz}$ and $\tilde{q}_z = k_z k_{iz} / (k_z + k_{iz})$. Substituting into the differential reflection coefficient expression gives

$$\frac{\partial^2 R}{\partial E \partial \Omega} = \frac{k_{iz} k}{8\pi^3 L^2 \hbar} \int_{-\infty}^{\infty} dt \int d\mathbf{R} d\mathbf{R}' \exp \left\{ -i \left[\frac{Et}{\hbar} + \mathbf{Q} \cdot (\mathbf{R}' - \mathbf{R}) \right] \right\} \mathcal{C}(\mathbf{R}, \mathbf{R}'; t), \quad (16.161)$$

where $\mathcal{C}(\mathbf{R}, \mathbf{R}'; t)$ is the correlation function:

$$\begin{aligned} \mathcal{C}(\mathbf{R}, \mathbf{R}'; t) = & \left\langle \exp \left[-iq_z \zeta(\mathbf{R}'; 0) - \frac{\alpha}{\tilde{q}_z} \left\{ 1 - \frac{1}{3} \xi(\mathbf{R}') \langle \hat{S}_z(\mathbf{R}') \rangle \right\} \right] \right. \\ & \times \exp \left[iq_z \zeta(\mathbf{R}; t) - \frac{\alpha}{\tilde{q}_z} \left\{ 1 - \frac{1}{3} \xi(\mathbf{R}) \langle \hat{S}_z(\mathbf{R}) \rangle \right\} \right] \Bigg\rangle. \end{aligned} \quad (16.162)$$

In order to introduce the Debye–Waller factor, we follow the recipe of Levi *et al.* [136, 137] and split the corrugation shape function $\zeta(\mathbf{R}, t)$ into a static part $\zeta_0(\mathbf{R})$ and a time-dependent part $v(\mathbf{R}, t)$:

$$\zeta(\mathbf{R}, t) = \zeta_0(\mathbf{R}) + v(\mathbf{R}, t), \quad (16.163)$$

where $v(\mathbf{R}, t)$ is given by

$$v(\mathbf{R}, t) = u_z(\mathbf{R}, t) + \mathbf{U}(\mathbf{R}, t) \cdot \nabla \zeta_0(\mathbf{R}), \quad (16.164)$$

where $\mathbf{u} = (\mathbf{U}, u_z)$ is the thermal displacement. The correlation function then becomes

$$\begin{aligned} \mathcal{C}(\mathbf{R}, \mathbf{R}'; t) = & \exp \left\{ -iq_z [\zeta_0(\mathbf{R}') - \zeta_0(\mathbf{R})] + \frac{\alpha}{3\tilde{q}_z} \left[\xi(\mathbf{R}') \langle \hat{S}_z(\mathbf{R}') \rangle + \xi(\mathbf{R}) \langle \hat{S}_z(\mathbf{R}) \rangle \right] \right\} \\ & \times \exp \left[-\frac{2\alpha}{\tilde{q}_z} \right] \langle \exp[-iq_z v(\mathbf{R}', 0)] \exp[iq_z v(\mathbf{R}, t)] \rangle. \end{aligned} \quad (16.165)$$

The term $\langle \dots \rangle$ is calculated in the traditional way by quantizing the normal modes of the surface motion $v(\mathbf{R}, t)$ to obtain

$$\begin{aligned} \mathcal{C}(\mathbf{R}, \mathbf{R}'; t) = & \exp \left\{ -iq_z [\zeta_0(\mathbf{R}') - \zeta_0(\mathbf{R})] + \frac{\alpha}{3\tilde{q}_z} \left[\xi(\mathbf{R}') \langle \hat{S}_z(\mathbf{R}') \rangle + \xi(\mathbf{R}) \langle \hat{S}_z(\mathbf{R}) \rangle \right] \right\} \\ & \times \exp \left[-\frac{2\alpha}{\tilde{q}_z} \right] \exp \left[-\frac{1}{2} q_z^2 [\langle v^2(\mathbf{R}) \rangle + \langle v^2(\mathbf{R}') \rangle] \right] \\ & \times \exp [-q_z \langle v(\mathbf{R}', 0) v(\mathbf{R}, t) \rangle] \\ = & \mathcal{A}^*(\mathbf{R}') \mathcal{A}(\mathbf{R}) \exp [-q_z \langle v(\mathbf{R}', 0) v(\mathbf{R}, t) \rangle], \end{aligned} \quad (16.166)$$

where the terms $\exp [-\frac{1}{2} q_z^2 [\langle v^2(\mathbf{R}) \rangle + \langle v^2(\mathbf{R}') \rangle]]$ is just the Debye–Waller term $\exp[-2W]$. The elastic contribution is then obtained by setting $E = 0$ in the differential reflection coefficient expression, or, alternatively, by taking $t \rightarrow \infty$ in the correlation function

$$\mathcal{C}(\mathbf{R}, \mathbf{R}'; \infty) = \mathcal{A}^*(\mathbf{R}') \mathcal{A}(\mathbf{R}), \quad (16.167)$$

with

$$\mathcal{A}(\mathbf{R}) = \exp \left\{ iq_z \zeta_0(\mathbf{R}) - W - \frac{\alpha}{\tilde{q}_z} \left[1 - (1/3) \xi(\mathbf{R}) \langle \hat{S}_z(\mathbf{R}) \rangle \right] \right\}. \quad (16.168)$$

Substituting back in the differential reflection coefficient expression we get

$$\left(\frac{\partial^2 R}{\partial E \partial \Omega} \right)_{\text{elastic}} \simeq \frac{k_{iz} k}{\pi^2 L^2} \delta(E) \left| \int d\mathbf{R} \exp(\mathbf{Q} \cdot \mathbf{R}) \mathcal{A}(\mathbf{R}) \right|^2. \quad (16.169)$$

Making use of the surface periodicity, the modulus squared can be written as

$$4\pi^2 \frac{L^2}{\Omega} \delta^2(\mathbf{Q} - \mathbf{G}) \left| \int_{\text{uc}} d\mathbf{R} \exp(\mathbf{Q} \cdot \mathbf{R}) \mathcal{A}(\mathbf{R}) \right|^2, \quad (16.170)$$

where uc stands for unit cell, and Ω is its area. We thus obtain the differential reflection coefficient

$$\left(\frac{\partial^2 R}{\partial E \partial \Omega} \right)_{\text{elastic}} \simeq k_{iz} k \sum_{\mathbf{G}} \delta^2(\mathbf{Q} - \mathbf{G}) \delta(E) |\tilde{\mathcal{A}}_{\mathbf{G}}|^2, \quad (16.171)$$

where

$$\tilde{\mathcal{A}}_{\mathbf{G}} = \frac{1}{\Omega} \int_{\text{uc}} d\mathbf{R} \exp \left\{ i[\mathbf{G} \cdot \mathbf{R} + q_z \zeta(\mathbf{R})] - W - \frac{\alpha}{\tilde{q}_z} \left[1 - (1/3) \xi(\mathbf{R}) \langle \hat{S}_z(\mathbf{R}) \rangle \right] \right\}. \quad (16.172)$$

Exercises

16.1 LiNbO_3 belongs to the space-group $R3c(C_{3v}^6)$, #161; its generators are $(C_3|\mathbf{0})$, $(\sigma_d|\boldsymbol{\tau})$, with $\boldsymbol{\tau} = (1/2, 1/2, 1/2)$. It has two formulas per primitive cell. The primitive lattice basis is $(2/3, 1/3, 1/3)$, $(-1/3, 1/3, 1/3)$, $(-1/3, -2/3, 1/3)$ with respect to hexagonal axes: $a = 5.15 \text{ \AA}$, $c = 13.86 \text{ \AA}$. The atomic positions in the rhombohedral primitive cell are given in Table 16.4.

- Determine the symmetries of the phonon modes at the Γ -point.
- Determine the symmetries of the acoustic modes at the Γ -point.
- Determine the Raman active modes.
- Derive the inelastic neutron scattering selection rules for $\mathbf{q}$ along a three-fold axis.

Table 16.4. *The positions of the 10 atoms in the rhombohedral primitive cell.*

Atom	Positions
Nb	$(0, 0, w)$, $(0, 0, \frac{1}{2} + w)$
Li	$(0, 0, \frac{1}{3} + w')$, $(0, 0, \frac{5}{6} + w')$
O	$(\frac{1}{3} - v, u - v, \frac{5}{12})$, $(v - u, \frac{1}{3} - u, \frac{5}{12})$, $(-\frac{1}{3} + u, -\frac{1}{3} + v, \frac{5}{12})$, $(-\frac{1}{3} - v, -u, \frac{7}{12})$, $(u, -\frac{1}{3} + u - v, \frac{7}{12})$, $(\frac{1}{3} - u + v, \frac{1}{3} + v, \frac{7}{12})$

$$w = 0.0186, \quad w' = -0.0318, \quad u = 0.0492, \quad v = 0.0113.$$

- 16.2 The rutile family includes FeF_2 and MgF_2 . It belongs to the space-group $P4_2/mnm$ (D_{4h}^{14} , #136); its generators are $(U_x|\boldsymbol{\tau})$, $(C_4|\boldsymbol{\tau})$, $(I|\mathbf{0})$, with $\boldsymbol{\tau} = (a/2, a/2, c/2)$.
- (i) Determine the symmetries of the phonon modes at the Γ -point.
 - (ii) Determine the symmetries of the acoustic modes at the Γ -point.
 - (iii) Determine the Raman active modes.
 - (iv) Derive the inelastic neutron scattering selection rules for $\mathbf{q}$ along the Δ - and Σ -directions.
- 16.3 Repeat Exercise 16.2 for $\alpha\text{-HgI}_2$, which belongs to the space-group $P4_2/nmc$ (D_{4h}^{15} , #137); its generators are $(U_x|\boldsymbol{\tau})$, $(C_4|\boldsymbol{\tau})$, $(I|\boldsymbol{\tau})$, with $\boldsymbol{\tau} = (a/2, a/2, c/2)$. The primitive cell contains two formulas with positions given in Table 16.5.

Table 16.5. *The positions of the six atoms in the primitive cell.*

Atom	Positions
Hg	$(0, 0, 0), (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$
I	$(0, \frac{1}{2}, u), (-\frac{1}{2}, 0, -u), (0 + u, \frac{1}{2}, \frac{1}{2} + u), (-\frac{1}{2}, 0, \frac{1}{2} - u)$

$$u = 0.14$$

17

Landau's theory of phase transitions

17.1 Phase transitions and their classification

A thermodynamic system can exist in a number of physical states whose macroscopic behavior can differ dramatically. Such states are known as phases. A thermodynamic system may then undergo transformations from one phase into another under certain ambient conditions [144, 145, 146]. In some instances, several phases may coexist in equilibrium with each other when certain common favorable external thermodynamic parameters, such as temperature, pressure, and magnetic field, are applied. The conditions for equilibrium that favor some phases over others will depend on the type of thermodynamic potential that is applicable under existing external constraints. The most common situation is when the thermodynamic system is in contact with both a heat and a pressure reservoir; in which case the Gibbs free energy is applicable and the phases should have the same chemical potential. Thus, at a phase transition, the chemical potential of the phases, and therefore the Gibbs free energy, must change continuously. However, the phase transitions can be sorted into two classes according to the behavior of the first derivatives of the Gibbs free energy.

17.1.1 Classification of phase transitions

For a single component system,

$$G = U - TS + PV = \mu N, \quad (17.1)$$

$$dG = -S dT + V dP + \mu dN; \quad (17.2)$$

and we find that the molar Gibbs free energy, for fixed N , is

$$g = \frac{G}{N} = \mu. \quad (17.3)$$

For simplicity, we consider the coexistence of two phases at equilibrium, and we require that

$$T_1 = T_2, \quad P_1 = P_2, \quad \mu_1 = \mu_2, \quad (17.4)$$

or $g_1 = g_2$. For processes that occur at constant T and Y , where Y is any other intensive variable such as the pressure P or the magnetic field H , changes in the Gibbs free energy

can be written as

$$[dG]_{Y,T} = \mu dN. \quad (17.5)$$

Thus, at a phase transition, the derivative $\mu = (\partial G/\partial N)_{Y,T}$ for both phases, must be equal, and the molar Gibbs energy of each phase shares the same value. However, no restriction is placed on the derivatives $X = (\partial G/\partial Y)_T$ and $S = -(\partial G/\partial T)_Y$. The behavior of these derivatives is used to classify phase transitions:

- If the derivatives $(\partial G/\partial Y)_T$ and $(\partial G/\partial T)_Y$ are discontinuous at the transition point (that is, the extensive variable X and the entropy S have different values in the two phases), the transition is called “first-order”.
- If these derivatives are continuous at the transition but higher-order derivatives are discontinuous, then the phase transition is continuous.

17.1.2 The Ehrenfest definition of second-order phase transition

In the case of a first-order phase transition, as manifest in the van der Waals system, we have two phases with chemical potentials, $\mu_1(T, P)$ and $\mu_2(T, P)$, which intersect at a first-order transition temperature T_0 leading to the coexistence of the two phases at T_0, P_0 , yet the slopes of the two curves are different, $(\partial\mu_1/\partial T)_P \neq (\partial\mu_2/\partial T)_P$, as shown in Figure 17.1. This indicates that at T_0 there is a discontinuity in the specific entropy, $\Delta s = s_1 - s_2$, which gives rise to a finite latent heat, signaling the phase transition as first-order. A similar discontinuity in $(\partial\mu_i/\partial P)_T$ leads to a Δv which corresponds to a discontinuous work $P_0\Delta v$ that can be associated with a mass exchange $\mu\Delta N$ between the two phases.

According to Ehrenfest, even if first-order derivatives of the chemical potentials are equal, two distinct phases could be in equilibrium, provided that the second- or higher-order derivatives of μ_1 and μ_2 are discontinuous at their crossing point. Such a case is

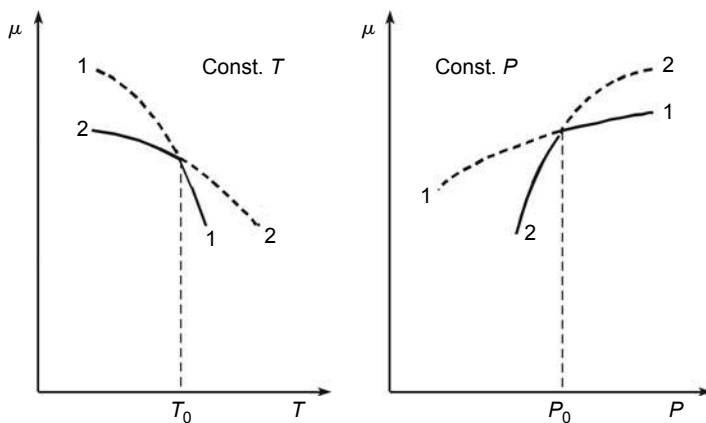


Fig. 17.1. Coexistence of two phases as a function of temperature and pressure.

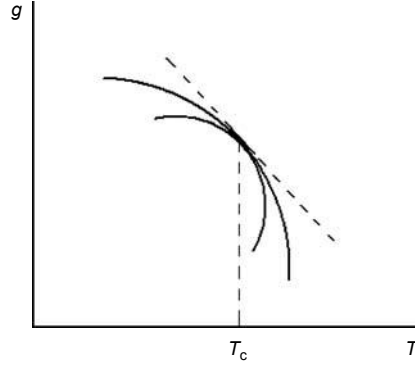


Fig. 17.2. Possible coexistence of two phases for $\Delta s = 0$. No phase transition takes place.

illustrated in Figure 17.2, in the μ – T diagram, where curves $\mu_1(T, P)$ and $\mu_2(T, P)$ are just touching at a single point T_c with a common tangent, and hence $-\Delta s = (\partial \Delta \mu / \partial T)_P = 0$. However, in this case, one of these curves is lower than the other on both sides of T_c , hence representing no transition between the two phases.

On the other hand, we notice that the Ehrenfest condition for a second-order phase transition can be fulfilled mathematically by considering only a single potential μ , instead of μ_1 and μ_2 , if a discontinuous change of the curvature, i.e. $(\partial^2 \Delta \mu / \partial T^2)_{T=T_c} \neq 0$, occurs at T_c . In this case we must consider a substance consisting of a single phase, where the chemical potential represents a continuous *macroscopic* change from one phase to another. Now that we consider a single thermodynamic phase where the number of constituent particles N is constant, it is more convenient to use the Gibbs function G than the chemical potential μ . Thus a second-order phase transition can be characterized by $\Delta(\partial G / \partial T)_P = 0$ and $\Delta(\partial^2 G / \partial T^2)_P \neq 0$ at T_c .

Under a constant P condition, we consider a Gibbs potential $G_0(T)$ for $T > T_c$, which changes continuously to $G(T)$ for $T < T_c$ when the temperature is varied through T_c such that $G_0(T_c) = G(T_c)$.

Expressing $G(T)$, for $T < T_c$, as

$$G(T) = G(T_c) + \Delta G(T), \quad (17.6)$$

and remembering that $\Delta(\partial G / \partial T)_P = 0$ at $T = T_c$, we write $\Delta G(T)$ in the vicinity of T_c as

$$\Delta G(T) = G(T) - G(T_c) = -\frac{1}{2} \left(\frac{\partial^2 \Delta G}{\partial T^2} \right)_{T=T_c} (T_c - T)^2 + \dots, \quad (17.7)$$

where the coefficient

$$\left(\frac{\partial^2 \Delta G}{\partial T^2} \right)_{T=T_c} = -(\Delta c_P)_{T=T_c}$$

represents a discontinuous change in the heat capacity at T_c .

To summarize, we find that phase transitions are of several types, the most common being:

- (i) First-order transitions in which there is a latent heat and possibly a change in symmetry.
- (ii) Second-order transitions with no latent heat but, as we argue below, with a change in symmetry.

17.1.3 Characteristics of phase transitions

Examples of the first type are highlighted by the vaporization of water, with no change in symmetry, and the sublimation of ice with a change in symmetry between the two phases. Typical of the second-order transitions are those of crystals going from a high-temperature paraelectric phase to a low-temperature ferroelectric phase.

The melting of ice and the vaporization of water are described as first-order transitions. The Gibbs free energy is continuous at a first-order transition, but its derivatives are discontinuous, leading to changes in entropy and volume as given by

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S, \quad \left(\frac{\partial \Delta G}{\partial P}\right)_T = \Delta V. \quad (17.8)$$

For some applications, the Helmholtz free energy may be more appropriate. Because of this we use Φ to denote the free energy but not specify whether it is the Gibbs or Helmholtz free energy.

Second-order transitions are characterized by continuous changes in Φ and its first derivatives, but by discontinuities in its second derivatives. In particular, the entropy is continuous across the phase transition, but its derivative is discontinuous, leading to a discontinuity in the heat capacity. In most higher-order phase transitions, the discontinuities are infinities, not simple jumps. The λ -point of the superfluid–normal fluid transition is an example.

Transitions between phases take place along a curve that separates the two phases. An example is shown in Figures 17.3 and 17.4. Along the curve separating the liquid and gas phases of Figure 17.1, the transition is first order. The system is unstable along this curve. That is, any small change in temperature or pressure that causes a deviation from the curve will result in the entire system settling in one phase or the other. As the critical point (T_c, P_c) is approached, the latent heat approaches zero.

A *second-order phase transition* occurs exactly at the critical point. Above the critical point one cannot define separate phases and the system is stable. Thus a second-order phase transition takes place at a very special set of values for pressure and temperature, namely, the critical point (P_c, T_c) , which marks the point between instability and stability.

Transitions between different crystal structures usually involve a discontinuous change. The path for the transition may be known from physical arguments or experiment, but one cannot generally use symmetry arguments and Landau theory to restrict the possible new structure, although it is possible to extend Landau theory to first-order transitions in some circumstances. The same difficulty is encountered for the surface reconstruction of solids. However, there are transitions in solids for which the *positions* of the atoms change

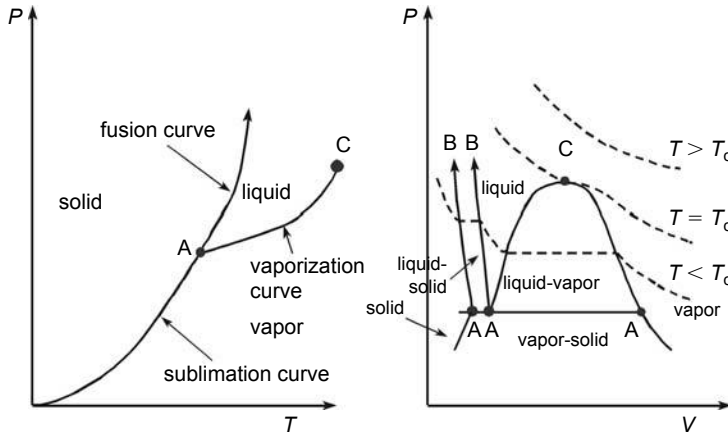


Fig. 17.3. Phase diagrams for a single-component PVT system.

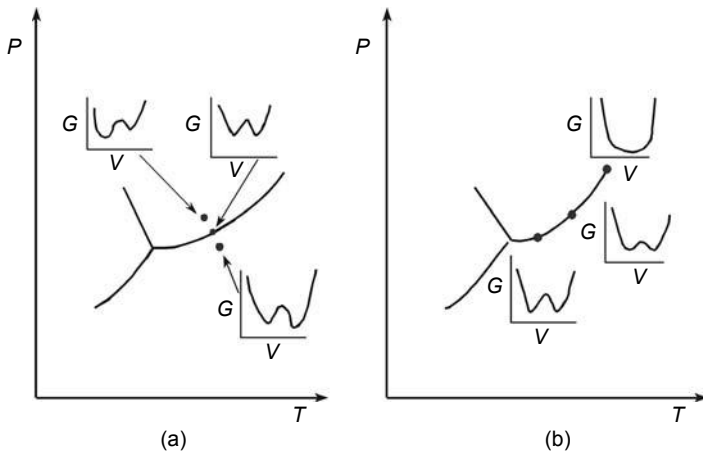


Fig. 17.4. (a) Competition of two minima of the Gibbs potential near the coexistence curve. (b) The coalescence of the minima of the Gibbs potential as the critical point is approached.

continuously even though the *symmetry* of the structure changes discontinuously. Such a transition is identified as a second-order phase transition. Landau theory uses group theory to define the sudden *qualitative* change occurring at the phase transition for these second-order transitions.

17.2 Landau theory of phase transitions: principles

Landau's theory of phase transitions deals primarily with *second-order transitions*, where a system undergoes a continuous change of its structure, but a discontinuous change of

its symmetry. The theory invokes a thermodynamic description of the phase change, with restrictions imposed by stability constraints. These restrictions are then used to impose constraints on the ensuing symmetry changes of the system [19, 144, 145, 146, 147, 148, 149, 150].

17.2.1 The density function

A natural description of a thermodynamic phase is achieved with the aid of a density function $\rho(\mathbf{r})$. It provides a statistical description of the configuration of a condensed matter system as given by the probability distribution of an electronic charge density, a particular type of atom, magnetic or electric moments, etc. By definition, this function must conform to the full symmetry of the system, i.e. to the operations of the space-group $\mathbb{S}_0$ characterizing the system. Consequently, the instantaneous distribution of this density, containing fluctuations, must be expressible, exclusively, in terms of the Irreps of $\mathbb{S}_0$. Its equilibrium configuration, by definition, belongs to the *invariant* Irrep of $\mathbb{S}_0$.

The density fluctuations, as a function of temperature or pressure, may be manifest as atomic vibrations about the equilibrium positions, when we employ an atomic density function, or magnetic or electric moments oscillating about their equilibrium state, when we choose the pertinent density function.

From a thermodynamic perspective we partition the density function into a static equilibrium component $\rho_{\text{eq}}^0(T, P, \dots; \mathbf{r})$, and a dynamic part $\delta\rho(T, P, \dots; \mathbf{r})$ that serves as the thermodynamic variable describing fluctuations in the free energy of the system. In ρ_{eq}^0 , we generally imagine an idealized system in which the density function is static, but may continuously change when a phase change takes place.

We now stipulate, following Landau, that the free energy can be expressed as a functional of the density, in addition to being a function of the usual thermodynamic variables. This stipulation safeguards the continuity of the extensive variables, while allowing for the discontinuity of the underlying symmetry at a phase transition. It also elucidates the classification of the different phases by their symmetry; i.e. we may identify a *high-symmetry* and a *low-symmetry* phase. We may write the Landau free energy as the functional of the density

$$\Phi[\rho(\mathbf{r})] = \int d^d x F(T, P, \dots, \rho(\mathbf{r})). \quad (17.9)$$

We begin with a system in thermodynamic equilibrium in the high-symmetry phase, which is invariant under the symmetry group $\mathbb{S}_0$, at each pressure and temperature (P, T) in that phase. Every operation $(R | \boldsymbol{\tau} + \mathbf{t}) \in \mathbb{S}_0$ leaves the density function $\rho_{\text{eq}}^0(T, P, \mathbf{r})$ invariant, namely,

$$\begin{aligned} (R | \boldsymbol{\tau} + \mathbf{t}) \rho_{\text{eq}}^0(T, P, \mathbf{r}) &= \rho_{\text{eq}}^0(T, P, R^{-1}(\mathbf{r} - \mathbf{v} - \mathbf{t})) \\ &= \rho_{\text{eq}}^0(T, P, \mathbf{r}) \quad \forall (R | \hat{R} | \mathbf{v} + \mathbf{t}) \in \mathbb{S}_0. \end{aligned} \quad (17.10)$$

Generally, this is the high-temperature phase, favored by entropy. For this high-symmetry phase, thermodynamic expectation values that are invariant with respect to operations of the group $\mathbb{S}_0$ are nonzero. All others are zero. Thus, we expect that $\langle \delta\rho(\mathbf{r}) \rangle = 0$, so that $\langle \rho(\mathbf{r}) \rangle = \rho_{\text{eq}}^0(\mathbf{r})$.

The low-temperature phase, which we always consider as the *ordered* phase, is characterized by the appearance of one or more expectation values that are *not* invariant under some operations of $\mathbb{S}_0$. These expectation values are known as *order-parameters*. They are invariant only under a subgroup, $\mathbb{S} \subset \mathbb{S}_0$. Thus the appearance of a more ordered phase is a symmetry-breaking operation; the ordered phase is a *broken-symmetry* phase.

Example 17.1

Phase transition in BaTiO_3

Here we consider barium titanate, BaTiO_3 , which is paraelectric at high temperatures but becomes ferroelectric at low temperatures. It has the *perovskite* structure at high temperatures, shown in Figure 17.5, which belongs to the space-group $\mathbb{S}_0 = Pm\bar{3}m$ (O_h^1), i.e. having cubic point-group symmetry. The property of ferroelectricity in this class of materials is associated with the displacement of the Ti and O atoms relative to the Ba atoms, in a direction parallel to one of the edges of the cube, as, for example, indicated by arrows in Figure 17.5.

It is the relative displacements of the ions that give rise to the existence of a spontaneous electric polarization of the crystal, i.e. the property of ferroelectricity. These displacements of the atoms reduce the symmetry of the crystal to $\mathbb{S} = I4/mcm$ with a tetragonal point-group symmetry. The displacements of the atoms are invariant under the operations of the space-group $\mathbb{S}$.

Alternatively, one can study the static displacements of the atoms, from their positions in the high-symmetry paraelectric phase, in terms of the Irreps of $\mathbb{S}_0$. This is analogous to the decomposition of the lattice vibrations of a crystal in terms of the normal modes

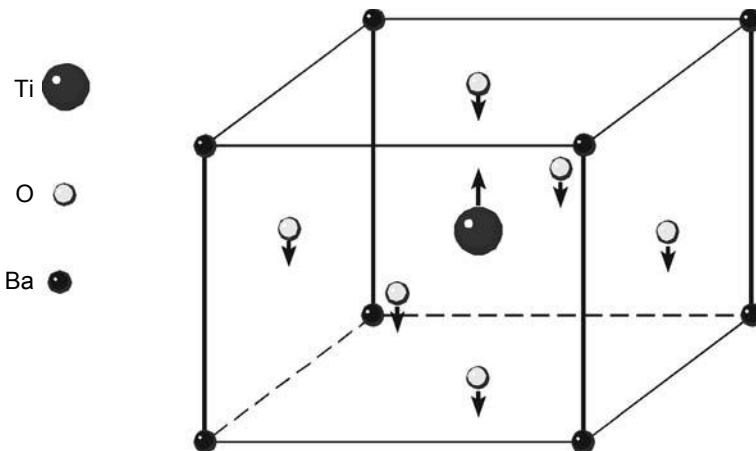


Fig. 17.5. Unit cell of BaTiO_3 . Arrows indicate displacements that occur in the ferroelectric phase.

belonging to the Irreps of $\mathbb{S}_0$. Thus, the displacements that produce the ferroelectric phase can be resolved in terms of Irreps of $\mathbb{S}_0$; the difference from the lattice vibrations case is that we are now concerned with a set of static displacements not dynamic displacements. It came to be realized, around 1960, that these displacements were in fact a *frozen-in* version, or replica, of one of the normal modes of the high-symmetry crystal. The relation between the dynamic and frozen-in displacement is achieved through the scenario of *mode softening*: the frequency of vibration of the “dynamic” mode decreases systematically as the temperature is lowered towards the transition point, and becomes zero at the transition temperature T_c .

As we stated above, usually the higher-temperature phase is the one of higher symmetry, though there is no thermodynamic law that requires it to be so. For example, when considering a crystal of cubic lattice symmetry which undergoes a transition, say, from a paramagnetic (paraelectric) phase at high temperatures to an ordered ferromagnetic (ferroelectric) phase at low temperatures, it automatically lowers its symmetry, due to the superposition of the magnetic (electric) moment direction onto the lattice cubic symmetry. We should point out that the lower-temperature phase is also the more *ordered* phase for these cases.

The change in symmetry that takes place at the phase transition is described, in general, by a *multicomponent order-parameter*, denoted by $\boldsymbol{\eta}$, which goes from zero value in the high-symmetry phase to a nonzero value in the low-symmetry phase. In the case of a paramagnetic to ferromagnetic transition, the order-parameter is the magnetization $\langle \mathbf{m} \rangle$. This is conceptually probably the simplest case to define: The magnetization is either zero or not zero.

Example 17.2

Phase transition of the order–disorder type

A somewhat more subtle transition is the disorder–order transition in alloys. This was the system first considered by Landau. In particular, he considered the case of β -brass (CuZn). In the perfectly ordered state, the alloy structure comprises two interpenetrating lattices, one of Cu, the other of Zn. In the disordered phase, at high temperatures, atoms can move from one lattice site to another and end up on the *wrong* sublattice. If we define the probability of an atom being in the *right* position as r and the probability of being in the *wrong* position as w , we can define a convenient order-parameter as

$$\eta = \frac{r - w}{r + w}, \quad r + w = 1. \quad (17.11)$$

Here η is the *long-range* order, since it can only be defined as an average over a large volume. At high temperatures, atoms are equally likely to be in *right* or *wrong* positions and $\eta = 0$. When all are either *right* or *wrong*, the alloy is perfectly ordered, since $\eta = \pm 1$ and there is no physical significance to the minus sign.

In the high-symmetry phase, away from a transition point $\{T_c, P_c\}$, when the temperature (pressure) is changed by an amount $dT(dP)$ the density changes infinitesimally, $\rho_{\text{eq}}(T, P, \bar{r}) \rightarrow \rho_{\text{eq}}(T + dT, P, \bar{r}) = \rho_{\text{eq}}(T, P, \bar{r}) + \delta\bar{\rho}$, while $\mathbb{S}_0$ remains the same. The change $\delta\bar{\rho}$ may correspond to an effective expansion or contraction of the system with no phase change. Such a $\delta\bar{\rho}$ must belong to the invariant Irrep of $\mathbb{S}_0$, which we denote by $(^1)\Gamma$. Note that because the invariant Irrep $(^1)\Gamma$ is an Irrep of the space-group $\mathbb{S}_0$, it corresponds to the wavevector $\mathbf{k} = \mathbf{0}$ and to the Irrep $(\mathbf{0}, 1+)$ of the little-group of the second kind.

The occurrence of a continuous transition at the *critical* point $\{T_c, P_c\}$ is marked by the following:

- (i) ρ_{eq} varies continuously as the system goes through the transition point.
- (ii) The high-symmetry phase, belonging to $\mathbb{S}_0$, changes to the low-symmetry phase, belonging to $\mathbb{S}$.
- (iii) At the critical point, the symmetry must include *all* the symmetry attributes of both phases, which, in fact, is manifest in the high-symmetry state.

17.2.2 Symmetry properties of the density increment

Because second-order transitions take place at the critical point, we use that point as the reference point with density $\rho_c(\mathbf{r})$ such that

$$\rho_c(\mathbf{r}) = \rho_{\text{eq}}(\{T_c, P_c, \dots\}; \mathbf{r}), \quad (17.12)$$

where $\{T_c, P_c, \dots\}$ denotes the values of all intensive thermodynamic parameters characterizing the transition point. The critical density $\rho_c(\mathbf{r})$ has the full symmetry of $\mathbb{S}_0$, i.e. it belongs to the invariant Irrep of $\mathbb{S}_0$.

We maintain $\mathbb{S}$ as the symmetry group of the low-temperature phase $T < T_c$. The equilibrium density of that phase in the vicinity of the critical point is described in terms of the critical density and the density increment by

$$\rho_{\text{eq}}(T, P, \mathbf{r}) = \rho_c(\mathbf{r}) + \delta\rho_{\text{eq}}(T, P, \mathbf{r}), \quad (17.13)$$

where $\rho_{\text{eq}}(T, P, \mathbf{r}) \rightarrow \rho_c(\mathbf{r})$ as $T, P \rightarrow T_c, P_c$. Thus $\delta\rho$ is a small correction in the vicinity of the critical point. We confine our studies to changes in free energy $\Phi[T, P, \rho_c + \delta\rho, \mathbf{r}]$ to such a region.

Above T_c , $\delta\rho_{\text{eq}}(\mathbf{r}) = 0$. The dynamic $\delta\rho(\mathbf{r})$, representing fluctuations, can be expanded in terms of basis functions belonging to the complete set of Irreps of $\mathbb{S}_0$, and we obtain

$$\delta\rho(\mathbf{r}) = \sum_{*\mathbf{k}\mu, l} \alpha_l(*\mathbf{k}\mu) (^*\mathbf{k}\mu) \psi_l(\mathbf{r}), \quad (17.14)$$

where the functions $\{ (^*\mathbf{k}\mu) \psi_l \}$ transform according to the l th row of the Irrep $(^*\mathbf{k}\mu)\Gamma$.

Below T_c , the equilibrium density function of a system changes slightly and continuously in such a manner that the symmetry of the system will be lowered. We therefore expect the average values of some of the $\alpha_l(*\mathbf{k}\mu)$ s to become nonzero, namely,

$$\langle \alpha_l(*\mathbf{k}\mu) \rangle \neq 0,$$

and the equilibrium form of $\delta\rho$ at a given (T, P) below T_c may be written as

$$\delta\rho_{\text{eq}}(T, P, \mathbf{r}) = \sum'_{\lambda=* \mathbf{k}\mu} \bar{\alpha}_l(\lambda) {}^{(\lambda)}\psi_l(T, P, \mathbf{r}), \quad (17.15)$$

where the prime in the summation precludes ${}^{(1)}\Gamma$, and thus renders $\delta\rho_{\text{eq}}$ not to be invariant under $\mathbb{S}_0$, signaling a lower symmetry than that of $\mathbb{S}_0$. We note that if the component of $\delta\rho$ that belongs to ${}^{(1)}\Gamma$, $\delta\rho(\mathbf{0}, 1)$, actually existed, it would present density contributions that lead to the expansion or contraction of the system that do not involve a symmetry change. Consequently, basis functions belonging to ${}^{(1)}\Gamma$ must be excluded from an expansion for $\delta\rho(\mathbf{r})$. In order to simplify the notation, we used (λ) to stand for the Irrep index $(*\mathbf{k}\mu)$.

The density increment is of lower symmetry than $\mathbb{S}_0$; its symmetry is that of $\mathbb{S}$. This argument then stipulates that $\mathbb{S}$ cannot contain symmetry operations not present in $\mathbb{S}_0$, and leads to the first condition of Landau's theory:

(I) Compatibility condition

A necessary condition for a second-order phase transition is that there must be a change of symmetry in such a way that the symmetry group of one phase is a subgroup of that of the other phase, namely

$$\mathbb{S} \subset \mathbb{S}_0. \quad (17.16)$$

To eliminate the dependence of the magnitude of ${}^{(\lambda)}\psi_l(\mathbf{r})$ on $\delta\rho(\mathbf{r})$, we normalize ${}^{(\lambda)}\psi_l(\mathbf{r})$ and transfer the associated amplitude into a set of *scalar quantities* $\eta_l(T, P, \lambda)$, such that

$$\alpha_l(\lambda) {}^{(\lambda)}\psi_l(T, P, \mathbf{r}) = \eta_l(T, P, \lambda) {}^{(\lambda)}\phi_l(\mathbf{r}). \quad (17.17)$$

Moreover, we allow the $\eta_l(T, P, \lambda)$ s to induce the Irrep ${}^{(\lambda)}\Gamma$, and thus render the ${}^{(\lambda)}\phi_l(\mathbf{r})$ s to remain invariant with respect to $\mathbb{S}_0$.

Example 17.3

We consider the expansion $\delta\rho = (\eta_1\phi_1 + \eta_2\phi_2)$, and stipulate that

$$R \begin{bmatrix} \phi_1 \\ \phi_2 \end{bmatrix} = \begin{bmatrix} \phi_2 \\ -\phi_1 \end{bmatrix},$$

so that we obtain the transformation

$$R\delta\rho = (\eta_1\phi_2 - \eta_2\phi_1).$$

Alternatively, this transformation can be achieved by setting

$$R \begin{bmatrix} \eta_1 \\ \eta_2 \end{bmatrix} = \begin{bmatrix} -\eta_2 \\ \eta_1 \end{bmatrix}.$$

The η s must transform in the *same way* as the ϕ s if $\rho(\mathbf{r})$, which is a *product* of η and ϕ is to be unique, independent of the coordinate system. That is,

$$\delta\rho(T, P, \mathbf{r}) = \sum'_{\lambda, l} \eta_l(T, P, \lambda) {}^{(\lambda)}\phi_l(\mathbf{r}). \quad (17.18)$$

As we stipulated above, the Landau theory assumes the existence of a single thermodynamic potential which is capable of describing the thermodynamic state of both the high- and low-symmetry phases of a system. By hypothesis, this potential is a function of the sets of quantities $\eta_l(\lambda)$ which span the vector space associated with the Irrep ${}^{(\lambda)}\mathbf{\Gamma}$ of the symmetry space-group $\mathbb{S}_0$. It is a scalar invariant of $\mathbb{S}_0$.

If $\mathbb{S}$ is a group compatible with $\mathbb{S}_0$, then $\delta\rho(\mathbf{r})$ is a basis of an invariant space with respect to all $(R \mid \mathbf{v} + \mathbf{t}) \in \mathbb{S}$. But by construction, $\delta\rho(\mathbf{r})$ is a space built from a complete set of basis vectors that engender the ${}^{(\lambda)}\mathbf{\Gamma}$ s of $\mathbb{S}_0$.

(II) Subduction condition

Thus we arrive at the requirement that for an Irrep ${}^{(\lambda)}\mathbf{\Gamma}$ to contribute to the transition it has to satisfy

$$\langle {}^{(\lambda)}\mathbf{\Gamma} \downarrow \mathbb{S} \mid {}^{(1)}\mathbf{\Delta} \rangle \neq 0, \quad (17.19)$$

where ${}^{(1)}\mathbf{\Delta}$ is the invariant Irrep of $\mathbb{S}$. Or, alternatively,

$${}^{(\lambda)}\mathbf{\Gamma} \downarrow \mathbb{S} \ni {}^{(1)}\mathbf{\Delta}. \quad (17.20)$$

Tensor field criterion

We proposed above that the density increment should be expanded in terms of Irreps of $\mathbb{S}_0$, yet we have to provide some qualifications as to which Irreps are to be included in the expansion. Birman [151] has demonstrated that such Irreps should be contained in a representation of a *physical tensor field*. We have presented the idea of physical tensor fields in Section 13.4, and described methods for their construction and decomposition into Irreps of the covering symmetry group. Here, we simply add this requirement to our list of conditions:

(III) Tensor field condition

An active Irrep, i.e. an Irrep qualified to drive a second-order phase transition, must be contained in the decomposition of a relevant physical tensor field,

$$\mathfrak{F}^{\text{TF}} = \Gamma^{\text{T}} \otimes \Gamma^{\text{Perm}} \ni {}^{(\lambda)}\Gamma, \quad (17.21)$$

where $\mathfrak{F}^{\text{TF}}$ is the tensor field representation. By definition, $\mathfrak{F}^{\text{TF}}$ has to be real.

As we argued in Chapter 13, Γ^{T} is some physical tensor representation, such as the polar representation in the case of atomic displacements or electric dipoles, or the axial representation in the case of magnetic moments or spins. Γ^{Perm} is the representation of site permutations under the operation of the group $\mathbb{S}_0$.

(IIIA) Tensor field condition

The reality of $\mathfrak{F}^{\text{TF}}$ introduces the constraint that the candidate Irrep has to be real, or, if an Irrep is complex, then an active Irrep is the direct sum of it and its complex conjugate.

17.2.3 The Landau free energy

The thermodynamic potential, or free energy, $\Phi[T, P, \rho(\mathbf{r})]$ is a functional of the coefficients $\eta_l(T, P, \lambda)$ and can be expressed as

$$\Phi[T, P, \rho(\mathbf{r})] = \int d^d x F \left(T, P; \rho_c(\mathbf{r}) + \sum_{\lambda, l} \eta_l(T, P, \lambda) {}^{(\lambda)}\phi_l(\mathbf{r}) \right), \quad (17.22)$$

where the free energy density F must belong to the invariant Irrep ${}^{(1)}\Gamma$. The variables T and P can be chosen arbitrarily, but the coefficients $\bar{\eta}_l(T, P, \lambda)$ must be chosen such that Φ is a minimum. These thermodynamically determined coefficients also determine the group $\mathbb{S}$ of the system in its state of reduced symmetry, according to (17.15).

A Taylor expansion of the Landau free energy

At the transition point (P_c, T_c) , all the coefficients $\bar{\eta}_l(T, P, \lambda)$ must vanish in order that $\delta\rho_{\text{eq}}(T, P, \mathbf{r})$ vanish. Only then does (17.12) reduce to (17.13). However, the vanishing of the coefficients must be continuous in order that the change of the density be continuous at the critical point. This allows us to expand the free energy in powers of $\eta_l(T, P, \lambda)$

about the critical point, namely

$$\begin{aligned}\Phi &= \int d^d x \left\{ F_c(T, P; \rho_c) + \mathcal{F}(\{({}^{(\lambda)}\eta_l(T, P)\}) \right\} \\ &= \Phi_c + \int d^d x \mathcal{F}(\{({}^{(\lambda)}\eta_l(T, P)\}), \\ \Delta\Phi &= \Phi - \Phi_c = \int d^d x \left[\sum_i \mathcal{F}^{(i)}(\{({}^{(\lambda)}\eta_l(T, P)\}) \right],\end{aligned}\quad (17.23)$$

where $\mathcal{F}^{(i)}$ are homogeneous polynomials in $({}^{(\lambda)}\eta_l(T, P))$ of order i .

We note that:

- Linear terms in the η_l s, represented by $\mathcal{F}^{(1)}$, are excluded in the Taylor series expansion of F , since such terms constitute $\delta\rho$ itself which, by definition, does not belong to the invariant Irrep, as F should.
- Because of (8.36)

$$\langle ({}^{(\mu)}\Gamma \otimes ({}^{(\nu)}\Gamma) \mid ({}^{(1)}\Gamma) \rangle = \frac{1}{S_0} \sum_R ({}^{(\mu)}\chi(R) ({}^{(\nu)}\chi^*(R)) = \delta_{\mu\nu},$$

we find that bilinear cross-terms among the different Irreps vanish identically, and that there is only *one* bilinear invariant for each Irrep λ .

Since each active Irrep is real and unitary, its matrices are orthogonal. It is then instructive to consider the case of two identical or equivalent Irreps λ , with basis $({}^{(\lambda)}\eta_{1i})$ and $({}^{(\lambda)}\eta_{2j})$, respectively, and to operate on the bilinear combination $({}^{(\lambda)}\eta_{1i}^* ({}^{(\lambda)}\eta_{2j}))$ with the projection operator $({}^{(1)}\mathcal{P})$

$$\begin{aligned}({}^{(1)}\mathcal{P}) ({}^{(\lambda)}\eta_{1i}^* ({}^{(\lambda)}\eta_{2j})) &= \frac{1}{S_0} \sum_{R \in S_0} R ({}^{(\lambda)}\eta_{1i}^* ({}^{(\lambda)}\eta_{2j})) \\ &= \frac{1}{S_0} \sum_{kl} \sum_{R \in S_0} ({}^{(\lambda)}\eta_{1k}^* ({}^{(\lambda)}\eta_{2l})) ({}^{(\lambda)}\Gamma_{ki}^*(R) ({}^{(\lambda)}\Gamma_{lj}(R)) \\ &= \frac{1}{d_\lambda} \sum_l ({}^{(\lambda)}\eta_{1l}^* ({}^{(\lambda)}\eta_{2l})).\end{aligned}\quad (17.24)$$

If we consider the special case of taking the Kronecker product of the same basis we obtain $\sum_l |({}^{(\lambda)}\eta_l)|^2$. Thus, the most general *second-degree invariant* has the form

$$\sum_\lambda a_\lambda \left(T, P, \rho_0(\mathbf{r}), ({}^{(\lambda)}\phi(\mathbf{r})) \right) \sum_l ({}^{(\lambda)}\eta_l^2), \quad (17.25)$$

where a_λ includes the various partial derivatives of Φ expressed symbolically in terms of T, P , equilibrium density and basis functions.

We now study the features that allow an Irrep λ to drive a continuous phase transition. We require that, for $T \geq T_c$, all $^{(\lambda)}\bar{\eta}_l = 0$, and that at least one $^{(\lambda)}\bar{\eta}_l \neq 0$, i.e. be finite, at $T < T_c$. Since Φ has to be a minimum at equilibrium, this would require that

$$a_\lambda(T, P) \begin{cases} > 0 & T > T_c, \\ = 0 & T = T_c, \\ < 0 & T < T_c. \end{cases} \quad (17.26)$$

Consequently, we find that the equation $a_\lambda(T, P) = 0$ defines a line of transition points T_c, P_c in the P - T plane. We may then associate such a line with every Irrep that satisfies all the conditions cited above, as well as those given below.

It is now necessary to discuss the possibility that more than one Irrep drives the transition at a given (T_c, P_c) . For the sake of simplicity, we consider the case of two such irreps λ and μ , and assume the order-parameter to have second-degree terms of the form

$$\frac{a_\lambda}{2} \sum_{i=1}^{d_\lambda} {}^{(\lambda)}\eta_i^2 + \frac{a_\mu}{2} \sum_{j=1}^{d_\mu} {}^{(\mu)}\eta_j^2. \quad (17.27)$$

Transition points associated with each of the coefficients are defined by the lines $a_\lambda(T, P) = 0$ and $a_\mu(T, P) = 0$. For both irreps to simultaneously drive the transition at (T_c, P_c) , the two lines have to cross at that point, as shown in Figure 17.6. However, we note that any infinitesimal change in P_c would lead to the elimination of one of the two irreps from driving the transition. Such crossing points are referred to as multicritical points (tricritical in the present example); and because of their instability against pressure fluctuations they are labeled *singular points*. Consideration of singular points

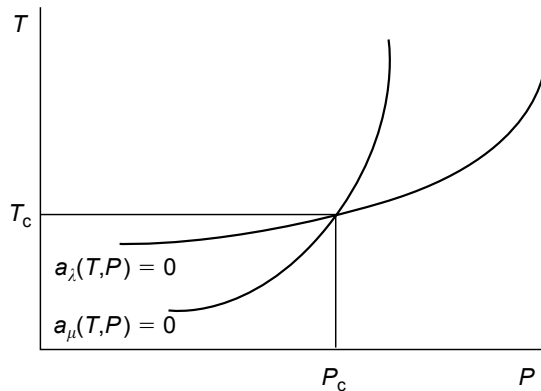


Fig. 17.6. Intersection of two critical lines, defining a multicritical or singular point (T_c, P_c) .

is waived from the mainstream Landau theory, and is beyond the purview of this book. Thus, we may introduce the nonsingularity condition of the Landau theory as:

(IV) Non-singularity condition

We postulate that only the basis of one Irrep, λ , of $\mathbb{S}_0$ “drives” the phase transition, and we express $\delta\rho$ as

$$\delta\rho(\mathbf{r}) = \sum_l {}^{(\lambda)}\eta_l(T, P) {}^{(\lambda)}\phi_l(\mathbf{r}), \quad (17.28)$$

and (17.27) is reduced to

$$a_\lambda(T, P) \sum_l | {}^{(\lambda)}\eta_l |^2, \quad (17.29)$$

with a_λ satisfying (17.26), and

$$a_\mu(T, P) > 0, \forall \mu \neq \lambda, \text{ at all } T. \quad (17.30)$$

Now, since we are only concerned with the region in the vicinity of T_c , we use the fact that the *single* a_λ vanishes at T_c to expand it in terms of a power series in the temperature difference $(T - T_c)$ in the neighborhood of the critical point. Thus,

$$a_\lambda = a(T - T_c) + a'(T - T_c)^2 + \dots, \quad (17.31)$$

For the Irrep ${}^{(\lambda)}\Gamma$, the set ${}^{(\lambda)}\bar{\eta}_l$ constitutes the order-parameter (OP) of the transition. Each ${}^{(\lambda)}\eta_l$ is an OP-component and the number of ${}^{(\lambda)}\eta_l$ s is both the dimension of ${}^{(\lambda)}\Gamma$ and the OP space.

Definition The *order-parameter* (OP) of a continuous phase transition that occurs at (T_c, P_c) comprises a set of scalar quantities η_l that induce an Irrep (λ) of $\mathbb{S}_0$. In order-parameter space, the set η_l form a vector $\boldsymbol{\eta} \equiv \{\eta_l\}$, and its components are associated with a single coefficient

$$a_\lambda \equiv a_\lambda(T, P),$$

that appears in a Taylor expansion of the Landau (Gibbs, Helmholtz, ...) free energy $\Delta\Phi$, and satisfies the condition

$$a_\lambda(T_c, P_c) = 0.$$

As we asserted above, the remaining coefficients a_μ associated with Irreps (μ) of $\mathbb{S}_0$, satisfy the condition

$$a_\mu(T, P) > 0, \quad \text{for all } T,$$

which forces the corresponding $^{(\mu)}\bar{\eta}_l = 0$ to minimize $\Delta\Phi$.

We now arrive at the following deductions:

- (i) The invariance of ρ_{eq} with respect to $\mathbb{S}_0$ in the high-symmetry phase leads to the condition that the minimum of the thermodynamic potential $\Delta\Phi$ with respect to the set $\{^{(\lambda)}\bar{\eta}_l(T, P)\}$ occurs at $^{(\lambda)}\bar{\eta}_l(T, P, \lambda) = 0, \forall l$.
- (ii) In the case of the low-symmetry phase, the minimum of Φ occurs for a set $\{^{(\lambda)}\bar{\eta}_l(T, P)\}$, where at least one of the $^{(\lambda)}\bar{\eta}_l(T, P)$ is nonzero. The corresponding density

$$\delta\bar{\rho}(\mathbf{r}) = \sum_l ^{(\lambda)}\bar{\eta}_l(T, P) ^{(\lambda)}\phi_l(\mathbf{r}), \quad (17.32)$$

is left invariant by a subset of elements $(\bar{R}|\mathbf{v} \mp \mathbf{t}) \in \mathbb{S}_0$. This subset defines the broken-symmetry subgroup $\mathbb{S}$, and the transition $\mathbb{S}_0 \rightarrow \mathbb{S}$ occurs via $^{(\lambda)}\mathbf{\Gamma}$. This can be stated as two postulates:

$$\begin{aligned} \text{(I)} \quad & \mathbb{S}_0 \supset \mathbb{S}. \\ \text{(II)} \quad & ^{(\lambda)}\mathbf{\Gamma} \downarrow \mathbb{S} \ni ^{(0,1)}\mathbf{\Delta}. \end{aligned}$$

Dimensionality of the OP

We now discuss the dimensionality of the OP describing a thermodynamic phase transition. For two- and three-dimensional systems, the Euclidean groups $\mathcal{E}(2)$ and $\mathcal{E}(3)$ or one of their subgroups, namely the space-groups, will constitute the group $\mathbb{S}_0$. As we explained in Chapter 11, the Irreps associated with such groups are identified by a star of the wavevector, $^*\mathbf{k}$, and by one of the Irreps (μ) of $\mathbb{S}_{\mathbf{k}}$, the little-group of $\mathbf{k}$. Each Irrep $(^*\mathbf{k}, \mu)$ has a basis of the form

$$^{(\mathbf{k}_m, \mu)}\psi_j(\mathbf{r}) = e^{i\mathbf{k}_m \cdot \mathbf{r}} ^{(\mu)}U_j(\mathbf{r}, \mathbf{k}_m) \quad \left\{ \begin{array}{l} m = 1, \dots, n(^*\mathbf{k}), \\ j = 1, \dots, d_\mu, \end{array} \right. \quad (17.33)$$

where $n(^*\mathbf{k}) = \mathbb{S}_0/\mathbb{S}_{\mathbf{k}}$ is the number of wavevectors $\mathbf{k}_m$ in the star of $\mathbf{k}$, and $^{(\mu)}U_j(\mathbf{r}, \mathbf{k}_m)$ are invariant functions under the translation group of $\mathbb{S}_0$. Thus the dimensionality of the Irrep $(^*\mathbf{k}, \mu)$ is

$$d(^*\mathbf{k}, \mu) = n(^*\mathbf{k}) \times d_\mu. \quad (17.34)$$

17.2.4 The low-temperature, low-symmetry phase

Just below the critical point (P_c, T_c) the high-temperature phase (HTP) is no longer stable. In particular, $a_\lambda(T, P_c) < 0$ for $T < T_c$, is consistent with the instability of the

HTP for $T < T_c$. Stability of the low-temperature phase (LTP) requires the introduction of high-order expansion terms in the OP:

$$\Delta\Phi = \frac{a(T - T_c)}{2} \left(\sum_i \eta_i^2 \right) + \mathcal{F}^{(3)}(\boldsymbol{\eta}) + \mathcal{F}^{(4)}(\boldsymbol{\eta}) + \dots, \quad (17.35)$$

where $\mathcal{F}^{(i)}$ is a homogeneous polynomial of the components of the OP $\boldsymbol{\eta}$ of degree i invariant under $\mathbb{S}_0$. The homogeneity of the monomials allows us to make the substitution $\eta_i = \xi \zeta_i$, and invoke the normalization $\sum_i \zeta_i^2 = 1$, to obtain

$$\begin{aligned} \Delta\Phi = & \frac{a(T - T_c)}{2} \xi^2 + \xi^3 \sum_p \frac{b_p(T, P)}{3} f_p^{(3)}(\boldsymbol{\zeta}) \\ & + \xi^4 \sum_q \frac{c_q(T, P)}{4} f_q^{(4)}(\boldsymbol{\zeta}) + \dots, \end{aligned} \quad (17.36)$$

where the sum over p and q assumes the presence of more than one homogeneous third- and fourth-degree invariant polynomials, respectively.

Example 17.4

Landau free energy expansion for BaTiO₃

Consider a change in the crystal due to small atomic displacements such that a ferroelectric state is obtained. Because the electric polarization vector transforms according to the vector representation $\Gamma_{15}(T_1^-)$ of $Pm3m$, with $\mathbf{q} = \mathbf{0}$, we seek the expansions $\mathcal{F}^{(i)}$ as invariants in the Kronecker products of Γ_{15} . The number of terms in each $\mathcal{F}^{(i)}$ is given by

$$\langle \Gamma_{15}^2 | \Gamma_1 \rangle = 1, \quad \langle \Gamma_{15}^4 | \Gamma_1 \rangle = 2, \quad \langle \Gamma_{15}^6 | \Gamma_1 \rangle = 3.$$

Since Γ_{15} is odd with respect to inversion, it can be easily shown that any odd Kronecker product does not contain the invariant Irrep Γ_1 . The general forms of the homogeneous polynomials are given by

$$\begin{aligned} \mathcal{F}_1^{(4)} &= (\eta_1^2 + \eta_2^2 + \eta_3^2)^2, & \mathcal{F}_2^{(4)} &= (\eta_1^4 + \eta_2^4 + \eta_3^4), \\ \mathcal{F}^{(4)} &= \xi^4 (1 + \alpha (\zeta_1^4 + \zeta_2^4 + \zeta_3^4)), \\ \mathcal{F}_1^{(6)} &= (\eta_1^2 + \eta_2^2 + \eta_3^2)^3, & \mathcal{F}_2^{(6)} &= (\eta_1^6 + \eta_2^6 + \eta_3^6), & \mathcal{F}^{(6)} &= \eta_1^2 \eta_2^2 \eta_3^2, \\ \mathcal{F}^{(6)} &= \xi^6 (1 + \beta (\zeta_1^6 + \zeta_2^6 + \zeta_3^6) + \gamma \zeta_1^2 \zeta_2^2 \zeta_3^2), \end{aligned}$$

where α , β , and γ are parameters which depend on the intensive variables $T, \dots$

In order to find the actual stable state of the crystal, we minimize with respect to the ζ_i s and ξ . We start with the former and use the constraint $\sum_i \zeta_i^2 = 1$, with the aid of

Lagrange multipliers. Retaining up to quartic terms, we obtain,

$$\frac{\partial \mathcal{F}^{(4)}}{\partial \zeta_i} - 2\lambda \zeta_i = 0, \implies \zeta_i (2\alpha \zeta_i^2 - \lambda) = 0,$$

where λ is a Lagrange multiplier. This set of equations yields three possible solutions, namely,

$$\begin{aligned} \text{(i)} \quad & \zeta_1 = 1, \quad \zeta_2 = 0, \quad \zeta_3 = 0, \\ \text{(ii)} \quad & \zeta_1 = \frac{1}{\sqrt{2}}, \quad \zeta_2 = \frac{1}{\sqrt{2}}, \quad \zeta_3 = 0, \\ \text{(iii)} \quad & \zeta_1 = \frac{1}{\sqrt{3}}, \quad \zeta_2 = \frac{1}{\sqrt{3}}, \quad \zeta_3 = \frac{1}{\sqrt{3}}. \end{aligned}$$

The minimization with respect to ξ in each of the three cases is left as Exercise 17.1.

The ferroelectric states corresponding to these solutions are the only states that are stable against arbitrarily small deviations from the cubic state. The three states (i), (ii), and (iii) represent three different ferroelectric phases of BaTiO_3 , with the polarization $\mathbf{P}$ parallel to the $[100]$ axes (tetragonal phase) $I4/mcm$, parallel to the $[110]$ axis (orthorhombic phase), and parallel to the $[111]$ axes (rhombohedral phase), respectively.

By writing $\eta_i = P_i$ we can express the Landau free energy in terms of the P_i as

$$\begin{aligned} \Phi = & \Phi_0 + A (P_x^2 + P_y^2 + P_z^2)^2 \\ & + B (P_x^2 + P_y^2 + P_z^2)^2 + C (P_x^4 + P_y^4 + P_z^4) \\ & + D (P_x^2 + P_y^2 + P_z^2)^3 + E (P_x^6 + P_y^6 + P_z^6) \\ & + F P_x^2 P_y^2 P_z^2 + \dots \end{aligned}$$

17.2.5 Instability in the presence of $\mathcal{F}^{(3)}$

The actual stable phase of the system is found by minimizing $\Delta\Phi$ with respect to ξ and ζ_i . From the conditions of stability,

$$\partial\Delta\Phi/\partial\xi = 0 \text{ and } \partial^2\Delta\Phi/\partial\xi^2 > 0,$$

we find that the state $\xi = 0$ is stable for $a > 0$, whereas for $a < 0$ the stable phase must have $\xi \neq 0$. Therefore, in order for a phase transition to take place from the high-symmetry phase $\xi = 0$ to a phase of lower symmetry at the point where $a = 0$ and $\xi = 0$, Φ must increase for both positive and negative changes in ξ . This can only be true if, in addition to the condition $a(T_c, P_c) = 0$, we impose the set of conditions

$b_p(T_c, P_c) = 0$, $\forall p$, a quite unlikely scenario. Therefore, the stability of the transition can only be ensured if the following condition is satisfied:

(V) Stability or Landau condition

A second-order phase transition is possible only if third-degree terms in the free energy are excluded by symmetry, i.e.

$$[({}^{(\lambda)}\Gamma \otimes {}^{(\lambda)}\Gamma \otimes {}^{(\lambda)}\Gamma)] \not\supset ({}^{(0,1)}\Gamma). \quad (17.37)$$

Using the expression for the symmetrized form of the cubic Kronecker product,

$$\chi[\Gamma^3(R)] = \frac{1}{6} \chi^3(R) + \frac{1}{2} \chi(R) \chi(R^2) + \frac{1}{3} \chi(R^3), \quad (17.38)$$

we write the Landau condition as

$$\left\langle [({}^{(\lambda)}\Gamma \otimes {}^{(\lambda)}\Gamma \otimes {}^{(\lambda)}\Gamma)] | ({}^{(1)}\Gamma) \right\rangle = \frac{1}{S_0} \sum_R \chi[\Gamma^3(R)] = 0, \quad (17.39)$$

or,

$$\frac{1}{S_0} \sum_R \left(\frac{1}{6} \chi^3(R) + \frac{1}{2} \chi(R) \chi(R^2) + \frac{1}{3} \chi(R^3) \right) = 0. \quad (17.40)$$

One-dimensional Irreps

For real one-dimensional Irreps, we find that the characters are just the matrix elements, $\chi(R) \equiv \Gamma_{11}(R)$, and, hence $\chi(R^n) = \chi^n(R)$. We then obtain

$$[\chi^3(R)] = \left(\frac{1}{6} + \frac{1}{2} + \frac{1}{3} \right) \chi^3(R) = \chi^3(R). \quad (17.41)$$

Since the compatible Irreps have to be real, then $\chi^3(R) = \chi(R)$, and using (17.38) we obtain

$$\begin{aligned} \left\langle [({}^{(\lambda)}\Gamma \otimes {}^{(\lambda)}\Gamma \otimes {}^{(\lambda)}\Gamma)] | ({}^{(1)}\Gamma) \right\rangle &= \frac{1}{S_0} \sum_R \chi(R) \\ &= \frac{1}{S_0} \sum_R \chi(R) ({}^{(1)}\chi^*(R) = 0, \end{aligned} \quad (17.42)$$

so that, excluding the invariant Irrep, all other one-dimensional real Irreps satisfy the Landau condition.

Subgroups of index 2 in S_0

With this result at hand, we can show that the Landau condition is always satisfied when S , the subgroup of S_0 associated with the lower-symmetry phase, is of index 2 in S_0 . Any

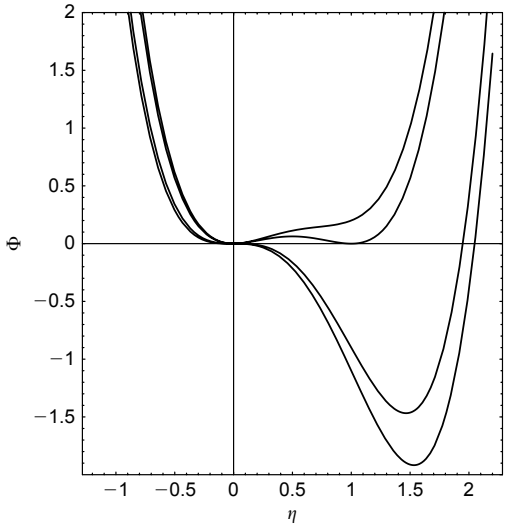


Fig. 17.7. Variation of Φ as a function of temperature.

subgroup of index 2 is a normal subgroup such that

$$\mathbb{S}_0 = \mathbb{S} + R\mathbb{S} \text{ and } R\mathbb{S} = \mathbb{S}R.$$

By definition, $\delta\rho_{\text{eq}}$ in the low-symmetry phase belongs to the invariant Irrep $^{(1)}\Delta$ of $\mathbb{S}$. And, since the quotient group $\mathbb{S}_0/\mathbb{S}$ is of order 2, it has an invariant Irrep (+), and an odd Irrep (−). The induction $^{(1)}\Delta \uparrow \mathbb{S}_0$ will yield two 1-dimensional Irreps of $\mathbb{S}_0$: the invariant Irrep $^{(1)}\Gamma$ and the noninvariant Irrep, which is the one driving the transition.

Example 17.5

Irreps of C_{3v} compatible with the Landau condition							
$^{(2)}\Gamma$	E	$2C_3$	3σ	$^{(3)}\Gamma$	E	$2C_3$	3σ
$^{(2)}\chi$	1	1	-1	$^{(3)}\chi$	2	-1	0
$\left[^{(2)}\chi^3 \right]$	1	1	-1	$\left[^{(3)}\chi^3 \right]$	4	1	0

$\left[^{(2)}\Gamma^3 \right]$ does not contain $^{(1)}\Gamma$, thus, symmetry rules out an invariant third-degree term. $\left[^{(3)}\Gamma^3 \right]$ contains $^{(1)}\Gamma$, i.e. symmetry does not rule out an invariant third-degree term.

Example 17.6

One-component OP with third-degree invariant

For pedagogical reasons, we consider here a hypothetical example of a one-component system whose symmetry allows an invariant term of the third-degree. We write the Landau

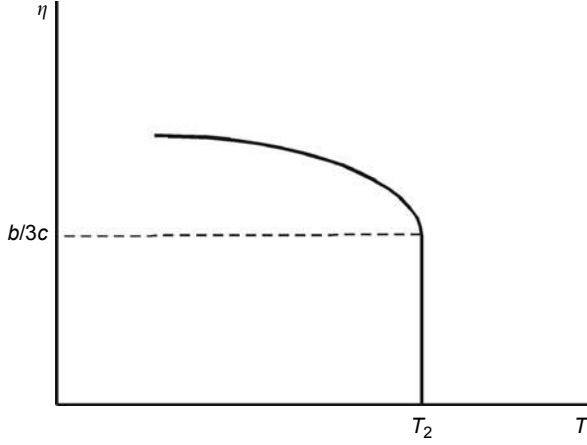


Fig. 17.8. Temperature dependence of OP.

free energy expansion as

$$\Phi(\eta) - \Phi_0 = \frac{a(T - T_c)}{2} \eta^2 - \frac{b}{3} \eta^3 + \frac{c}{4} \eta^4,$$

and we are interested in the case $b > 0$ and $c > 0$. The free energy has minima at

$$\begin{aligned} \eta [a(T - T_c) - b\eta + c\eta^2] &= 0, \\ a(T - T_c) - 2b\eta + 3c\eta^2 &\geq 0. \end{aligned}$$

We find that the root

$$\eta = 0, \quad \Phi(\eta_0) - \Phi_0 = 0$$

is a minimum in the range $T > T_c$; it is a stable minimum for $T \geq T_2$, T_2 to be defined shortly, and becomes metastable for $T < T_2$.

Moreover, an inflection appears at

$$\eta' = \frac{b}{2c} \Rightarrow T_1 = T_c + \frac{b^2}{4ac},$$

and for $T_2 < T < T_1$ it becomes a metastable minimum. This minimum reaches the value

$$\Phi(\eta') - \Phi_0 = 0, \quad T_2 = T_c + \frac{2}{9} \frac{b^2}{ac},$$

marking the coexistence of the two phases $\eta_0 = 0$ and $\eta' = \frac{b}{3c}$, where the system undergoes a first-order transition. For $T < T_2$, η' becomes the stable phase with

$$\eta' = \frac{b}{2c} + \sqrt{\left(\frac{b}{2c}\right)^2 - \frac{a}{c}(T_c - T)}.$$

The η_0 phase becomes metastable for $T < T_2$, and disappears at the second metastability limiting point $T = T_c$, below which a maximum appears at $\eta_0 = 0$.

Example 17.7

Landau condition for space-groups

It is quite useful to consider how the Landau condition may be formulated for Irreps of space-groups. As we have demonstrated, such Irreps are constructed from the Irreps of $\mathbb{T}$, namely,

$$e^{i\mathbf{k} \cdot \mathbf{t}}, \quad \mathbf{k} \in {}^*\mathbf{k}, \quad \mathbf{t} \in \mathbb{T},$$

together with allowable Irreps of the little-group $\mathbb{S}_{\mathbf{k}}$, which we labeled μ . The admissibility of a third-degree invariant term will depend on Kronecker cubic products of both types of Irreps. We first consider the simpler case of Kronecker cubic products of $e^{i\mathbf{k} \cdot \mathbf{t}}$, which involve the sum of three members of ${}^*\mathbf{k}$:

$$\mathbf{k} + \mathbf{k}' + \mathbf{k}'' . \quad (17.43)$$

The invariance of such terms would require that

$$\mathbf{k} + \mathbf{k}' + \mathbf{k}'' = \mathbf{0}. \quad (17.44)$$

Condition (17.44) cannot be satisfied for Irreps associated with one- or two-member stars since

$$\mathbf{k} + \mathbf{k} + \mathbf{k} \neq \mathbf{0} \quad \text{and} \quad \mathbf{k} + \mathbf{k} + \mathbf{k}' \neq \mathbf{0}. \quad (17.45)$$

This invariance condition can only be realized when $\mathbf{k} = \mathbf{0}$, or, possibly, for ${}^*\mathbf{k}$ consisting of at least three wavevectors.

In order to guarantee the absence of cubic invariants when some ${}^*\mathbf{k}$ satisfies (17.44), we need to examine the invariance of the symmetrized Kronecker cubic products of the Irrep $({}^*\mathbf{k}, \mu)$. To this end, the Landau condition can be written as

$$\frac{1}{s_0} \sum_{\mathbf{t}} \sum_{R \in \mathbb{P}_0} \left[({}^*\mathbf{k}, \mu) \chi^3 \left((R|\boldsymbol{\tau} + \mathbf{t}) \right) \right] = \frac{N}{s_0} \sum_{R \in \mathbb{P}_0} \left[({}^*\mathbf{k}, \mu) \chi^3 \left((R|\boldsymbol{\tau}) \right) \right] = 0, \quad (17.46)$$

where we used (17.44) to obtain $\sum_{\mathbf{t}} e^{i(\mathbf{k} + \mathbf{k}' + \mathbf{k}'') \cdot \mathbf{t}} = \sum_{\mathbf{t}} 1 = N$, the number of primitive lattice vectors, or lattice sites; we also have $N/s_0 = 1/p_0$, where p_0 is the order of the point-group $\mathbb{P}_0$. Next, we write condition (17.46) in terms of the characters of the Irrep μ of $\mathbb{P}_{\mathbf{k}}$

$$\frac{1}{p_{\mathbf{k}}} \sum_{R \in \mathbb{P}_{\mathbf{k}}} \left[({}^{\mathbf{k}, \mu}) \chi^3 \left((R|\boldsymbol{\tau}) \right) \right] = 0, \quad (17.47)$$

where, according to Chapter 11, we have

$$({}^{\mathbf{k}, \mu}) \chi(S) = e^{-i\mathbf{k} \cdot \boldsymbol{\tau}} ({}^{\mu}) \chi(R), \quad (17.48)$$

$$({}^{\mathbf{k}, \mu}) \chi(S^2) = e^{-i\mathbf{k} \cdot (E + R)\boldsymbol{\tau}} ({}^{\mu}) \chi(R^2), \quad (17.49)$$

$$({}^{\mathbf{k}, \mu}) \chi(S^3) = e^{-i\mathbf{k} \cdot (E + R + R^2)\boldsymbol{\tau}} ({}^{\mu}) \chi(R^3), \quad (17.50)$$

where $S = (R|\boldsymbol{\tau})$. Substituting (17.38) and (17.48)–(17.50) in (17.47), we obtain

$$\begin{aligned} \frac{1}{g_{\mathbf{k}0}} \sum_{R \in \mathcal{S}_{\mathbf{k}0}} & \left[\frac{1}{6} e^{-i3\mathbf{k} \cdot \boldsymbol{\tau}} {}^{(\mu)}\chi^3(R) \right. \\ & + \frac{1}{2} e^{-i\mathbf{k} \cdot [(2E + R)\boldsymbol{\tau}]} {}^{(\mu)}\chi(R) {}^{(\mu)}\chi(R^2) \\ & + \left. \frac{1}{3} e^{-i\mathbf{k} \cdot [(E + R + R^2)\boldsymbol{\tau}]} {}^{(\mu)}\chi(R^3) \right] \\ & = 0. \end{aligned} \quad (17.51)$$

If (17.51) is satisfied then cubic terms are absent in the free energy expansion.

17.2.6 Fourth-degree term

So far, we found that the existence of a second-order phase transition at some temperature T_c requires the Landau free energy to have the form

$$\Delta\Phi = \frac{a(T - T_c)}{2} \xi^2 + \xi^4 \sum_q \frac{c_q(T, P)}{4} \mathcal{F}_q^{(4)}(\boldsymbol{\zeta}) + \cdots, \quad (17.52)$$

We should point out that by writing

$$\delta\rho(\bar{\mathbf{r}}) = \xi \left[\sum_l \zeta_l \phi_l(\bar{\mathbf{r}}) \right],$$

and using the normalization $\sum_l \zeta_l^2 = 1$, we have allowed the symmetry of $\delta\rho(\mathbf{r})$ to be determined only by the relations among the coefficients ζ_l . The variables ζ_l specify the direction, at equilibrium, of a unit vector in OP-space, and the variable ξ its amplitude. These quantities are obtained through minimizing $\Delta\Phi$. Because of the normalization relation, the ζ_l s do not appear in the quadratic term. Consequently, the direction of the OP will be determined by the quartic invariants of the free energy $\Delta\Phi$. The changes in $\Delta\Phi$ will be solely contingent upon the properties of these quartic invariants. Moreover, a close examination of (17.52) reveals that in order to have a minimum of $\Delta\Phi$ we require that

$$\sum_q c_q(T, P) \mathcal{F}_q^{(4)}(\boldsymbol{\zeta}) > 0, \quad (17.53)$$

at (T_c, P_c) in every direction $\{\boldsymbol{\zeta}\}$ of OP-space. We make the simplifying assumption that in the neighborhood of (T_c, P_c) the values of c_q that satisfy (17.53) at (T_c, P_c) are slowly varying functions of T and P , and hence, for all practical reasons, can be taken as constants equal to their values at (T_c, P_c) . Equation (17.53) imposes some restrictions on the coefficients c_q .

For a given set of c_q s that satisfy (17.53), the sum $\sum_q c_q \mathcal{F}_q^{(4)}$ will have at least one absolute minimum at $\{\boldsymbol{\zeta}_0\}$ with

$$\sum_c c_q \mathcal{F}_q^{(4)}(\boldsymbol{\zeta}_0) = c > 0;$$

then we may write (17.52) as

$$\Delta\Phi = \frac{a(T - T_c)}{2} \xi^2 + \frac{c}{4} \xi^4. \quad (17.54)$$

Minimizing (17.54) with respect to ξ we obtain for the order-parameter $\bar{\xi}$,

$$\bar{\xi} = \begin{cases} 0, & T \geq T_c, \\ \sqrt{\frac{a(T_c - T)}{c}}, & T < T_c, \end{cases} \quad (17.55)$$

which is the well-known mean-field form.

17.2.7 Group-subgroup relations: isotropy subgroups

The set of values $\{\bar{\eta}(T); \zeta_0\}$ corresponding to the absolute minimum defines the stable phase. The Landau condition ensures that the phase transition is continuous. Here, we relax this condition and extend our analysis to encompass possible discontinuous transitions. In other words, we only require that the low-symmetry phase is invariant under the operations of the space-group $\mathbb{S} \subset \mathbb{S}_0$: The operations of $\mathbb{S}$ must leave

$$\rho_{\text{eq}}(\mathbf{r}) = \rho_0(\mathbf{r}) + \bar{\xi}(T) \left[\sum_l \zeta_l^0 \phi_l(\mathbf{r}) \right]$$

invariant. Subgroups of $\mathbb{S}_0$ that satisfy this requirement are called *isotropy* subgroups of $\mathbb{S}_0$.

Our analysis still conforms with the subduction condition, and pertains to all Irreps of $\mathbb{S}_0$ – except the invariant Irrep. We then find that for a given Irrep $(^{*\mathbf{k},\lambda})\mathbf{\Gamma}$, an isotropy subgroup $\mathbb{S}$ comprises all operations $K \in \mathbb{S}_0$ satisfying the relation

$$(^{*}\mathbf{k},\lambda)\mathbf{\Gamma}(K) = \mathbb{I}.$$

$\mathbb{S}$ is actually the kernel of the Irrep $(^{*\mathbf{k},\lambda})\mathbf{\Gamma}$, and it leaves ζ_0 invariant.

As we have seen, the subduction criterion is a necessary condition that an Irrep $(^{*\mathbf{k},\lambda})\mathbf{\Gamma}$ of $\mathbb{S}_0$ has to satisfy in order to be a candidate associated with the space-group $\mathbb{S}$. It is then worthwhile to study, in more detail, the relation between $(^{*\mathbf{k},\lambda})\mathbf{\Gamma}$ and $\mathbb{S}_0$.

We start by expanding $\mathbb{S}_0$ in left-cosets of $\mathbb{S}$,

$$\mathbb{S}_0 = \sum_i \mathbb{S}_i \mathbb{S}.$$

We note that each S_{ci} generates an OP vector ζ_0^i , which is distinct from $\zeta_0 \equiv \zeta_0^1$. However, we surmise that $\mathcal{F}^{(4)}(\zeta_0^i) = \mathcal{F}^{(4)}(\zeta_0^1)$ since Φ is, by definition invariant under all operations of $\mathbb{S}_0$.

In all, there are s_0/s , the index of $\mathbb{S}$ in $\mathbb{S}_0$, distinct vectors, and an equal number of distinct, degenerate absolute minima. The number of minima physically translates to the number of possible domains.

We may restate these findings as follows: The distinct set of vectors, ζ_0^i , form the orbit of ζ_0 ; and each component vector of the orbit of ζ_0^i has its stabilizer subgroup as one of the conjugate subgroups of $\mathbb{S}$ in $\mathbb{S}_0$.

Chain subduction criterion and isotropy groups

When we apply the subduction criterion to an Irrep of $\mathbb{S}_0$ to determine its suitability to drive the transition $\mathbb{S}_0 \rightarrow \mathbb{S}$, we realize that if $\mathbb{S} \subset \mathbb{S}_0$ satisfies (II), so will every subgroup of $\mathbb{S}$, because if $\delta\rho$ is invariant under $\mathbb{S}$, it must be invariant under every subgroup of $\mathbb{S}$. Hence, this test is not sufficiently restrictive. We may conclude that the actual symmetry group of $\delta\rho$ is the maximal subgroup of this sequence. However, a more careful consideration of this sequence will allow us to formulate a more restrictive selection rule [151, 152]. We consider the simplest maximal subgroup chain, namely,

$$\mathbb{S}_0 \supset \mathbb{S} \supset \mathbb{S}'. \quad (17.56)$$

The subduction of Irrep $(^{*\mathbf{k},\lambda})\Gamma$ gives

$$(^{*}\mathbf{k},\lambda)\Gamma \downarrow \mathbb{S} \ni (^{0,1+})\Delta, \quad (^{*}\mathbf{k},\lambda)\Gamma \downarrow \mathbb{S}' \ni (^{0,1+})\Sigma, \quad (17.57)$$

where $(^{0,1+})\Delta$ and $(^{0,1+})\Sigma$ are the invariant irreps of $\mathbb{S}$ and $\mathbb{S}'$, respectively. If the subductions (17.57) onto $\mathbb{S}$ and $\mathbb{S}'$ contain the identity Irrep only once in each, we then establish a chain subduction rule stating that

$$\mathbb{S}_0 \rightarrow \mathbb{S} \text{ may occur, but } \mathbb{S}_0 \rightarrow \mathbb{S}' \text{ may not,}$$

based on the fact the system has to pass through the $\mathbb{S}$ before reaching $\mathbb{S}'$. We can extend the argument to cases where the multiplicities of the subduction are greater than 1. We argue that if in the case

$$(^{*}\mathbf{k},\lambda)\Gamma \downarrow \mathbb{S} \ni m(^{0,1+})\Delta, \quad (^{*}\mathbf{k},\lambda)\Gamma \downarrow \mathbb{S}' \ni n(^{0,1+})\Sigma, \quad (17.58)$$

$m = n$, then each of the subduced identity irreps $(^{0,1+})\Delta$ maps onto one counterpart $(^{0,1+})\Sigma$, and the above subduction rule holds. However, if $n > m$, then there are $n - m$ identity irreps $(^{0,1+})\Sigma$, which can be accessed through an independent path; these appear to contribute to higher-order critical transitions. We then modify the chain subduction criterion to read:

If $n > m$,
 $\mathbb{S}_0 \rightarrow \mathbb{S}$ may occur as a simple second-order transition,
 and
 $\mathbb{S}_0 \rightarrow \mathbb{S}'$ may occur as a higher-order critical transition.

It then becomes apparent that we need to enumerate the different subgroup chains of the high-symmetry group $\mathbb{S}_0$. Here is one place where Hermann's theorem (Section 10.5.6) comes to the rescue: We recall that it states that the maximal subgroups are either t -equal

or k -equal. So, it is preferable to start the “tree” of group–subgroup with the t -equal subgroups, since there is a finite number of them; then work down the tree through the k -equals. Since there is infinite number of k -equal subgroups, only a subset of these is usually required. We note that any generated subgroup has to be equivalent to one of the 230 three-dimensional or the 17 two-dimensional space-group types. Hence, we need to identify the standard equivalent in this case.

A general subgroup $\mathbb{S} \subset \mathbb{S}_0$ has to satisfy the following conditions:

- (i) Their respective translation subgroups satisfy the relation $\mathbb{T} \subset \mathbb{T}_0$.
- (ii) Their respective point (or isogonal) groups satisfy $\mathbb{P} \subset \mathbb{P}_0$.
- (iii) The lattice $\mathcal{L}$, associated with $\mathbb{S}$, is invariant under the operations of $\mathbb{P}$.
- (iv) The coset representatives $(R_i | \boldsymbol{\tau}_i)$ in $\mathbb{S}$ have the form $(R_i^0 | \boldsymbol{\tau}_i^0 + \mathbf{t}_i^0)$ in $\mathbb{S}_0$. This restricts the determination of the nonprimitive translation $\boldsymbol{\tau}_i$ associated with R_i in $\mathbb{S}$ to the relation

$$\boldsymbol{\tau}_i = \boldsymbol{\tau}_i^0 + \mathbf{t}_i^0, \quad \mathbf{t}_i^0 \notin \mathbb{S}, \\ \in \mathbb{S}_0.$$

- (v) To satisfy the space-group binary composition law, the following relations must be satisfied

$$R_k = R_i R_j, \quad \boldsymbol{\tau}_i^0 + R_i^0 \boldsymbol{\tau}_j^0 - \boldsymbol{\tau}_k^0 + \mathbf{t}_i^0 + R_i^0 \mathbf{t}_j^0 - \mathbf{t}_k^0 \in \mathbb{T}. \quad (17.59)$$

Note that any $\mathbf{t}'_0 = \mathbf{t}_i^0 + \mathbf{t}$, $\mathbf{t} \in \mathbb{T}$ satisfies (17.59).

Example 17.8

The X -point of the 2D space-group $p4mm$ (#11)

$$^* \mathbf{X} = (b_1/2, 0), (0, b_2/2); \quad b_1 = b_2 = 2\pi/a.$$

The subgroup of this point is $p2mm$ (t -equal), (2×1) (k -equal); the matrices of its four 2D Irreps were derived in Section 11.2.2.

We define the components of the corresponding 2D OP as $[\zeta_1, \zeta_2]$, which, under the action of the translation group $\mathbb{T}$, transform as

$$\hat{\mathbf{t}} \begin{cases} \zeta_1 = \exp[-i(1/2)\mathbf{b}_2 \cdot \mathbf{t}] \zeta_1, \\ \zeta_2 = \exp[-i(1/2)\mathbf{b}_1 \cdot \mathbf{t}] \zeta_2, \end{cases}$$

	E	C_2	C_4^+	C_4^-	σ_d^1	σ_d^2	σ_x	σ_y
X_1	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$
ζ_1	ζ_1	ζ_1	ζ_2	ζ_2	ζ_2	ζ_2	ζ_1	ζ_1
ζ_2	ζ_2	ζ_2	ζ_1	ζ_1	ζ_1	ζ_1	ζ_2	ζ_2
	$(E \mathbf{0})$	$(C_2 \mathbf{0})$	—	—	—	—	$(\sigma_x \mathbf{0})$	$(\sigma_y \mathbf{0})$
ζ^+	ζ^+	ζ^+	ζ^+	ζ^+	ζ^+	ζ^+	ζ^+	ζ^+
	$(E \mathbf{0})$	$(C_2 \mathbf{0})$	$(C_4^+ \mathbf{0})$	$(C_4^- \mathbf{0})$	$(\sigma_d^1 \mathbf{0})$	$(\sigma_d^2 \mathbf{0})$	$(\sigma_x \mathbf{0})$	$(\sigma_y \mathbf{0})$
ζ^-	ζ^-	ζ^-	$-\zeta^-$	$-\zeta^-$	$-\zeta^-$	$-\zeta^-$	ζ^-	ζ^-
	$(E \mathbf{0})$	$(C_2 \mathbf{0})$	$(C_4^+ \boldsymbol{\tau}')$	$(C_4^- \boldsymbol{\tau}')$	$(\sigma_d^1 \boldsymbol{\tau}')$	$(\sigma_d^2 \boldsymbol{\tau}')$	$(\sigma_x \mathbf{0})$	$(\sigma_y \mathbf{0})$

	E	C_2	C_4^+	C_4^-	σ_d^1	σ_d^2	σ_x	σ_y
X_2	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$
ζ_1	ζ_1	ζ_1	ζ_2	ζ_2	$-\zeta_2$	$-\zeta_2$	$-\zeta_1$	$-\zeta_1$
ζ_2	ζ_2	ζ_2	ζ_1	ζ_1	$-\zeta_1$	$-\zeta_1$	$-\zeta_2$	$-\zeta_2$
	$(E \mathbf{0})$	$(C_2 \mathbf{0})$	—	—	—	—	$(\sigma_x \boldsymbol{\tau}_i)$	$(\sigma_y \boldsymbol{\tau}_i)$
ζ^+	ζ^+	ζ^+	ζ^+	ζ^+	$-\zeta^+$	$-\zeta^+$	$-\zeta^+$	$-\zeta^+$
	$(E \mathbf{0})$	$(C_2 \mathbf{0})$	$(C_4^+ \mathbf{0})$	$(C_4^- \mathbf{0})$	$(\sigma_d^1 \boldsymbol{\tau}')$	$(\sigma_d^2 \boldsymbol{\tau}')$	$(\sigma_x \boldsymbol{\tau}')$	$(\sigma_y \boldsymbol{\tau}')$
ζ^-	ζ^-	ζ^-	$-\zeta^-$	$-\zeta^-$	ζ^-	ζ^-	$-\zeta^-$	$-\zeta^-$
	$(E \mathbf{0})$	$(C_2 \mathbf{0})$	$(C_4^+ \boldsymbol{\tau}')$	$(C_4^- \boldsymbol{\tau}')$	$(\sigma_d^1 \mathbf{0})$	$(\sigma_d^2 \mathbf{0})$	$(\sigma_x \boldsymbol{\tau}')$	$(\sigma_y \boldsymbol{\tau}')$

$$\boldsymbol{\tau}' = \mathbf{a}_1 + \mathbf{a}_2; \quad \boldsymbol{\tau}_i = \mathbf{a}_2, \quad i = 1; \quad \boldsymbol{\tau}_i = \mathbf{a}_1, \quad i = 2.$$

E	C_2	C_4^+	C_4^-	σ_{d}^1	σ_{d}^2	σ_x	σ_y	
$X_3 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix} \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$								
ζ_1	ζ_1	$-\zeta_1$	$-\zeta_2$	ζ_2	ζ_2	$-\zeta_2$	$-\zeta_1$	ζ_1
$(E \mathbf{0})$	$(C_2 \mathbf{a}_2)$	—	—	—	—	—	$(\sigma_x \mathbf{a}_2)$	$(\sigma_y \mathbf{0})$
ζ_2	ζ_2	$-\zeta_2$	ζ_1	$-\zeta_1$	ζ_1	$-\zeta_1$	ζ_2	$-\zeta_2$
$(E \mathbf{0})$	$(C_2 \mathbf{a}_1)$	—	—	—	—	—	$(\sigma_x \mathbf{0})$	$(\sigma_y \mathbf{a}_1)$
ζ^+	ζ^+	$-\zeta^+$	ζ^-	$-\zeta^-$	ζ^+	$-\zeta^+$	ζ^-	$-\zeta^-$
$(E \mathbf{0})$	$(C_2 \boldsymbol{\tau}')$	—	—	$(\sigma_{\text{d}}^1 \mathbf{0})$	$(\sigma_{\text{d}}^2 \boldsymbol{\tau}')$	—	—	—
ζ^-	ζ^-	$-\zeta^-$	$-\zeta^+$	ζ^+	$-\zeta^-$	ζ^-	ζ^+	$-\zeta^+$
$(E \mathbf{0})$	$(C_2 \boldsymbol{\tau}')$	—	—	$(\sigma_{\text{d}}^1 \boldsymbol{\tau}')$	$(\sigma_{\text{d}}^2 \mathbf{0})$	—	—	—
E	C_2	C_4^+	C_4^-	σ_{d}^1	σ_{d}^2	σ_x	σ_y	
$X_4 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$								
ζ_1	ζ_1	$-\zeta_1$	$-\zeta_2$	ζ_2	$-\zeta_2$	ζ_2	ζ_1	$-\zeta_1$
$(E \mathbf{0})$	$(C_2 \mathbf{a}_2)$	—	—	—	—	—	$(\sigma_x \mathbf{0})$	$(\sigma_y \mathbf{a}_2)$
ζ_2	ζ_2	$-\zeta_2$	ζ_1	$-\zeta_1$	$-\zeta_1$	ζ_1	$-\zeta_2$	ζ_2
$(E \mathbf{0})$	$(C_2 \mathbf{a}_1)$	—	—	—	—	—	$(\sigma_x \mathbf{a}_1)$	$(\sigma_y \mathbf{0})$
ζ^+	ζ^+	$-\zeta^+$	ζ^-	$-\zeta^-$	$-\zeta^+$	ζ^+	$-\zeta^-$	ζ^-
$(E \mathbf{0})$	$(C_2 \boldsymbol{\tau}')$	—	—	$(\sigma_{\text{d}}^1 \boldsymbol{\tau}')$	$(\sigma_{\text{d}}^2 \mathbf{0})$	—	—	—
ζ^-	ζ^-	$-\zeta^-$	$-\zeta^+$	ζ^+	ζ^-	$-\zeta^-$	$-\zeta^+$	ζ^+
$(E \mathbf{0})$	$(C_2 \boldsymbol{\tau}')$	—	—	$(\sigma_{\text{d}}^1 \mathbf{0})$	$(\sigma_{\text{d}}^2 \boldsymbol{\tau}')$	—	—	—

We now consider the transformation of ζ under the action of the four 2×2 matrix irreps of $p4mm$ engendered at the $\bar{X}$ -point. A one-armed phase transition will involve only one OP component ζ_i , and the periodicity will be doubled in the x_i -direction. We point out here that when the action of a point-group operation R on the component

OP yields $R\zeta_i = -\zeta_i$, it should leave it invariant if we augment R with the *now* non-primitive translation $\boldsymbol{\tau}_i = \mathbf{a}_j$, $i \neq j$. Thus, $(R|\mathbf{a}_i)$ is a symmetry operation of the new phase!

A two-armed phase transition will involve the linear combinations $\zeta_1 \pm \zeta_2$, which we denote by $\zeta^\pm$. In this case, the action $R\zeta^\pm = -\zeta^\pm$ would lead to a symmetry operation $(R|\boldsymbol{\tau}')$.

We remind the reader that a nonprimitive translation associated with a rotation about an axis normal to the 2D plane of symmetry can be eliminated simply by an origin shift.

Subgroup identification with a standard space-group

Our next task is to identify a space-subgroup $\mathbb{S} \subset \mathbb{S}_0$ with one of the standard space-groups [153, 154, 155]. The most convenient method is based on the arithmetic matrix representation of the operations of $\mathbb{S}_0$ and its subgroup $\mathbb{S}$, Section 10.3.3, i.e. with respect to the basis $\{\mathbf{a}_j^0\}$ of its lattice, $\mathcal{L}_0$. This has the advantage that all matrix representatives belong to $GL(n, \mathbb{Z}^n)$, $n = 1, 2, 3$, namely

$$\mathbf{t}^0 = \sum_{j=1}^n m_j \mathbf{a}_j^0, \quad (17.60)$$

$$R_i \mathbf{a}_j^0 = \sum_{k=1}^n \mathbf{a}_k^0 M_{kj}^0(R_i), \quad (17.61)$$

$$\mathbf{a}_j = \sum_{k=1}^n \mathbf{a}_k^0 A_{kj}, \quad (17.62)$$

where $\mathbf{M}^0(R)$ is a unimodular integer matrix and $\mathbf{A}$ is a nonsingular matrix with integer entries and $\det \mathbf{A} > 0$. This also has the advantage that R_i is represented by the same matrix, since they are referred to the same origin, and we have

$$(R_i|\boldsymbol{\tau}_i) = (R_i|\boldsymbol{\tau}_i^0 + \mathbf{t}_i^0). \quad (17.63)$$

Equations (17.60)–(17.63) define the elements of the subgroup $\mathbb{S}$. In order to identify the space-group type that $\mathbb{S}$ belongs to, among the 230 (or 17) space-groups, we recall that two space-groups $\mathbb{S}'$ and $\mathbb{S}''$ are of the same type if they are equivalent with respect to a unimodular transformation $(\mathcal{U}|\mathbf{v})$, $\mathcal{U} \in GL(n, \mathbb{Z}^n)$, such that

$$(\mathcal{U}|\mathbf{v})(\mathbb{S}'|\boldsymbol{\tau}' + \mathbf{t}')(\mathcal{U}|\mathbf{v})^{-1} = (\mathbb{S}''|\boldsymbol{\tau}'' + \mathbf{t}''),$$

and we use the following procedure to determine the conventional form, $\mathbb{S}^c$, of $\mathbb{S}$:

- (i) The equivalence $\mathbb{S} \sim \mathbb{S}^c$ requires that their isogonal point-groups are isomorphic and have the same geometric meaning.

An isomorphism between $\mathbb{P}$ of $\mathbb{S}$ and one of the conventional point-groups $\mathbb{P}_c$ can be established by *comparing their traces and determinants*.

We need only consider the generators of $\mathbb{P}$.

A one-to-one correspondence is then made with respect to the nature of the operations (C_n , σ , $\mathcal{I}$, etc.) and we ensure that their multiplication tables coincide.

- (ii) Since the point-groups have equivalent arithmetic representations, we attempt to construct the unimodular transformation $\mathcal{U} \in GL(n, \mathbb{Z}^n)$ such that

$$\begin{aligned} \mathbf{a}_j^c &= \sum_{k=1}^n \mathbf{a}_k \mathcal{U}_{kj}, \\ (R_i^c | \boldsymbol{\tau}_i^c + \mathbf{t}_i^c) &= (\mathcal{U} | \mathbf{v}) (R_i | \boldsymbol{\tau}_i + \mathbf{t}_i) (\mathcal{U} | \mathbf{v})^{-1}, \end{aligned} \quad (17.64)$$

or,

$$\begin{aligned} R_i^c &= \mathcal{U} R_i \mathcal{U}^{-1}, \\ \boldsymbol{\tau}_i^c - (\mathbb{I} - \mathcal{U} R_i \mathcal{U}^{-1}) \mathbf{v} - \mathcal{U} \boldsymbol{\tau}_i &\in \mathbb{T}^c, \end{aligned} \quad (17.65)$$

since $\mathcal{U} \mathbf{t}_i \in \mathbb{T}^c$. To obtain the representative matrices of the linear operations R_i , we write

$$R_i \mathbf{a}_j^c = \sum_{k=1}^n \mathbf{a}_k^c \mathbf{M}_{kj}^c(R_i),$$

then, using (17.61) and (17.62) we obtain

$$\mathbf{M}^c(R_i) = \mathcal{U}^{-1} \mathbf{A}^{-1} \mathbf{M}(R_i) \mathbf{A} \mathcal{U},$$

or

$$\mathcal{U} \mathbf{M}^c(R_i) = \mathbf{A}^{-1} \mathbf{M}(R_i) \mathbf{A} \mathcal{U}. \quad (17.66)$$

Remember, in order to determine $\mathcal{U}$ we need only consider the generators of $\mathbb{P}$.

- (iii) With the matrix $\mathcal{U}$ known, we proceed to determine the translation $\mathbf{v}$ such that

$$\mathcal{U} \boldsymbol{\tau}_i - \mathbf{v} + \mathbf{M}_i^c \mathbf{v} = \boldsymbol{\tau}_i^c + \mathbf{t}_i^c, \quad (17.67)$$

for each R_i , where $\mathbf{t}^c$ may be different for each R_i . We express all vectors in (17.67) in terms of the standard bases $\mathbf{a}_i^c$,

$$\mathcal{U} \boldsymbol{\tau}_i = \sum_j \tau_{ij} \mathbf{a}_j^c, \quad \mathbf{v} = \sum_j v_j \mathbf{a}_j^c, \quad \boldsymbol{\tau}_i^c = \sum_j \tau_{ij}^c \mathbf{a}_j^c,$$

and (17.67) becomes

$$v_j - \sum_k M_{jk}^c v_k = \tau_{ij} - \tau_{ij}^c + m_{ij}, \quad (17.68)$$

where $\mathbf{t}^c = \sum_j m_{ij} \mathbf{a}_j^c$. Notice that, in addition to the v_j s, we have the m_{ij} s as unknowns. However, the v_j s are expected to be simple rationals.

- (iv) Using a solution for $\mathcal{U}$ we seek a solution for $\mathbf{v}$ using (17.68), which will define $\mathbb{S}^c$. If this fails, we construct another matrix $\mathcal{U}$.

Example 17.9

Identification of isotropy subgroups of the X -point of $p4mm$

In this example we use the results of Example 17.8. The point-group $mm4$ is

	E	C_2	C_4^+	C_4^-	σ_d^1	σ_d^2	σ_x	σ_y
$\mathbf{M}^0$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

We start with the isotropy subgroups derived from the Irrep X_1 . We define the $\mathbf{A}$ matrix as

$$\begin{aligned} \zeta_1 &\Rightarrow \mathbf{A} = \begin{bmatrix} 2 & 0 \\ 0 & 1 \end{bmatrix}, & \zeta_2 &\Rightarrow \mathbf{A} = \begin{bmatrix} 1 & 0 \\ 0 & 2 \end{bmatrix}, \\ \zeta^+ &\Rightarrow \mathbf{A} = \begin{bmatrix} 2 & 0 \\ 0 & 2 \end{bmatrix}, & \zeta^- &\Rightarrow \mathbf{A} = \begin{bmatrix} 2 & 0 \\ 0 & 2 \end{bmatrix}. \end{aligned}$$

We find that the space-subgroups for ζ_i and ζ^+ are symmorphic, and are isomorphic with $p2mm$ and $p4mm$, respectively. The subgroup of ζ^- needs a little more consideration. In terms of the new primitive basis, we have

$$(E|\mathbf{0}), (C_2|\mathbf{0}), \left(C_4^+ \left| \begin{smallmatrix} 1 & 1 \\ 2 & 2 \end{smallmatrix} \right.\right), \left(C_4^- \left| \begin{smallmatrix} 1 & 1 \\ 2 & 2 \end{smallmatrix} \right.\right), \left(\sigma_d^1 \left| \begin{smallmatrix} 1 & 1 \\ 2 & 2 \end{smallmatrix} \right.\right), \left(\sigma_d^2 \left| \begin{smallmatrix} 1 & 1 \\ 2 & 2 \end{smallmatrix} \right.\right), (\sigma_x|\mathbf{0}), (\sigma_y|\mathbf{0}).$$

There are three planar space-groups in the $4mm$ system. Starting with $p4mm$, we find that its point-group is isomorphic to that of the ζ^- subgroup. We choose C_4^+ and σ_x as generators, and conclude that $\mathcal{U} = \mathbb{I}$. Equation (17.67) then gives

$$\begin{aligned} \sigma_x &\Rightarrow \begin{bmatrix} 2 & 0 \\ 0 & 0 \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} - \begin{bmatrix} 0 \\ 0 \end{bmatrix} + \begin{bmatrix} m_1 \\ m_2 \end{bmatrix}, \quad \text{mod } 1 \Rightarrow v_1 = 0, \quad \text{mod } 1 \\ C_4^+ &\Rightarrow \begin{bmatrix} 1 & 1 \\ -1 & 1 \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \end{bmatrix} = \begin{bmatrix} \frac{1}{2} \\ \frac{1}{2} \end{bmatrix} - \begin{bmatrix} 0 \\ 0 \end{bmatrix} + \begin{bmatrix} m'_1 \\ m'_2 \end{bmatrix}, \quad \text{mod } 1 \Rightarrow \begin{aligned} v_1 &= 0, & \text{mod } 1, \\ v_2 &= 0, & \text{mod } 1. \end{aligned} \end{aligned}$$

Thus, the ζ^- subgroup is equivalent to $p4mm$.

OP Irrep	Point-group	Relations	$\begin{bmatrix} v_1 & v_2 \end{bmatrix}$
X_1	$2mm$	Symmorphic $p2mm$ space-groups	
X_2	$2mm$	$\left\{ \begin{array}{l} \zeta_1, \zeta_2 : p2mg : (C_2 \mathbf{0}), (\sigma_y \mathbf{a}_1) \\ \begin{bmatrix} 0 & 0 \\ 0 & 2 \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \end{bmatrix} = \begin{bmatrix} \frac{1}{2} \\ 0 \end{bmatrix} - \begin{bmatrix} \frac{1}{2} \\ 0 \end{bmatrix} + \begin{bmatrix} m_1 \\ m_2 \end{bmatrix}, \text{ mod } 1 \\ \begin{bmatrix} 2 & 0 \\ 0 & 2 \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} - \begin{bmatrix} 0 \\ 0 \end{bmatrix} + \begin{bmatrix} m'_1 \\ m'_2 \end{bmatrix}, \text{ mod } 1 \end{array} \right.$	$\begin{bmatrix} 0 & 0 \end{bmatrix}$
ζ_i			
X_3	$2mm$	$\left\{ \begin{array}{l} \zeta_1 : p2gm : (C_2 \mathbf{0}), (\sigma_x \mathbf{a}_2); \zeta_2 : p2mg \\ \begin{bmatrix} 2 & 0 \\ 0 & 0 \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \end{bmatrix} = \begin{bmatrix} 0 \\ \frac{1}{2} \end{bmatrix} - \begin{bmatrix} 0 \\ \frac{1}{2} \end{bmatrix} + \begin{bmatrix} m_1 \\ m_2 \end{bmatrix}, \text{ mod } 1 \\ \begin{bmatrix} 2 & 0 \\ 0 & 2 \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \end{bmatrix} = \begin{bmatrix} 0 \\ \frac{1}{2} \end{bmatrix} - \begin{bmatrix} 0 \\ 0 \end{bmatrix} + \begin{bmatrix} m'_1 \\ m'_2 \end{bmatrix}, \text{ mod } 1 \end{array} \right.$	$\begin{bmatrix} 0 & \frac{1}{4} \end{bmatrix}$
X_4	$2mm$	$\left\{ \begin{array}{l} \zeta_1 : p2mg : (C_2 \mathbf{0}), (\sigma_y \mathbf{a}_1); \zeta_2 : p2mg \\ \begin{bmatrix} 0 & 0 \\ 0 & 2 \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \end{bmatrix} = \begin{bmatrix} 0 \\ \frac{1}{2} \end{bmatrix} - \begin{bmatrix} \frac{1}{2} \\ 0 \end{bmatrix} + \begin{bmatrix} m_1 \\ m_2 \end{bmatrix}, \text{ mod } 1 \\ \begin{bmatrix} 2 & 0 \\ 0 & 2 \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \end{bmatrix} = \begin{bmatrix} 0 \\ \frac{1}{2} \end{bmatrix} - \begin{bmatrix} 0 \\ 0 \end{bmatrix} + \begin{bmatrix} m'_1 \\ m'_2 \end{bmatrix}, \text{ mod } 1 \end{array} \right.$	$\begin{bmatrix} 0 & \frac{1}{4} \end{bmatrix}$
$\zeta^\pm$			
X_1	$4mm$	$\left\{ \begin{array}{l} \zeta^- : p4mm : (C_4^+ \mathbf{0}), (\sigma_x \mathbf{0}) \\ \begin{bmatrix} 2 & 0 \\ 0 & 0 \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} - \begin{bmatrix} 0 \\ 0 \end{bmatrix} + \begin{bmatrix} m_1 \\ m_2 \end{bmatrix}, \text{ mod } 1 \\ \begin{bmatrix} 1 & 1 \\ -1 & 1 \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \end{bmatrix} = \begin{bmatrix} \frac{1}{2} \\ \frac{1}{2} \end{bmatrix} - \begin{bmatrix} 0 \\ 0 \end{bmatrix} + \begin{bmatrix} m'_1 \\ m'_2 \end{bmatrix}, \text{ mod } 1 \end{array} \right.$	$\begin{bmatrix} 0 & \frac{1}{2} \end{bmatrix}$
X_2	$4mm$	$\left\{ \begin{array}{l} p4gm : (C_4^+ \mathbf{0}), (\sigma_x \mathbf{r}') \\ \begin{bmatrix} 2 & 0 \\ 0 & 0 \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \end{bmatrix} = \begin{bmatrix} \frac{1}{2} \\ \frac{1}{2} \end{bmatrix} - \begin{bmatrix} \frac{1}{2} \\ \frac{1}{2} \end{bmatrix} + \begin{bmatrix} m_1 \\ m_2 \end{bmatrix}, \text{ mod } 1 \\ \begin{bmatrix} 1 & 1 \\ -1 & 1 \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} - \begin{bmatrix} 0 \\ 0 \end{bmatrix} + \begin{bmatrix} m'_1 \\ m'_2 \end{bmatrix}, \text{ mod } 1 \end{array} \right.$	$\begin{bmatrix} 0 & 0 \end{bmatrix}$

(cont.)

OP	Irrep	Point-group	Relations	$\begin{bmatrix} v_1 & v_2 \end{bmatrix}$
	X_3	$2m_d m_d$	$\begin{cases} \begin{bmatrix} 2 & 0 \\ 0 & 0 \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} - \begin{bmatrix} 0 \\ 0 \end{bmatrix} + \begin{bmatrix} m_1 \\ m_2 \end{bmatrix}, \text{ mod } 1 \\ \begin{bmatrix} 1 & 1 \\ -1 & 1 \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \end{bmatrix} = \begin{bmatrix} \frac{1}{2} \\ \frac{1}{2} \end{bmatrix} - \begin{bmatrix} 0 \\ 0 \end{bmatrix} + \begin{bmatrix} m'_1 \\ m'_2 \end{bmatrix}, \text{ mod } 1 \end{cases}$	
	X_4	$2mm$	$\begin{cases} \begin{bmatrix} 2 & 0 \\ 0 & 0 \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} - \begin{bmatrix} 0 \\ 0 \end{bmatrix} + \begin{bmatrix} m_1 \\ m_2 \end{bmatrix}, \text{ mod } 1 \\ \begin{bmatrix} 1 & 1 \\ -1 & 1 \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \end{bmatrix} = \begin{bmatrix} \frac{1}{2} \\ \frac{1}{2} \end{bmatrix} - \begin{bmatrix} 0 \\ 0 \end{bmatrix} + \begin{bmatrix} m'_1 \\ m'_2 \end{bmatrix}, \text{ mod } 1 \end{cases}$	

The tables in this example show detailed analysis of all the isotropy subgroups of the X -point.

Table 17.2. *Allowed Irreps, and corresponding chain-subduction selection rules (Example 17.9).*

Irrep	Arms	OP	$\mathbb{S}$	m^a	$[\chi^3]$	$\{\chi^2\} \otimes^{(v)} \Gamma$	Basis vectors	Size	Origin
X_1	1		$p2mm$	1	0	0	(2,0), (0,1)	2	0, 0
	2	ζ^+	$p4mm$	1	0	0	(2,0), (0,2)	4	0, 0
		ζ^-		2			(2,0), (0,2)		0, 0
X_2	1	$\begin{cases} \zeta_1, \tau = \mathbf{a}_1 \\ \zeta_2, \tau = \mathbf{a}_2 \end{cases}$	$p2mg$	1	0	0	(2,0), (0,1)	2	$\frac{1}{2}, 0$
	2	ζ^+	$p4mm$	1	0	0	(2,0), (0,2)	4	$\frac{1}{2}, \frac{1}{2}$
		ζ^-	$p2mm(d)$ $p2mg(v)$	2	0	0	(2,0), (0,2)		$\frac{1}{2}, \frac{1}{2}$
X_3	1		$p2mg$	1	0	0	(2,0), (0,1)	2	0, 0
	2	ζ^+	$p4gm$	1	0	0	(2,0), (0,2)	4	0, 0
		ζ^-	$p2mm$	2	0	0	(2,0), (0,2)		0, 0
X_4		1	$p2mg$	1	0	0	(2,0), (0,1)	2	$\frac{1}{2}, 0$
	2	ζ^+	$p4gm$	1	0	0	(2,0), (0,2)	4	$\frac{1}{2}, \frac{1}{2}$
		ζ^-	$p2gg$	2	0	0	(2,0), (0,2)		$\frac{1}{2}, \frac{1}{2}$

$$^a m = \left\langle \left({}^*(\mathbf{k}, \lambda) \Gamma \downarrow \mathbb{S} |^{(0,1+)} \Delta \right) \right\rangle.$$

To further illustrate the method, we examine the isotropy subgroups of X_2 . The subgroups of ζ_i are nonsymmorphic with a $2mm$ point-group. We only show here that these sub-space-groups are equivalent to $p2mg$, which has $(C_2|\mathbf{0})$ and $(\sigma_y|\mathbf{a}_1)$ as generators.

Equation(17.67) reads

$$\begin{aligned}\sigma_y &\Rightarrow \begin{bmatrix} 0 & 0 \\ 0 & 2 \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \end{bmatrix} = \begin{bmatrix} \frac{1}{2} \\ 0 \end{bmatrix} - \begin{bmatrix} \frac{1}{2} \\ 0 \end{bmatrix} + \begin{bmatrix} m_1 \\ m_2 \end{bmatrix}, \quad \text{mod } 1 \Rightarrow v_2 = 0, \quad \text{mod } 1 \\ C_2 &\Rightarrow \begin{bmatrix} 2 & 0 \\ 0 & 2 \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} - \begin{bmatrix} 0 \\ 0 \end{bmatrix} + \begin{bmatrix} m'_1 \\ m'_2 \end{bmatrix}, \quad \text{mod } 1 \Rightarrow \begin{aligned} v_1 &= 0, & \text{mod } 1 \\ v_2 &= 0, & \text{mod } 1 \end{aligned} \\ &\begin{bmatrix} 2 & 0 \\ 0 & 0 \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} - \begin{bmatrix} 0 \\ 0 \end{bmatrix} + \begin{bmatrix} m_1 \\ m_2 \end{bmatrix}, \quad \text{mod } 1 \\ &\begin{bmatrix} 1 & 1 \\ -1 & 1 \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \end{bmatrix} = \begin{bmatrix} \frac{1}{2} \\ \frac{1}{2} \end{bmatrix} - \begin{bmatrix} 0 \\ 0 \end{bmatrix} + \begin{bmatrix} m'_1 \\ m'_2 \end{bmatrix}, \quad \text{mod } 1\end{aligned}$$

Table 17.2 summarizes the results of this example.

Example 17.10

The trigonal space-group $\mathbb{S}_0 = R\bar{3}c(D_{3d}^6)$

Although crystals belonging to the calcite and corundum families have different structures, they share the symmetry of this space-group.

The trigonal lattice $\mathcal{L}_0$ has basis vectors

$$\mathbf{a}_1^0 = (0, -a, c), \quad \mathbf{a}_2^0 = \frac{1}{2}(\sqrt{3}a, a, 2c), \quad \mathbf{a}_3^0 = \frac{1}{2}(-\sqrt{3}a, a, 2c),$$

and coset representatives

$$(E|\mathbf{0}), (C_3^+|\mathbf{0}), (C_3^-|\mathbf{0}), (\mathcal{I}|\mathbf{0}), (S_3^-|\mathbf{0}), (S_3^+|\mathbf{0}), \\ (U_1|\boldsymbol{\tau}), (U_2|\boldsymbol{\tau}), (U_3|\boldsymbol{\tau}), (\sigma_{d1}|\boldsymbol{\tau}), (\sigma_{d2}|\boldsymbol{\tau}), (\sigma_{d3}|\boldsymbol{\tau}).$$

where $\boldsymbol{\tau} = \frac{1}{2}\frac{1}{2}\frac{1}{2}$.

We consider the subgroup $\mathbb{S}$ with $\mathcal{L}$

$$\mathbf{a}_1 = \mathbf{a}_1^0, \quad \mathbf{a}_2 = \mathbf{a}_2^0 - \mathbf{a}_3^0, \quad \mathbf{a}_3 = \mathbf{a}_2^0 + \mathbf{a}_3^0,$$

and coset representatives

$$(E|\mathbf{0}), (\mathcal{I}|\mathbf{0}), (U_1|\boldsymbol{\tau}), (\sigma_{d1}|\boldsymbol{\tau}),$$

with matrices

$$\mathbf{M}(\mathcal{I}) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \quad \mathbf{M}(U_1) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix}, \quad \mathbf{M}(\sigma_{d1}) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}.$$

The matrix $\mathbf{A}$ is given by

$$\mathbf{A} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 1 \\ 0 & -1 & 1 \end{pmatrix}.$$

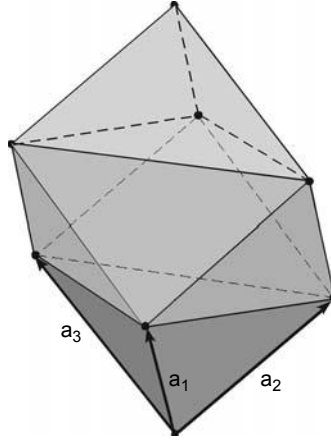


Fig. 17.9. Trigonal primitive cell.

We compare $\mathbb{S}$ with the standard space-groups in three-dimensions: The point-group is $\mathcal{C}_{2h}$, with the identification

$$E \rightarrow E, \quad \mathcal{I} \rightarrow \mathcal{I}, \quad U_1 \rightarrow C_2, \quad \sigma_{d1} \rightarrow \sigma_z,$$

with matrices

$$\mathbf{M}^c(\mathcal{I}) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \quad \mathbf{M}^c(C_2) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \mathbf{M}^c(\sigma_{d1}) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}.$$

This point-group is compatible with space-groups $\mathbb{C}_{2h}^1 \rightarrow \mathbb{C}_{2h}^6$. In hindsight, we try space-groups

$$P2/m(\mathbb{C}_{2h}^1), \quad P2_1/m(\mathbb{C}_{2h}^2), \quad P2/b(\mathbb{C}_{2h}^4), \quad P2_1/b(\mathbb{C}_{2h}^5)$$

corresponding to the primitive monoclinic lattice with basis vectors

$$\mathbf{a}_1^c = (0, -b, 0), \quad \mathbf{a}_2^c = (a \sin \gamma, -a \cos \gamma, 0), \quad \mathbf{a}_3^c = (0, 0, c).$$

From (17.66) we obtain

$$\mathcal{U} = \begin{pmatrix} U_{11} & U_{12} & U_{13} \\ U_{21} & 0 & U_{23} \\ U_{31} & U_{32} & 0 \end{pmatrix}, \quad \det U = 1,$$

$$\mathcal{U} = \begin{pmatrix} U_{11} & U_{12} & 0 \\ 0 & 0 & U_{23} \\ U_{31} & U_{32} & 0 \end{pmatrix}, \quad \det U = 1.$$

We choose

$$\mathcal{U} = \begin{pmatrix} -1 & -1 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \Rightarrow \begin{cases} \mathbf{a}_1^c = -\mathbf{a}_1^0 \\ \mathbf{a}_2^c = -\mathbf{a}_1^0 + \mathbf{a}_2^0 + \mathbf{a}_3^0 \\ \mathbf{a}_3^c = \mathbf{a}_2^0 - \mathbf{a}_3^0 \end{cases}$$

which shows that $\mathbf{M}$ and $\mathbf{M}^c$ are in the same arithmetic class. We write the coset representatives of $\mathbb{S}$ in terms of the monoclinic basis vectors, as

$$(E|000), (\mathcal{I}|000), \left(C_2 \left| \frac{1}{2} 0 \frac{1}{2} \right. \right), \left(\sigma_z \left| \frac{1}{2} 0 \frac{1}{2} \right. \right).$$

We try to match $\mathbb{S}$ with $P2_1/b$ with coset representatives

$$(E|000), \left(\mathcal{I} \left| \frac{1}{2} 0 \frac{1}{2} \right. \right), \left(C_2 \left| 00 \frac{1}{2} \right. \right), \left(\sigma_z \left| \frac{1}{2} 00 \right. \right),$$

and with the aid of (17.68) we obtain

$$-2v_1 = \frac{1}{2} + m_{21}, \quad -2v_2 = m_{22}, \quad -2v_3 = \frac{1}{2} + m_{23}.$$

Choosing $m_{21} = m_{23} = -1$, $m_{22} = 0$, we obtain

$$\mathbf{v} = \left(\frac{1}{4} 0 \frac{1}{4} \right),$$

so, indeed $\mathbb{S} \sim P2_1/b$.

17.2.8 Homogeneity of the order-parameter

The order-parameter describes some form of the density which, in classical thermodynamics, can be construed as the ratio of two extensive variables: the particle number and the volume, each of which is homogeneous of degree one. This implies that the order-parameter should be homogeneous of degree zero, i.e. uniform across the system.

In order to identify the conditions necessary to ensure homogeneity [156, 157, 158], we first consider the characteristics of inhomogeneous contributions to the density and their manifestations in the structure of the Landau free energy density. Spatial inhomogeneities in the density naturally give rise to nonvanishing density-spatial-gradients, which in turn introduce nonvanishing gradients of the OP. Consequently, the expansion of the Landau free energy should include terms of the form

$$\sum_{i,j=1}^{d_\lambda} \sum_{k=1}^n A_{ijk} \eta_i \frac{\partial \eta_j}{\partial x_k} + \sum_{i,j=1}^{d_\lambda} \sum_{k,l=1}^d B_{ijkl} \frac{\partial \eta_i}{\partial x_k} \frac{\partial \eta_j}{\partial x_l} + \cdots, \quad (17.69)$$

where λ corresponds to active Irreps, and n is the physical space dimension. The appearance of each term in the expansion is contingent upon its conformity with the invariant Irrep of $\mathbb{S}_0$. The expansion does not contain terms linear in the derivatives,

$$\sum_{i=1}^{d_\lambda} \sum_{k=1}^d C_{ik} \frac{\partial \eta_i}{\partial x_k}, \quad (17.70)$$

because these are surface terms that are neglected in the thermodynamic limit. For the same reason, the symmetric terms constructed from the A_{ijk} summation, namely,

$$\frac{1}{2} \sum_{i,j=1}^{d_\lambda} \sum_{k=1}^d (A_{ijk} + A_{jik}) \frac{\partial(\eta_i \eta_j)}{\partial x_k}, \quad (17.71)$$

lead to surface terms and should be neglected. Consequently, we consider only the tensors A_{ijk} that are antisymmetric in the first two indices, and give rise to terms of the form

$$\frac{1}{2} \sum_{i,j=1}^{d_\lambda} \sum_{k=1}^d (A_{ijk} - A_{jik}) \eta_i \frac{\partial \eta_j}{\partial x_k}. \quad (17.72)$$

(VI) The Lifshitz homogeneity condition

Lifshitz proposed that in order to guarantee a priori the homogeneity of the low-symmetry phase, terms in (17.72) should be excluded in the Landau free energy expansion by symmetry restrictions.

A condition that insures the absence of such terms implies that the Irrep “driving” the transition should not possess an invariant component in the antisymmetrized Kronecker product $\{\lambda^2\}$ with the vector representation $^{(v)}\Gamma$, namely,

$$\{^{(\lambda)}\Gamma^2\} \otimes ^{(v)}\Gamma \not\supset ^{(0,1)}\Gamma. \quad (17.73)$$

This is known as the Lifshitz condition.

Comment on the vector representation for space-groups A polar vector representation of a group is one that is engendered when operating on the components of a vector $\mathbf{r}$ by the operators of the group. When a typical space-group element $(R | \mathbf{t} + \boldsymbol{\tau})$ operates on a vector $\mathbf{r}$ in a Euclidean space of dimension n , we obtain

$$(R | \mathbf{t} + \boldsymbol{\tau}) \mathbf{r} = R\mathbf{r} + \mathbf{t} + \boldsymbol{\tau}, \quad (17.74)$$

where R is an orthogonal $n \times n$ matrix. It is then clear that the polar vector Irrep $^{(v)}\Gamma$ must be associated with the Irreps of null wavevector $\mathbf{0}$, and we write it as $^{(0,v)}\Gamma$.

The physical interpretation of this condition is best seen by rewriting the modified form of Φ , namely,

$$\Delta\Phi = \frac{a(T - T_c)}{2} \left(\sum_i \eta_i^2 \right) + \mathcal{F}^{(3)}(\boldsymbol{\eta}) + \mathcal{F}^{(4)}(\boldsymbol{\eta}) + \mathcal{F}^{(\nu)}(\boldsymbol{\eta}) + \mathcal{F}^{(\mu)}(\boldsymbol{\eta}) + \cdots, \quad (17.75)$$

$$\begin{aligned} \mathcal{F}^{(\nu)}(\boldsymbol{\eta}) &= \sum_{i,j=1}^{d_\lambda} \sum_{k=1}^d A_{ijk} \eta_i \frac{\partial \eta_j}{\partial x_k}, \\ \mathcal{F}^{(\mu)}(\boldsymbol{\eta}) &= \sum_{i,j=1}^{d_\lambda} \sum_{k,l=1}^d B_{ijkl} \frac{\partial \eta_i}{\partial x_k} \frac{\partial \eta_j}{\partial x_l}, \end{aligned}$$

in terms of the Fourier components of the OP. To second order, we get

$$\Delta\Phi = \frac{1}{2} \sum_{\mathbf{q}} \sum_i F_i(\mathbf{q}) \eta_{i\mathbf{q}} \eta_{i-\mathbf{q}} + \cdots \quad (17.76)$$

where

$$F_i(\mathbf{q}) = \frac{a(T - T_c)}{2} + \mathbf{A}_i \cdot \mathbf{q} + B_{\alpha\beta}^i q_\alpha q_\beta. \quad (17.77)$$

Since the homogeneity condition requires the order-parameter component that becomes critical at $T = T_c$ to be $\eta_{i\mathbf{0}}$ (the $\mathbf{q} = \mathbf{0}$ Fourier component of η_i), the coefficient $F_i(\mathbf{q})$ should satisfy

$$F_i(\mathbf{0}) = 0, \quad (17.78)$$

$$F_i(\mathbf{q}) > 0, \quad \text{for } \mathbf{q} \neq \mathbf{0}, \quad (17.79)$$

at the transition. This may happen only if the linear term in (17.77) vanishes at T_c , that may ensue under two different scenarios:

- (i) **Homogeneous low-symmetry phase** The expansion (17.75) does not include $\mathcal{F}^{(\nu)}(\boldsymbol{\eta})$ due to symmetry, and the minimum of $F_i(\mathbf{q})$ is obtained at $\mathbf{q} = \mathbf{0}$ in a temperature interval that includes T_c , as shown in Figure 17.10(a).
- (ii) **Modulated low-symmetry phase** The expansion (17.75) does include $\mathcal{F}^{(\nu)}(\boldsymbol{\eta})$, but the coefficients A_{ijk} vanish at T_c . For $T \neq T_c$ the coefficients do not vanish, and therefore, the minimum of $F_i(\mathbf{q})$ is expected to be at $\mathbf{q}_0 \neq \mathbf{0}$. The order-parameter that appears below T_c is $\eta_{i\mathbf{q}_0}$, where $\mathbf{q}_0(T)$ is expected to vary continuously with temperature, and $\mathbf{q}_0(T_c) = \mathbf{0}$. The OP that appears below T_c is the $\mathbf{q}_0$ Fourier component $^{(\lambda)}\eta_i(\mathbf{q}_0)$, where $\mathbf{q}_0(T)$ is expected to vary continuously with temperature, and $\mathbf{q}_0(T_c) = \mathbf{0}$, as shown in Figure 17.10(b).

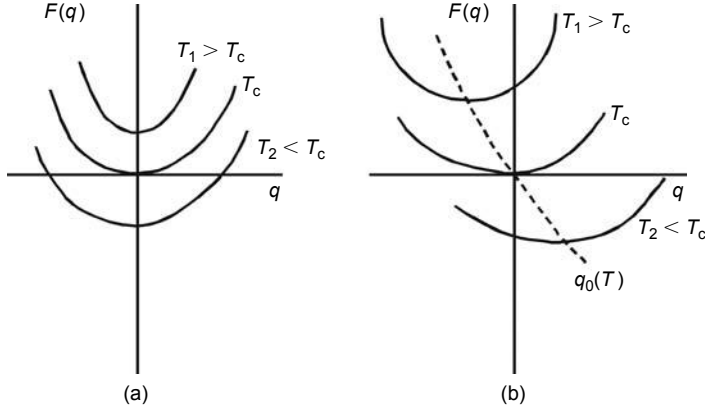


Fig. 17.10. Schematic form of the function $F_i(\mathbf{q})$ for (a) the Lifshitz condition is satisfied, and (b) the modulated low-symmetry phase.

Application of the Lifshitz condition to space-groups

The antisymmetrized Kronecker bilinear product $\{({}^*\mathbf{k}, \mu)\Gamma \otimes ({}^*\mathbf{k}, \mu)\Gamma\} \equiv \{({}^*\mathbf{k}, \mu)\Gamma^2\}$ of an Irrep $({}^*\mathbf{k}, \mu)\Gamma$ of $\mathbb{S}_0$ will contain terms of the form

$$\exp[i(\mathbf{k} + \mathbf{k}') \cdot \mathbf{t}], \quad \mathbf{k}, \mathbf{k}' \in {}^*\mathbf{k}.$$

For the vector Irrep $({}^{0,v})\Gamma$ to appear in the reduction of $\{({}^*\mathbf{k}, \mu)\Gamma^2\}$, the condition

$$\mathbf{k} + \mathbf{k}' = \mathbf{0} \implies \mathbf{k}' = -\mathbf{k} + \mathbf{G} \quad \text{or} \quad \mathbf{k}' \equiv -\mathbf{k} \quad (17.80)$$

must be satisfied. We note that a general orbit (star of $\mathbf{k}$) contains $\pm\mathbf{k}$, and thus satisfies (17.80). If we write the basis of $\{({}^*\mathbf{k}, \mu)\Gamma \otimes ({}^*\mathbf{k}, \mu)\Gamma\}$ as

$$\phi_{\mathbf{k}} \psi_{\mathbf{k}'} - \phi_{\mathbf{k}'} \psi_{\mathbf{k}},$$

then for $\mathbf{k}' = -\mathbf{k}$ we have

$$\phi_{\mathbf{k}} \psi_{-\mathbf{k}} - \phi_{-\mathbf{k}} \psi_{\mathbf{k}},$$

which forms a basis for the regular representation of the point-group $\mathbb{P}_0$ of $\mathbb{S}_0$. This in turn contains all Irreps, including $({}^{0,v})\Gamma$. Therefore, a general k -orbit is not admissible as an active Irrep by the Lifshitz condition.

We are then left with the BZ center (null star), $\mathbf{k} = \mathbf{0}$, and k -orbits on the BZ boundaries as possible candidates for Lifshitz-active Irreps. For the latter cases, (17.80) may be satisfied for some components of ${}^*\mathbf{k}$, and the representation $\{({}^*\mathbf{k}, \mu)\Gamma^2\}$

decomposes into two representations

$$\begin{aligned} \left\{ ({}^*\mathbf{k}, \mu) \Gamma^2 \right\} &= \Gamma_0 \oplus \Gamma_K, \\ \Gamma_0 &\Rightarrow \mathbf{k} + \mathbf{k}' = \mathbf{0}, \\ \Gamma_K &\Rightarrow \mathbf{K} = \mathbf{k} + \mathbf{k}'. \end{aligned} \quad (17.81)$$

where Γ_0 contains the null-star components, and Γ_K includes all the remaining nonzero stars of $\mathbf{k} + \mathbf{k}'$.

In this case, we find that for a pair $\mathbf{k}, \mathbf{k}' \in {}^*\mathbf{k}$ that satisfy (17.81), the *symmetry operations that leave $\mathbf{k}'$ invariant, must also leave $\mathbf{k}$ invariant*. This implies that

$$\mathbb{S}_{\mathbf{k}} = \mathbb{S}_{\mathbf{k}'}, \quad (17.82)$$

where $\mathbb{S}_{\mathbf{k}}$ and $\mathbb{S}_{\mathbf{k}'}$ are the space-subgroups associated with the wavevectors $\mathbf{k}$ and $\mathbf{k}'$, respectively.

Since the vector $\text{Irrep}^{(0,v)}\Gamma$ belongs to the null-wavevector, *only Γ_0 may have Irreps equivalent to it*. Consequently, we focus our presentation on what properties Γ_0 should have in order to satisfy the Lifshitz condition.

- (i) First, we note that there are two possible scenarios for (17.81) to be satisfied, and hence for Γ_0 to be present in the reduction of $\left\{ ({}^*\mathbf{k}, \mu) \Gamma^2 \right\}$, namely,

$$\begin{aligned} \text{(a)} \quad \mathbf{k}_i &= -\mathbf{k}_i + \mathbf{G}, \quad \forall \mathbf{k}_i \in {}^*\mathbf{k}, \\ \text{(b)} \quad \mathbf{k}_j &= -\mathbf{k}_i + \mathbf{G}, \quad \forall \mathbf{k}_i, \mathbf{k}_j \in {}^*\mathbf{k}. \end{aligned} \quad (17.83)$$

To visualize these cases we consider the Brillouin zone corresponding to the hexagonal mesh $P6mm$, shown in Figure 17.11. Case (a) identifies the situation where each $\mathbf{k}_i \in {}^*\mathbf{k}$ is equivalent to $-\mathbf{k}_i$, and we find $p_0/p_{\mathbf{k}}$ components, where p_0 and $p_{\mathbf{k}}$ are the orders of the point-groups of $\mathbb{S}_0$ and $\mathbb{S}_{\mathbf{k}}$, respectively; while case (b) depicts the situation where a member of ${}^*\mathbf{k}$, namely $\mathbf{k}_j$, is equivalent to a wavevector $-\mathbf{k}_i$, where $\mathbf{k}_i \not\equiv -\mathbf{k}_i$ is another member of ${}^*\mathbf{k}$, in which case $p_0/2p_{\mathbf{k}}$ components arise.

We generalize this idea, by considering the left coset expansion of the space-group $\mathbb{S}_0$ in terms of its space-subgroup $\mathbb{S}_{\mathbf{k}_1}$

$$\mathbb{S}_0 = \sum_{i=1}^{s/s_{\mathbf{k}_1}} (R_i | \boldsymbol{\rho}_i) \mathbb{S}_{\mathbf{k}_1},$$

where $(R_i | \boldsymbol{\rho}_i)$ are the coset representatives, and each $\mathbf{k}_i = R_i \mathbf{k}_1$ is a distinct member of ${}^*\mathbf{k}$. We now consider special cases of condition (17.83)

$$\begin{aligned} \text{(a)} \quad \mathbf{k}_1 &= -\mathbf{k}_1 + \mathbf{G}, \\ \text{(b)} \quad \mathbf{k}_2 &= -\mathbf{k}_1 + \mathbf{G}, \end{aligned} \quad (17.84)$$

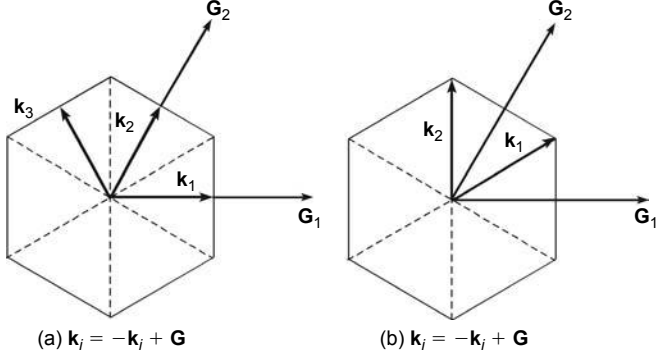


Fig. 17.11. Illustration of conditions (a) and (b) in (17.83) for the hexagonal Brillouin zone.

and, operating on (17.84) by the various R_i s, we obtain the complementing conditions

$$\begin{aligned} (a) \quad R_i \mathbf{k}_1 &= \mathbf{k}_i = -R_i \mathbf{k}_1 + \mathbf{G} = -\mathbf{k}_i + \mathbf{G}, \\ (b) \quad R_i \mathbf{k}_2 &= \mathbf{k}_{2i} = -R_i \mathbf{k}_1 + \mathbf{G} = -\mathbf{k}_{1i} + \mathbf{G}. \end{aligned} \quad (17.85)$$

Thus, we notice that if either of conditions (17.84) is satisfied for $\mathbf{k}_1$ or $(\mathbf{k}_1, \mathbf{k}_2)$, then conditions (17.85) must be satisfied: in case (a) we obtain $s/s_{\mathbf{k}_1} = p/p_{\mathbf{k}_1}$ such conditions, and in case (b) we obtain $s/2s_{\mathbf{k}_1} = p/2p_{\mathbf{k}_1}$ conditions.

- (ii) Second, we construct an expression for the frequency F_v of the vector Irrep in $\{\Gamma_0\}$, namely,

$$F_v = \left\langle \{\Gamma_0\} \mid {}^{(0,v)}\Gamma \right\rangle = \frac{1}{p} \sum_{R \in \mathbb{P}} \{ \chi^0(R \mid \tau) \} {}^{(0,v)}\chi(R \mid \tau), \quad (17.86)$$

where we summed over the elements of the translation group.

In order to obtain expressions for χ^0 we recall that the character $^{(*\mathbf{k},\mu)}\chi(R|\tau+\mathbf{t})$ of Irrep $^{(*\mathbf{k},\mu)}\Gamma$ is obtained by induction from an allowable Irrep $^{(\mathbf{k}_1,\mu)}\Lambda(R|\tau+\mathbf{t})$ of $\mathbb{S}_{\mathbf{k}_1}$,

$$^{(\mathbf{k}_1,\mu)}\Lambda(R \mid \tau + \mathbf{t}) = {}^{(\mu)}\Omega(R \mid \tau + \mathbf{t}) e^{-i\mathbf{k}_1 \cdot (\mathbf{t} + \tau)},$$

where $^{(\mu)}\Omega(R \mid \tau + \mathbf{t})$ is an Irrep of the little-cogroup $\mathbb{G}_{\mathbf{k}_1} = \mathbb{S}_{\mathbf{k}_1}/\mathbb{T}$, which is isomorphic to the point-subgroup $\mathbb{P}_{\mathbf{k}_1} \sim \mathbb{G}_{\mathbf{k}_1}$, $p_{\mathbf{k}_1} = g_{\mathbf{k}_1}$. $^{(*\mathbf{k},\mu)}\chi(R|\tau + \mathbf{t})$ is given as

$$\begin{aligned} ^{(*\mathbf{k},\mu)}\chi(R|\tau + \mathbf{t}) &= \sum_i {}^{(\mu)}\chi \left((R_i | \rho_i) (R|\tau) (R_i | \rho_i)^{-1} \right) \\ &\quad \times e^{-i\mathbf{k}_i \cdot (\mathbf{t} + \tau)} \Theta_i(\mathbf{k}), \end{aligned} \quad (17.87)$$

where

$$\Theta_i(\mathbf{k}) = \begin{cases} 1, & \text{if } (R_i | \rho_i) (R | \tau + \mathbf{t}) (R_i | \rho_i)^{-1} \in \mathbb{S}_{\mathbf{k}_i}, \\ & \text{or } (R | \tau + \mathbf{t}) \in \mathbb{S}_{\mathbf{k}_i}, \\ 0, & \text{otherwise.} \end{cases}$$

We use (17.87) to write the character of the Kronecker product $(*\mathbf{k}, \mu) \Gamma^2$

$$\begin{aligned} (*\mathbf{k}, \mu) \otimes (*\mathbf{k}, \mu) \chi(R | \tau + \mathbf{t}) &= \sum_{ij=1}^{p/g_{\mathbf{k}_1}} \binom{(\mu)}{(\mu)} \chi \left((R_i | \rho_i) (R | \tau) (R_i | \rho_i)^{-1} \right) \\ &\quad \times \binom{(\mu)}{(\mu)} \chi \left((R_j | \rho_j) (R | \tau) (R_j | \rho_j)^{-1} \right) \\ &\quad \times e^{-i(\mathbf{k}_i + \mathbf{k}_j) \cdot (\mathbf{t} + \tau)} \Theta_i(\mathbf{k}) \Theta_j(\mathbf{k}). \end{aligned} \quad (17.88)$$

We are now ready to derive expressions for χ^0 and for the Lifshitz conditions. We treat cases (a) and (b) of (17.83) separately:

- (a) $\mathbf{k}_i = -\mathbf{k}_i$ **case** Here, we set $j = i$ in the summation of (17.88) and, remembering that $\mathbf{k}_i + \mathbf{k}_i = 0$, we obtain

$$\begin{aligned} \{\chi^0(R | \tau)\} &= \sum_i \chi_{ii}^0(R | \tau) \Theta_i(\mathbf{k}) \\ &= \frac{p}{g_{\mathbf{k}_1}} \left\{ \binom{(\mu)}{(\mu)} \chi^2(R | \tau) \right\} \Theta_1(\mathbf{k}) \\ &= \frac{p}{2g_{\mathbf{k}_1}} \Theta_1(\mathbf{k}) \left(\binom{(\mu)}{(\mu)} \chi^2(R | \tau) e^{-2i\mathbf{k}_1 \cdot \tau} \right. \\ &\quad \left. - \binom{(\mu)}{(\mu)} \chi((R | \tau)^2) e^{-i\mathbf{k}_1 \cdot (\tau + R\tau)} \right). \end{aligned} \quad (17.89)$$

In the second line of (17.89) we used the fact that $\mathbf{k}_1$ could be any member of $*\mathbf{k}$; in the third line we used the expression for the character of the antisymmetrized representation,

$$\{\chi(R)\} = \frac{1}{2} (\chi^2(R) - \chi(R^2)).$$

We now derive the Lifshitz conditions by substituting the expression (17.89) for $\{\chi^0(R | \tau)\}$ in (17.86) and setting $F_v = 0$, and get

$$\begin{aligned} \sum_{R \in \mathbb{P}_{\mathbf{k}}} &\left(\binom{(\mu)}{(\mu)} \chi^2(R | \tau) e^{-2i\mathbf{k} \cdot \tau} \right. \\ &\quad \left. - \binom{(\mu)}{(\mu)} \chi((R | \tau)^2) e^{-i\mathbf{k} \cdot (\tau + R\tau)} \right) (0, v) \chi(R | \tau) = 0. \end{aligned}$$

(17.90)

- (b) $\mathbf{k}_j = -\mathbf{k}_i$, $i \neq j$, or $\mathbf{k}_2 = -\mathbf{k}_1$ **case** Here, we need to do a little preliminary work before deriving an expression for the Lifshitz condition. First, we note that the only elements that contribute to the summation in (17.86) are those that either leave $\mathbf{k}_1$ invariant, or change it to $-\mathbf{k}_1$. We then rewrite (17.86) as

$$F_v = \frac{1}{g_{\mathbf{k}_1}} \sum_{R\mathbf{k}_1 = \pm\mathbf{k}_1} \{ \chi^0(R|\boldsymbol{\tau}) \}^{(0,v)} \chi(R|\boldsymbol{\tau}). \quad (17.91)$$

Second, we partition the sum over R in (17.91) into the sets:

$$\begin{aligned} \text{(i)} \quad R_+ \mathbf{k}_1 &\equiv \mathbf{k}_1, & R_+ &\in \mathbb{P}_{\mathbf{k}_1}, \\ \text{(ii)} \quad R_- \mathbf{k}_1 &\equiv -\mathbf{k}_1, & R_- &\notin \mathbb{P}_{\mathbf{k}_1}, \quad -\mathbf{k}_1 \notin \mathbf{k}_1, \end{aligned} \quad (17.92)$$

and we select an element R_2 , such that $\mathbf{k}_2 = R_2\mathbf{k}_1$. We then find that

$$\begin{aligned} R_2 R_- \mathbf{k}_1 &= -\mathbf{k}_2 = \mathbf{k}_1 = R_+ \mathbf{k}_1, \\ R_- R_2 \mathbf{k}_1 &= R_- \mathbf{k}_2 = \mathbf{k}_1 = R_+ \mathbf{k}_1, \\ R_2^{-1} R_+ R_2 \mathbf{k}_1 &= R_2^{-1} R_+ \mathbf{k}_2 = R_2^{-1} \mathbf{k}_2 = \mathbf{k}_1, \end{aligned} \quad (17.93)$$

which implies that $R_2 R_-$, $R_- R_2$, $R_2^{-1} R_+ R_2 \in \mathbb{P}_{\mathbf{k}_1}$. We use the relation

$$(R_-|\boldsymbol{\tau}_-) = (R_2|\boldsymbol{\rho}_2)^{-1} (R_+|\boldsymbol{\tau}_+) = (R_2^{-1} R| R_2^{-1}(\boldsymbol{\tau}_+ - \boldsymbol{\rho}_2))$$

to limit the summation in (17.91) to $R \in \mathbb{P}_{\mathbf{k}_1}$, and we obtain

$$\frac{1}{2g_{\mathbf{k}_1}} \sum_{G \in \mathbb{G}_{\mathbf{k}_1}} \left(\{ \chi_{12}^0(G) \}^{(0,v)} \chi(G) + \{ \chi_{12}^0(G_2^{-1}G) \}^{(0,v)} \chi(G_2^{-1}G) \right) \quad (17.94)$$

where, for the sake of simplicity, we used $G \equiv (R|\boldsymbol{\tau})$ and $G_2 \equiv (R_2|\boldsymbol{\rho}_2)$. Consider two distinct bases, $(^*\mathbf{k}, \mu)\Psi$ and $(^*\mathbf{k}, \mu)\Phi$, for Irrep $(^*\mathbf{k}, \mu)$. Moreover, let the sub-bases $(\mathbf{k}_1, \mu)\Psi_1$, and $(\mathbf{k}_1, \mu)\Phi_1$ correspond to $(\mathbf{k}_2, \mu)\Psi_2$ and $(\mathbf{k}_2, \mu)\Phi_2$. Then for $G \in \mathbb{G}_{\mathbf{k}_1}$, we obtain

$$G^{(\mathbf{k}_i, \mu)} \Psi_i =^{(\mathbf{k}_i, \mu)} \Psi_i^{(\mathbf{k}_i, \mu)} \Omega(G), \quad (17.95)$$

$$G^{(\mathbf{k}_i, \mu)} \Phi_i =^{(\mathbf{k}_i, \mu)} \Phi_i^{(\mathbf{k}_i, \mu)} \Omega(G), \quad (17.96)$$

where $i = 1, 2$. We also have

$$\begin{aligned} G_2^{(\mathbf{k}_1, \mu)} \Psi_1 &=^{(\mathbf{k}_2, \mu)} \Psi_2, \\ G_2^{(\mathbf{k}_1, \mu)} \Phi_1 &=^{(\mathbf{k}_2, \mu)} \Phi_2. \end{aligned} \quad (17.97)$$

We now form the antisymmetrized basis

$$\Xi = (\mathbf{k}_1, \mu) \Psi_1 (\mathbf{k}_2, \mu) \widetilde{\Phi}_2 - (\mathbf{k}_1, \mu) \Phi_1 (\mathbf{k}_2, \mu) \widetilde{\Psi}_2,$$

and operate on by G , to obtain

$$G \Xi = \left(G^{(\mathbf{k}_1, \mu)} \Psi_1 \right) \left(G G_2^{(\mathbf{k}_1, \mu)} \tilde{\Phi}_1 \right) - \left(G^{(\mathbf{k}_1, \mu)} \Phi_1 \right) \left(G G_2^{(\mathbf{k}_1, \mu)} \tilde{\Psi}_1 \right). \quad (17.98)$$

By rewriting

$$G G_2^{(\mathbf{k}_1, \mu)} \tilde{\Psi}_1 = G_2 \left(G_2^{-1} G G_2 \right)^{(\mathbf{k}_1, \mu)} \tilde{\Psi}_1,$$

we obtain

$$\begin{aligned} G \Xi = & \left({}^{(\mathbf{k}_1, \mu)} \Psi_1 {}^{(\mathbf{k}_2, \mu)} \tilde{\Phi}_2 - {}^{(\mathbf{k}_1, \mu)} \Phi_1 {}^{(\mathbf{k}_2, \mu)} \tilde{\Psi}_2 \right) \\ & \times {}^{(\mathbf{k}_1, \mu)} \Omega(G) {}^{(\mathbf{k}_1, \mu)} \tilde{\Omega} \left(G_2^{-1} G G_2 \right), \end{aligned} \quad (17.99)$$

and

$$\chi^0(G) = {}^{(\mu)} \chi(G) {}^{(\mu)} \chi(G_2^{-1} G G_2). \quad (17.100)$$

When we operate on Ξ by $(R_2 | \rho_2) (R | \tau)$ we obtain

$$\begin{aligned} G_2 G \Xi = & \left(G_2 G^{(\mathbf{k}_1, \mu)} \Psi_1 \right) \left(G_2 G G_2^{(\mathbf{k}_1, \mu)} \tilde{\Phi}_1 \right) \\ & - \left(G_2 G^{(\mathbf{k}_1, \mu)} \Phi_1 \right) \left(G_2 G G_2^{(\mathbf{k}_1, \mu)} \tilde{\Psi}_1 \right) \\ = & {}^{(\mathbf{k}_2, \mu)} \Psi_2 {}^{(\mathbf{k}_1, \mu)} \tilde{\Phi}_1 {}^{(\mathbf{k}_1, \mu)} \Omega(G) {}^{(\mathbf{k}_1, \mu)} \tilde{\Omega} (G_2 G G_2) \\ & - {}^{(\mathbf{k}_2, \mu)} \Phi_2 {}^{(\mathbf{k}_1, \mu)} \tilde{\Psi}_1 {}^{(\mathbf{k}_1, \mu)} \Omega(G) {}^{(\mathbf{k}_1, \mu)} \tilde{\Omega} (G_2 G G_2) \\ = & -\Xi \left({}^{(\mathbf{k}_1, \mu)} \Omega (G_2 G G_2) {}^{(\mathbf{k}_1, \mu)} \tilde{\Omega}(G) \right), \end{aligned} \quad (17.101)$$

which, by contrast, gives

$$\chi^0(G_2 G) = - {}^{(\mu)} \chi(G_2 G G_2 G). \quad (17.102)$$

Substituting (17.100) and (17.101) back in (17.94), and setting $F_v = 0$, we obtain the Lifshitz condition

$$\begin{aligned} \frac{1}{2g_{\mathbf{k}_1}} \sum_{G \in \mathbb{G}_{\mathbf{k}_1}} & \left({}^{(\mu)} \chi(G) {}^{(\mu)} \chi(G_2^{-1} G G_2) {}^{(0, v)} \chi(G) \right. \\ & \left. - {}^{(\mu)} \chi(G_2 G G_2 G) {}^{(0, v)} \chi(G_2 G) \right) = 0. \end{aligned} \quad (17.103)$$

Types of phase transitions in crystals

***t*-Equal transitions** Such transitions are associated exclusively with the null-star Irreps $^{(0,\mu)}\Gamma$. By definition, they do not involve a change of the unit cell, and have *t*-equal low-symmetry phase subgroups:

$$\mathbb{S} \subset \mathbb{S}_0: \quad \mathbb{T} = \mathbb{T}_0 \text{ and } \mathbb{P} \subset \mathbb{P}_0.$$

Since, in this case, the space-group Irreps are just those of $\mathbb{P}_0$ with $d_\mu \leq 3$, the corresponding OPs have $n \leq 3$ independent components.

Example 17.11

The A-15 compounds

The high-symmetry phase in these A_3B compounds, such as Nb_3Sn and V_3Si , belongs to the nonsymmorphic space-group $Pm3n$ (O_h^3), which comprises

$$\mathbb{T}_h \oplus \left(\sigma^{\bar{x}y} \left| \begin{smallmatrix} a & a & a \\ 2 & 2 & 2 \end{smallmatrix} \right. \right) \mathbb{T}_h.$$

The *A* atoms occupy the (d) Wyckoff positions $(-4m \cdot 2)$:

$$\left(\frac{1}{4}, \frac{1}{2}, 0 \right), \left(\frac{3}{4}, \frac{1}{2}, 0 \right), \left(0, \frac{1}{4}, \frac{1}{2} \right), \left(0, \frac{3}{4}, \frac{1}{2} \right), \left(\frac{1}{2}, 0, \frac{1}{4} \right), \left(\frac{1}{2}, 0, \frac{3}{4} \right),$$

and form three sets of orthogonal chains.

The *B* atoms occupy the (a) Wyckoff positions $(0, 0, 0)$ and $\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2} \right)$.

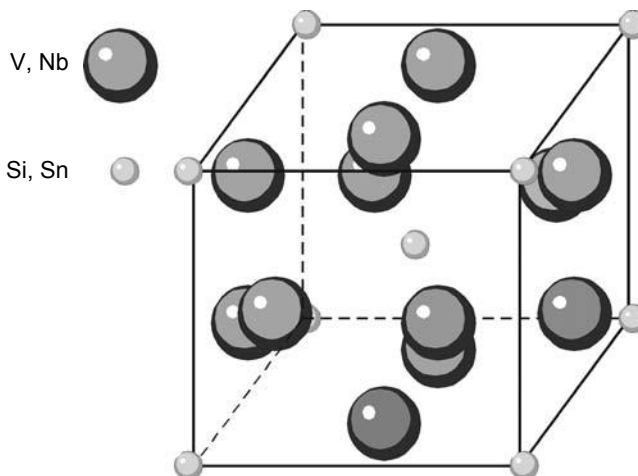


Fig. 17.12. A-15 unit cell with two formulas.

Table 17.3. Generation of the Wyckoff (d)-orbit from position $(\frac{3}{4}, \frac{1}{2}, 0)$.

Operation	Permutation	Coset
$E, C_2^x, C_2^{yz}, C_2^{y\bar{z}}, \sigma^y, \sigma^z, S_4^x, \bar{S}_4^x$	$(\frac{3}{4}, \frac{1}{2}, 0)$	E
$C_2^y, C_2^z, C_4^x, \bar{C}_4^x, I, \sigma^x, \sigma^{yz}, \sigma^{y\bar{z}}$	$(\frac{1}{4}, \frac{1}{2}, 0)$	C_2^y
$C_3^{xyz}, C_3^{\bar{x}\bar{y}z}, \bar{C}_3^z, C_2^{\bar{x}\bar{y}}, \bar{S}_4^z, \bar{S}_6^{\bar{x}\bar{y}z}, \bar{S}_6^{x\bar{y}\bar{z}}, \sigma^{xy}$	$(0, \frac{3}{4}, \frac{1}{2})$	C_3^{xyz}
$C_3^{x\bar{y}\bar{z}}, C_3^{\bar{x}y\bar{z}}, C_4^z, C_2^{xy}, S_4^z, \bar{S}_6^{xyz}, \bar{S}_6^{\bar{x}\bar{y}z}, \sigma^{x\bar{y}}$	$(0, \frac{1}{4}, \frac{1}{2})$	$C_3^{x\bar{y}\bar{z}}$
$\bar{C}_3^{xyz}, \bar{C}_3^{x\bar{y}\bar{z}}, C_4^y, C_2^{z\bar{x}}, S_4^y, S_6^{\bar{x}\bar{y}\bar{z}}, S_6^{x\bar{y}z}, \sigma^{xz}$	$(\frac{1}{2}, 0, \frac{3}{4})$	$\bar{C}_3^{xyz}$
$\bar{C}_3^{\bar{x}\bar{y}z}, C_3^{x\bar{y}\bar{z}}, \bar{C}_4^y, C_2^{xz}, \bar{S}_4^y, S_6^{yz}, S_6^{\bar{x}\bar{y}\bar{z}}, \sigma^{\bar{x}z}$	$(\frac{1}{2}, 0, \frac{1}{4})$	$\bar{C}_3^{\bar{x}\bar{y}z}$

Table 17.4. Subduction compatibility.

$(\mu)\Gamma$ of $\mathbb{S}_0$	$(^1)\Gamma$ of $\mathbb{S}$
$E_g (\Gamma_{12})$	A_{1g} of D_{4h}^9
$E_g, A_{1u} (\Gamma'_1), E_u (\Gamma'_{12})$	A_1 of D_4^5
$E_g, T_{1u} (\Gamma_{15})$	A_1 of C_{4v}^7
$E_g, A_{2u} (\Gamma'_2), E_u$	A_1 of D_{2d}^2
$E_g, T_{2u} (\Gamma_{25})$	A_1 of D_{2d}^5

Group generation of the Wyckoff (d)-orbit is given in Table 17.3.

A second-order phase change to a tetragonal structure occurs at $T = T_m$ without change in the unit cell. We give the following observations [151]:

- (i) The tetragonal sub-space-groups compatible with $Pm3n$ are

$$P\frac{4}{mmc} (D_{4h}^9), P4_22 (D_4^5), P\bar{4}2c (D_{2d}^2), P4mc (C_{4v}^7), P\bar{4}m2 (D_{2d}^5).$$

- (ii) Since the unit cell is unchanged, we must have an Irrep belonging to the Γ -point.
- (iii) Since the two phases are t -equal, we obtain by the subduction criterion Table 17.4.
- (iv) The Landau condition eliminates E_g and T_{2g} , which disqualifies D_{4h}^9 .
- (v) Invoking the physical tensor field criterion, we associate the structural phase transition with phonon modes; and recognizing that the acoustic modes have

zero frequencies at Γ , we should consider only the optical modes at Γ , namely,

$$A_{2g} \oplus E_g \oplus T_{1g} \oplus 2T_{1u} \oplus T_{2g} \oplus 2T_{2u}.$$

Since there are no modes belonging to Irreps A_{1u} , A_{2u} , and E_u we eliminate D_4^5 and D_{2d}^2 .

k -Equal and commensurate transitions Phase transitions associated with BZ boundary stars have k -equal or general space-subgroups. These transitions are associated with BZ boundary points characterized by high symmetry relative to all surrounding points. Such points are sometimes referred to as *Lifshitz points*. The type of lattice that emerges in the low-symmetry phase depends critically on which arms of the star of $\mathbf{k}$ contribute to the density of the new phase. In each case one considers the shortest translation vectors $\mathbf{t} \in \mathbb{T}_0$ that satisfy

$$\exp[i2\pi \mathbf{k}^{(i)} \cdot \mathbf{t}] = 1,$$

where i runs over the indices of the participating arms.

Example 17.12

Lifshitz points of the b.c.c. lattice

It has the primitive and reciprocal lattice bases

$$\begin{aligned} \mathbf{a}_1 &= \left(-\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right), \mathbf{a}_2 = \left(\frac{1}{2}, -\frac{1}{2}, \frac{1}{2}\right), \mathbf{a}_3 = \left(\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}\right), \\ \mathbf{b}_1 &= (0, 1, 1), \mathbf{b}_2 = (1, 0, 1), \mathbf{b}_3 = (1, 1, 0). \end{aligned}$$

There are three Lifshitz points on the b.c.c. BZ boundary:

- (i) **The H -point**, $\mathbf{k}_H = \frac{1}{2}(\mathbf{b}_1 + \mathbf{b}_2 - \mathbf{b}_3)$ $^*\mathbf{k}_H$ consists of one arm. The new lattice vectors have to satisfy the conditions

$$\exp[i2\pi \mathbf{k}_H \cdot \mathbf{t}] = 1, \quad \Rightarrow \quad \mathbf{t} = m_1 \mathbf{a}_1 + m_2 \mathbf{a}_2 + m_3 \mathbf{a}_3.$$

This yields the conditions $m_1 + m_2 - m_3 = 2$, with shortest vectors

$$\begin{aligned} m_1 = 1, m_2 = 1, m_3 = 0 &\Rightarrow \mathbf{a}'_3 = (0, 0, 1), \\ m_1 = 1, m_2 = 0, m_3 = -1 &\Rightarrow \mathbf{a}'_2 = (0, 1, 0), \\ m_1 = 0, m_2 = 1, m_3 = -1 &\Rightarrow \mathbf{a}'_1 = (1, 0, 0), \end{aligned}$$

Table 17.5. Possible lattices emerging from an N -point transition.

Number of arms	Participating arms	Shortest lattice vectors	Lattice type
1	1, 2, 3, 4, 5, 6		Orthorhombic-C
2	14, 25, 36		Tetragonal-P
2	remaining pairs		Rhombohedral
3	126, 135, 234, 456		Rhombohedral
3	remaining triplets		b.c.c.
4 or 5 or 6			b.c.c.

which defines a primitive cubic lattice.

- (ii) **The P -point**, $\mathbf{k}_P = \frac{1}{4}(\mathbf{b}_1 + \mathbf{b}_2 + \mathbf{b}_3)$ $^*\mathbf{k}_P$ consists of two arms, $\pm\mathbf{k}_P$. The new lattice vectors have to satisfy the conditions $\exp[\pm i2\pi\mathbf{k}_P \cdot \mathbf{t}] = 1$, or

$$m_1 + m_2 + m_3 = 4.$$

The shortest vectors satisfying this condition are

$$(1, 1, 0), (1, 0, 1), (0, 1, 1),$$

which define an f.c.c. lattice.

- (iii) **The N -point** The $^*\mathbf{k}_N$ consists of six arms:

$$\begin{aligned} \mathbf{k}_N^{(1)} &= \frac{1}{2}\mathbf{b}_3, \mathbf{k}_N^{(2)} = \frac{1}{2}\mathbf{b}_2, \mathbf{k}_N^{(3)} = \frac{1}{2}\mathbf{b}_1, \\ \mathbf{k}_N^{(4)} &= \frac{1}{2}(\mathbf{b}_2 - \mathbf{b}_1), \mathbf{k}_N^{(5)} = \frac{1}{2}(\mathbf{b}_3 - \mathbf{b}_1), \mathbf{k}_N^{(6)} = \frac{1}{2}(\mathbf{b}_3 - \mathbf{b}_2). \end{aligned}$$

Four possible lattice types may result for transitions associated with this point, depending on the number of participating arms. These possibilities are listed in Table 17.5, and the derivations are left to the reader.

Incommensurate transitions When the transition wavevector $\mathbf{k}$ lies on high-symmetry lines, such as the $\Delta, \Lambda, \Sigma, A, B, N$, and M for the f.c.c. Brillouin zone, there is a continuously varying parameter defining $\mathbf{k}$, for example

$$\mathbf{k}_\Delta = (k, 0, 0), \quad 0 < k < 2\pi/a.$$

It is then possible that the minimization of the Landau free energy coincides with an incommensurate value of such a parameter, and the emerging low-symmetry phase is an incommensurate one.

Example 17.13

Phase transitions in potassium selenate, K_2SeO_4

In Chapter 15 we presented dynamical modes of K_2SeO_4 that are related to structural phase transitions observed in this compound: paraelectric($Pnam$)–incommensurate at $T_i = 130$ K, and a subsequent transition to an improper ferroelectric phase at $T_f = 93$ K. The IC phase is characterized by an incommensurate wavevector

$$\mathbf{q}_\delta = \frac{1}{3}(1 - \delta) \mathbf{b}_1, \quad (\text{i})$$

where δ decreases, with decrease in temperature, from $\delta_0 = 0.07$ at T_i and abruptly vanishes at T_f . Here, we provide a theoretical description of these transitions within the Landau theory framework. The primary order parameter is the amplitude of the lattice distortion $\boldsymbol{\eta}(\mathbf{q}_\delta, \Sigma_2)$. To include a description of the transition to the ferroelectric phase, we must introduce a secondary OP which couples to the $\boldsymbol{\eta}(\mathbf{q}_\delta, \Sigma_2)$ distortion to produce a spontaneous z -polarization in the ferro-phase. In order to satisfy translational invariance, an n th-order monomial in the Landau free energy of the form

$$\mathcal{F}^{(n)}(\mathbf{q}_1\sigma_1, \mathbf{q}_2\sigma_2, \dots, \mathbf{q}_n\sigma_n) \boldsymbol{\eta}(\mathbf{q}_1, \sigma_1) \boldsymbol{\eta}(\mathbf{q}_2, \sigma_2) \dots \boldsymbol{\eta}(\mathbf{q}_n, \sigma_n) \quad (\text{ii})$$

must satisfy the conditions

$$\mathbf{q}_1 + \mathbf{q}_2 + \dots + \mathbf{q}_n = \mathbf{G}, \quad (\text{iii})$$

$$(\mathbf{q}_1, \sigma_1) \Gamma \otimes (\mathbf{q}_2, \sigma_2) \Gamma \otimes \dots \otimes (\mathbf{q}_n, \sigma_n) \Gamma \ni (\mathbf{0}, 1) \Gamma. \quad (\text{iv})$$

Given $\mathbf{q}_\delta$, we may introduce the coupling of the secondary OP $\boldsymbol{\xi}(\mathbf{q}_s, \sigma_s)$ in an n th-order monomial, satisfying (ii)–(iv), of the form

$$\begin{aligned} & \mathcal{F}^{(n)} \boldsymbol{\eta}^{n-1}(\mathbf{q}_\delta, \Sigma_2) \boldsymbol{\eta}(\mathbf{q}_s, \sigma_s), \\ & \left(\bigotimes_{i=1}^{n-1} (\mathbf{q}_\delta, \Sigma_2) \Gamma \right) \otimes (\mathbf{q}_s, \Sigma_s) \Gamma \ni (\mathbf{0}, 1) \Gamma, \\ & \mathbf{q}_s = \mathbf{b}_1 - (n-1)\mathbf{q}_\delta = \frac{1}{3}[(4-n) + (n-1)\delta] \mathbf{b}_1. \end{aligned}$$

Such coupling terms guarantee that a nonzero primary OP $\boldsymbol{\eta}(\mathbf{q}_\delta, \Sigma_2)$ would enforce the nonvanishing of the secondary *induced* OP $\boldsymbol{\xi}(\mathbf{q}_s, \sigma_s)$. With a two-component star of $\mathbf{q}_\delta$, the space-group Irreps induced from Σ_2 , Σ_3 , and Σ_4 are given in Table 17.6.

Table 17.6. *Space-group Irreps for primary and secondary OPs.*

$$(\mu = e^{-i\pi(1-\delta)/3}, \nu = e^{-i\pi\delta}, \zeta = e^{-i\pi(1+2\delta)/3}).$$

Irrep	$(E \mathbf{0})$	$(C_{2x} \frac{1}{2}\frac{1}{2}\frac{1}{2})$	$(C_{2y} \frac{1}{2}\frac{1}{2}0)$	$(C_{2z} 00\frac{1}{2})$	$(\mathcal{T} 000)$	$(\sigma_x \frac{1}{2}\frac{1}{2}\frac{1}{2})$	$(\sigma_y \frac{1}{2}\frac{1}{2}0)$	$(\sigma_z 00\frac{1}{2})$
Σ_2	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} \mu & 0 \\ 0 & \mu^* \end{bmatrix}$	$\begin{bmatrix} 0 & -\mu^* \\ -\mu & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & -1 \\ -1 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & \mu^* \\ \mu & 0 \end{bmatrix}$	$\begin{bmatrix} -\mu & 0 \\ 0 & -\mu^* \end{bmatrix}$	$\begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix}$
Σ_3	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -\nu & 0 \\ 0 & -\nu^* \end{bmatrix}$	$\begin{bmatrix} 0 & \nu^* \\ \nu & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & -1 \\ -1 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & -\nu^* \\ -\nu & 0 \end{bmatrix}$	$\begin{bmatrix} \nu & 0 \\ 0 & \nu^* \end{bmatrix}$	$\begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix}$
Σ_4	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -\zeta & 0 \\ 0 & -\zeta^* \end{bmatrix}$	$\begin{bmatrix} 0 & -\zeta^* \\ -\zeta & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & -\zeta^* \\ -\zeta & 0 \end{bmatrix}$	$\begin{bmatrix} -\zeta & 0 \\ 0 & -\zeta^* \end{bmatrix}$	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$

First, we find from Table 17.6 that both the primary and secondary OPs are two-dimensional. Second, terms of the form $\eta_1\eta_2$ and $\xi_1\xi_2$ are invariant under the operations of D_{2h} . Third, we may construct the monomials

$$n = 3 \Rightarrow \mathbf{q}_s = (1 + 2\delta) \frac{\mathbf{b}_1}{3} = \mathbf{q}_{2\delta}, \quad \Sigma_s = \Sigma_4,$$

$$n = 4 \Rightarrow \mathbf{q}_s = 3\delta \frac{\mathbf{b}_1}{3} = \mathbf{q}_{3\delta}, \quad \Sigma_s = \Sigma_3;$$

however, in the third-degree monomial wavevector $\mathbf{q}_{2\delta}$ becomes $\mathbf{b}_1/3$ when $\delta = 0$, which cannot establish a spontaneous macroscopic polarization. By contrast, the fourth-degree monomial has a wavevector $\mathbf{q}_{3\delta} = \delta \mathbf{b}_1$, which vanished when $\delta = 0$ and gives rise to a macroscopic polarization. We may write the Landau free energy as

$$\Delta\Phi = a\eta_1\eta_2 + b\xi_1\xi_2 + c(\eta_1\eta_2)^2 + d(\eta_1\eta_2)^3 + e(\eta_1^3\xi_1 + \eta_2^3\xi_2) + \dots$$

Since $\boldsymbol{\eta}$ is the primary OP, we write

$$a = a_0(T - T_i) + a_2(\delta - \delta_0)^2, \quad (\text{v})$$

$$b = b_0 + b_2\delta^2, \quad (\text{vi})$$

where at T_i , $\delta = \delta_0$. We assume that both a and b depend quadratically on δ , which, in turn, leads to the dependence of δ on temperature. Moreover, the transformations given in Table 17.6 allow us to write the OPs as

$$\eta_1 = \eta_0 e^{i\varphi}, \eta_2 = \eta_0 e^{-i\varphi}, \xi_1 = \xi_0 e^{i\vartheta}, \xi_2 = \xi_0 e^{-i\vartheta},$$

and obtain

$$\Delta\Phi = a\eta_0^2 + b\xi_0^2 + c\eta_0^4 + d\eta_0^6 + 2e\eta_0^3\xi_0 \cos(3\varphi + \vartheta) + \dots$$

Minimization with respect to φ and ϑ gives

$$3\varphi + \vartheta = \begin{cases} 0 & \text{if } e < 0, \\ \pi & \text{if } e > 0; \end{cases}$$

and with respect to ξ_0 yields

$$\xi_0 = \frac{|e|}{b} \eta_0^3,$$

and we obtain for the IC phase

$$\Delta\Phi_{\text{IC}} = a\eta_0^2 + c\eta_0^4 + \left(d - \frac{e^2}{b}\right)\eta_0^6 + \dots \quad (\text{vii})$$

In order to obtain an expression for the temperature dependence of δ we neglect the sixth-degree term, and then minimize $\Delta\Phi_{\text{IC}}$ with respect to η_0 to obtain

$$\eta_0 = \begin{cases} 0, & \text{unstable solution for } T < T_i \\ \pm \sqrt{\frac{-a}{2c}} & \text{stable solution for } T < T_i. \end{cases} \quad (\text{viii})$$

We also minimize $\Delta\Phi_{\text{IC}}$ with respect to δ , using (v) and (vi), getting

$$\delta \simeq \frac{\delta_0}{1 + \frac{e^2 b_2}{b^2 a_2} \eta_0^4}. \quad (\text{ix})$$

Next, solving (viii) and (ix) self-consistently gives the sought after expression for $\delta(T)$. However, close to T_i , we can approximate (viii) as $\eta_0 \simeq \sqrt{a_1(T_i - T)/c}$ and obtain

$$\delta(T) \simeq \frac{\delta_0}{1 + \gamma(T_i - T)^2},$$

where

$$\gamma = \frac{e^2 b_2 a_1}{4b^2 a_2 C^2}.$$

Magnetic phase transitions

There are several distinctive features that regulate the method of determining the nature and characteristics of a magnetic phase transition [58, 73, 147, 148, 159, 160].

- (i) The most obvious feature is that magnetic groups contain Θ , the operation of time-reversal, which is either present on its own as a symmetry operation of the crystal in the paramagnetic phase, above the transition temperature, or in combination with spatial symmetry operations, as in polychromatic groups.

- (ii) The presence of $\Theta \in \mathbb{S}_0$ means that $\mathbb{S}_0 \rightarrow \mathbb{M}_0$ is a gray group. If the OP η represents the magnetization in the ordered phase, the action of Θ on η will therefore produce $-\eta$; thus, all the homogeneous polynomials of odd order will not be invariant under the operations of $\mathbb{M}_0$, and have to be excluded from $\Delta\Phi$. This means that the Landau condition is automatically satisfied for a transition between a paramagnetic phase and a magnetically ordered phase.

In the case of a phase transition from a paramagnetic state to a magnetically ordered state it is never possible to construct an odd-order invariant [145]. This arises because of the special transformation properties of the spin-component vectors of which any magnetic order parameters are constructed; they must change sign under the time-reversal operation, which is a symmetry operation of the paramagnetic phase. Thus, this condition is automatically satisfied in these cases.

- (iii) In the case of a phase transition between two magnetically ordered phases, the Landau condition will also be satisfied, automatically, when the high-symmetry dichromatic space-group, $\mathbb{M}_0$, contains the element $\Theta I \in P_0$, where I is the space-inversion operation, in its point-group; since η is an axial vector, $\Theta I \eta = -\eta$ (meta-magnetic and spin-flip transitions).

This argument fails for dichromatic space-groups where $\Theta I \notin P_0$, and a more detailed analysis of the Landau condition will be required. This is the case for many of the dichromatic point-groups that do not contain the element ΘI .

- (iv) To identify a spin arrangement with some Rep or Irrep Γ of the point-group P_0 of $\mathbb{M}_0$, we have to confirm the following requirement, as derived by Opechowski and Dreyfuss [63]: The direct product of Γ and the axial-vector Rep $^{(a)}\Gamma$ must subduce the identity representation $^{(1)}\Gamma(P_s)$, where P_s is the site group, at least once.

$$\langle \Gamma \otimes ^{(a)}\Gamma | ^{(1)}\Gamma(P_s) \rangle \geq 1. \quad (17.104)$$

The moral here is that we must consider only those Irreps which allow for a basis of axial-vector components.

- (v) Since both gray and dichromatic groups are nonunitary, we have to employ CoReps and CoIrreps, $\theta\Gamma$, in the analysis of magnetic transitions.
- (vi) An unusual situation arises when we consider exchange-related invariant terms of the form $J \mathbf{S}_i \cdot \mathbf{S}_j$. Such terms are invariant under the action of all elements of $\mathcal{O}(3)$, the 3D isotropy group. We note that this group defines the underlying symmetry of the Heisenberg magnetic Hamiltonian, which comprises solely exchange terms.

The exchange terms define the relative orientations of the magnetic moments, or spins, at the different crystal sites. They do not define the absolute orientations relative to the crystallographic axes. The latter are usually determined by the *single-site anisotropy* terms arising from spin-orbit couplings at magnetic ion sites; although sometimes they may be ultimately determined by weak dipolar interactions.

We surmise from the above discussion that we have to distinguish between two possible types of magnetic phase transitions:

- (i) a transition from a paramagnetic to a magnetically ordered phase,
- (ii) a transition from one magnetically ordered phase to another.

Example 17.14

The paramagnetic–antiferromagnetic transition in $\alpha\text{-Fe}_2\text{O}_3$

$\alpha\text{-Fe}_2\text{O}_3$ has the corundum structure discussed in Example 17.10, with $\mathbb{S}_0 = R\bar{3}c$. It undergoes a magnetic t -equal phase transition to the AFM structure at $T_N = 250\text{ K}$. Thus, we have a transition associated with the trigonal BZ center, and we have to consider the Colreps at the Γ -point, with the gray space-group $\mathbb{M}_0 = R\bar{3}c1'$, whose Colrep generator matrices are given in Table 17.7.

Since, in magnetic groups, Θ appears only in combination with spatial operators, we only consider Colreps in which Θ is not represented by an identity matrix; this confines our analysis to $\Gamma_4^\pm$, $\Gamma_5^\pm$, $\Gamma_6^\pm$.

Table 17.7. *ColIrrep matrices of the $\bar{3}c1'$ generators.*

	E	Θ	C_3	U_1	$\mathfrak{J}$	Kernel subgroup
Γ_1^+	1	1	1	1	1	
Γ_2^+	1	1	1	-1	1	
Γ_3^+	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\frac{1}{2} \begin{bmatrix} -1 & -\sqrt{3} \\ \sqrt{3} & -1 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	
Γ_1^-	1	1	1	1	-1	
Γ_2^-	1	1	1	-1	-1	
Γ_3^-	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\frac{1}{2} \begin{bmatrix} -1 & -\sqrt{3} \\ \sqrt{3} & -1 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$	$\begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix}$	
Γ_4^+	1	-1	1	1	1	$R\bar{3}c$ (AF)
Γ_5^+	1	-1	1	-1	1	$R\bar{3}c'$ (F)
Γ_6^+	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix}$	$\frac{1}{2} \begin{bmatrix} -1 & -\sqrt{3} \\ \sqrt{3} & -1 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\frac{C_2}{c}$ (F)
Γ_4^-	1	-1	1	1	-1	$\frac{C_2'}{c'} (F)$
Γ_5^-	1	-1	1	-1	-1	$R\bar{3}'c'$ (AF)
						$R\bar{3}'c$ (AF)
Γ_6^-	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix}$	$\frac{1}{2} \begin{bmatrix} -1 & -\sqrt{3} \\ \sqrt{3} & -1 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$	$\begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix}$	$\frac{C_2}{c}$ (AF)
						$\frac{C_2'}{c'} (AF)$

The Fe atoms occupy the Wyckoff (c) positions

$$(x, x, x), (\bar{x}, \bar{x}, \bar{x}), \left(\frac{1}{2} + x, \frac{1}{2} + x, \frac{1}{2} + x\right), \left(\frac{1}{2} + \bar{x}, \frac{1}{2} + \bar{x}, \frac{1}{2} + \bar{x}\right)$$

with 3· site-symmetry.

17.3 Construction and minimization techniques for $\Delta\Phi$

In this section, we describe some useful techniques that can be employed in the construction of the Taylor expansion of the Landau free energy $\Delta\Phi$ and in its subsequent minimization. We start by enumerating the number of linearly independent p th-degree terms invariant under $\mathbb{S}_0$, up to the highest degree admitted in the expansion. Next, we describe how to determine the forms of the polynomial invariants, once an active Irrep of $\mathbb{S}_0$ is identified. Finally, we discuss technical procedures for minimizing $\Delta\Phi$.

17.3.1 Construction of the Landau free energy: invariant polynomials

Here, we present some useful techniques for the construction of the Landau free energy, or *generalized polynomials*. These techniques are based on the algebraic *theory of invariants*, which deals with the ring of group-invariant ($\mathcal{G}$ -invariant) polynomials.

We consider a d -dimensional vector space with variables $x_1, x_2, \dots, x_d$. A general polynomial of degree n , defined on this space, comprises a linear combination of homogeneous monomials of degree $m \leq n$. The set $\mathfrak{P}$ of all possible such polynomials forms a vector space of infinite dimension, which can be decomposed into the direct sum of vector spaces $\mathfrak{P}^{(m)}$

$$\mathfrak{P} = \bigoplus_{m=0}^{\infty} \mathfrak{P}^{(m)},$$

where $\mathfrak{P}^{(m)}$ contains all homogeneous polynomials of degree m .

Since the action of an element R of a group $\mathcal{G}$ on a polynomial $p(\mathbf{r})$, given by

$$Rp(\mathbf{r}) = p(R^{-1}\mathbf{r}),$$

preserves its degree, each $\mathfrak{P}^{(m)}$ carries a Rep of $\mathcal{G}$ whose character $\chi^{(m)}(R)$ is given by the generating function

$$\sum_{m=0}^{\infty} \chi^{(m)}(R) t^m = [\det(\mathbb{I} - tR)]^{-1},$$

as was demonstrated in Section 8.5.2. Such Reps are, in general, reducible into direct sums of the Irreps of $\mathcal{G}$, and we may write

$$\mathfrak{P} = \bigoplus_{\alpha} \mathfrak{P}_{\alpha}; \quad \mathfrak{P}_{\alpha}^{(m)} = \mathfrak{P}^{(m)} \cap \mathfrak{P}_{\alpha}.$$

The set $\mathfrak{P}_1$, $\alpha = 1$ the invariant Irrep, forms the ring of $\mathcal{G}$ -invariant polynomials.

Reduction of polynomials of p th degree into irreducible sets

We are interested here in the number and structure of distinct homogeneous monomials of degree p , constructed from the d_μ components of an OP, $(\eta_1, \dots, \eta_{d_\mu})$, associated with an active d_μ -dimensional Irrep $^{(\mu)}\Gamma$ of $\mathbb{S}_0$. Since any such monomial can be written as $\eta_1^{m_1} \eta_2^{m_2} \dots \eta_{d_\mu}^{m_{d_\mu}}$, the problem of finding the number of distinct monomials then reduces to that of the partition

$$(m_1 | m_2 | \dots | m_{d_\mu}), \quad \sum_i m_i = p,$$

which is well known to have $\binom{p+d_\mu-1}{p}$ configurations. These monomials form a basis that engenders a Rep of $\mathbb{S}_0$ of dimension $\binom{p+d_\mu-1}{p}$, which is generally reducible.

The space spanned by this basis is actually the same as that spanned by the symmetrized p th tensor product of the space $(\eta_1, \dots, \eta_{d_\mu})$. Again, any component of the tensor product basis can be written as some permutation of the product $\eta_1^{m_1} \eta_2^{m_2} \dots \eta_{d_\mu}^{m_{d_\mu}}$, with $\sum_i m_i = p$. A basis vector of the symmetrized space is just a linear combination of these permuted bases, namely

$$\xi = \sum_{k=1}^{p!} \mathcal{P}_k \left(\underbrace{\eta_1 \eta_1 \dots \eta_1}_{m_1 \text{ times}} \underbrace{\eta_2 \eta_2 \dots \eta_2}_{m_2 \text{ times}} \dots \underbrace{\eta_{d_\mu} \eta_{d_\mu} \dots \eta_{d_\mu}}_{m_{d_\mu} \text{ times}} \right),$$

which establish a one-to-one correspondence between the monomials and the symmetrized basis vectors.

This finding allows us to identify the number of independent homogeneous polynomials of degree p , $\mathcal{M}_1^{(p)}(\mu)$, that are invariant under the operations of $\mathbb{S}_0$ as the frequency of the invariant Irrep in the subduction $\left(^{(\mu)}\Gamma^p \downarrow ^{(1)}\Gamma \right)$, namely,

$$\mathcal{M}_1^{(p)}(\mu) = \frac{d^p}{dx^p} \mathcal{M}(\mu, x) \big|_{x=0}, \quad (17.105)$$

where $\mathcal{M}(\mu, x)$ is the Molien function introduced in Chapter 8. $\mathcal{M}_1^{(p)}(\mu)$ linearly independent polynomials of degree p , invariant under the operations of $\mathbb{S}_0$, can be constructed from the corresponding monomials with the aid of the projection operator $\mathcal{P}_1$, as

$$\mathcal{P}_1 \left(\eta_1^{m_1} \eta_2^{m_2} \dots \eta_{d_\mu}^{m_{d_\mu}} \right) = \frac{1}{i_0} \sum_{R \in \mathcal{I}_0} \hat{R} \left(\eta_1^{m_1} \eta_2^{m_2} \dots \eta_{d_\mu}^{m_{d_\mu}} \right), \quad \sum_i m_i = p.$$

Symmetric polynomials We can obtain a set of d independent symmetric polynomials over the d -dimensional vector space $x_1, x_2, \dots, x_d$ by the following construct:

$$\begin{aligned} f(t) &= (t - x_1)(t - x_2) \dots (t - x_d) \\ &= t^d + p_1 t^{d-1} + p_2 t^{d-2} - \dots + (-1)^d p_d, \end{aligned}$$

where t is a dummy variable. The p_i s are the sought-after polynomials,

$$\begin{aligned} p_1 &= x_1 + x_2 + \cdots + x_d, \\ p_2 &= x_1x_2 + x_1x_3 + \cdots + x_1x_d + x_2x_3 + \cdots + x_{d-1}x_d, \\ p_3 &= x_1x_2x_3 + x_1x_2x_4 + \cdots + x_{d-2}x_{d-1}x_d, \\ &\vdots \\ p_d &= x_1x_2x_3 \dots x_d, \end{aligned}$$

which are symmetric in the variables $x_1, x_2, \dots, x_d$ and are called *elementary symmetric polynomials*.

Every symmetric polynomial can be written uniquely as a polynomial,

$$P(x_1, x_2, \dots, x_d) = q(p_1(x_1, x_2, \dots, x_d), \dots, p_d(x_1, x_2, \dots, x_d)),$$

in the elementary symmetric polynomials.

Example 17.15

Polynomials of degree 2 and 3 of the space (η_1, η_2) , invariant under the Irrep ${}^{(3)}\Gamma$ of the group $\mathcal{C}_{3v}$.

- (i) Second-degree polynomials: The number of monomials is $\binom{3}{2} = 3$, namely, $\eta_1^2, \eta_1\eta_2, \eta_2^2$, which are also bases for ${}^{(3)}\Gamma^2$. Using the information given in Table 17.8, we first determine the number of invariant polynomials as

$$\mathcal{M}_1^{(2)} = \frac{1}{6} [3 + 2 \times 0 + 3 \times 1] = 1.$$

Second, we obtain the polynomial by constructing the projection operator $\mathcal{P}_1$, using the information of Table 17.9, and projecting the invariant space spanned by the monomials as

$$\mathcal{P}_1 \eta_1^2 = \frac{1}{6} \sum_i \hat{R}_i \eta_1^2 = \frac{1}{2} (\eta_1^2 + \eta_2^2).$$

Table 17.8.

	E	$2C_3$	3σ
${}^{(3)}\chi$	2	-1	0
$[{}^{(3)}\chi^2]$	3	0	1
$[{}^{(3)}\chi^3]$	4	1	0
$[{}^{(3)}\chi^4]$	5	-1	1

Table 17.9. *Monomial transformation.*

Monomial	E	$C_3 C_3^2$	$\sigma_1 \sigma_2 \sigma_3$
η_1^2	η_1^2	$\eta_1'^2 = \frac{1}{4}(\eta_1^2 + 3\eta_2^2 + 2\sqrt{3}\eta_1\eta_2)$ $\eta_1''^2 = \frac{1}{4}(\eta_1^2 + 3\eta_2^2 - 2\sqrt{3}\eta_1\eta_2)$	$\eta_1^2, \eta_1'^2$ $\eta_1''^2$
η_1^3	η_1^3	$\eta_1'^3 = -\frac{1}{8} [\eta_1^3 + 3\sqrt{3}\eta_2^3 + 3\sqrt{3}\eta_1^2\eta_2 + 9\eta_1\eta_2^2]$ $\eta_1''^3 = -\frac{1}{8} [\eta_1^3 - 3\sqrt{3}\eta_2^3 - 3\sqrt{3}\eta_1^2\eta_2 + 9\eta_1\eta_2^2]$	$\eta_1^3, \eta_1'^3$ $\eta_1''^3$
η_1^4	η_1^4	$\eta_1'^4 = \frac{1}{16}(\eta_1 + \sqrt{3}\eta_2)^4$ $\eta_1''^4 = \frac{1}{16}(\eta_1 - \sqrt{3}\eta_2)^4$	$\eta_1^4, \eta_1'^4$ $\eta_1''^4$

- (ii) Third-degree polynomials: The number of monomials is $\binom{4}{3} = 4$, namely, $\eta_1^3, \eta_1^2\eta_2, \eta_1\eta_2^2, \eta_2^3$, which are also bases for ${}^{(3)}\Gamma^3$. The number of invariant polynomials is

$$\mathcal{M}_1^{(3)} = \frac{1}{6} [4 + 2 \times 1 + 3 \times 0] = 1,$$

which we obtain with the aid of the projection operator $\mathcal{P}_1$ as

$$\mathcal{P}_1 \eta_1^3 = \frac{1}{6} \sum_i \hat{R}_i \eta_1^3 = \frac{1}{4} \eta_1 (\eta_1^2 - 3\eta_2^2).$$

- (iii) Fourth-degree polynomials: The number of monomials is $\binom{5}{4} = 5$, namely, $\eta_1^4, \eta_1^3\eta_2, \eta_1^2\eta_2^2, \eta_1\eta_2^3, \eta_2^4$, which are also bases for ${}^{(3)}\Gamma^4$. The number of invariant polynomials is

$$\mathcal{M}_1^{(4)} = \frac{1}{6} [5 + 2 \times (-1) + 3 \times 1] = 1,$$

and projecting the invariant polynomial, we obtain

$$\mathcal{P}_1 \eta_1^4 = 3(\eta_1^2 + \eta_2^2)^2.$$

We thus have the Landau free energy expansion

$$\Phi = \frac{\alpha}{2} (T - T_c) (\eta_1^2 + \eta_2^2) + \frac{\beta}{3} \eta_1 (\eta_1^2 - 3\eta_2^2) + \frac{\gamma}{4} (\eta_1^2 + \eta_2^2)^2.$$

Setting $\eta_1 = \rho \cos \phi$, $\eta_2 = \rho \sin \phi$, we obtain

$$\Phi = \frac{\alpha}{2} (T - T_c) \rho^2 + \frac{\beta}{3} \rho^3 \cos 3\phi + \frac{\gamma}{4} \rho^4,$$

which has only a first-order phase transition.

Clearly if $p(\boldsymbol{\eta})$ and $q(\boldsymbol{\eta})$ are invariants of $\mathbb{S}_0$, so are $p(\boldsymbol{\eta}) + q(\boldsymbol{\eta})$, $p(\boldsymbol{\eta})q(\boldsymbol{\eta})$, and $cp(\boldsymbol{\eta})$ (c complex). This is just saying that the set of invariants of $\mathbb{S}_0$, $\mathbb{R}^{\mathbb{S}_0}$, forms a *ring*. Since

the linear transformations of a group do not change the degree of a polynomial, it is enough to describe the homogeneous invariants.

Integrity basis

Hilbert showed that there exist some fundamental polynomials among certain sets of polynomials. In the present case we are interested in identifying a minimal set of invariant polynomials that generates all other invariant polynomials. Such a set is called the *integral rational basis* or the *integrity basis*. Thus, an integrity basis is a set of homogeneous polynomials in the η_i in terms of which all polynomial invariants may be expressed as a sum of products of the integrity basis functions. In other words, if the integrity basis functions are $\mathbb{J}, \mathbb{J}_1, \mathbb{J}_2, \dots, \mathbb{J}_l$ every polynomial invariant of the group is a polynomial in the $\mathbb{J}_i$, where $i = 1, \dots, l$.

Emmy Noether has shown that the integrity bases of finite groups are finite:

For a Rep of a group $\mathcal{G}$, of order g , engendered on a vector space of dimension d the integrity basis cannot exceed $\binom{d+g}{d}$ homogeneous invariants whose degree is bounded by g . (Noether's degree bound.)

Example 17.16

The action of $\mathcal{C}_n$ on the two-dimensional space (η_1, η_2)

We consider the simple example of the action of the Abelian group $\mathcal{C}_n$ on the two-dimensional space (η_1, η_2) . Changing variables to $\mathbf{r} = \rho e^{i\phi} = \eta_1 + i\eta_2$, we immediately find the invariants $\mathbf{r}\mathbf{r}^* = \eta_1^2 + \eta_2^2$, and $\mathbf{r}^n|_{\phi=2\pi/n}$ give two linearly independent invariants of degree n , namely $\Re(\eta_1 + i\eta_2)^n = \rho^n \cos(n\phi)$ and $\Im(\eta_1 + i\eta_2)^n = \rho^n \sin(n\phi)$. However, the relation

$$(\mathbf{r}\mathbf{r}^*)^n = \mathbf{r}^n(\mathbf{r}^n)^* \Rightarrow (\eta_1^2 + \eta_2^2)^n = (\Re(\eta_1 + i\eta_2)^n)^2 + (\Im(\eta_1 + i\eta_2)^n)^2$$

restricts the algebraic independence of the three polynomials, and we choose $(\eta_1^2 + \eta_2^2)$ and $\Re(\eta_1 + i\eta_2)^n$ as the two independent invariants. A general invariant polynomial P can be constructed by forming two polynomials from these two *basic* or *primary invariants*, namely, $p(\eta_1^2 + \eta_2^2, \Re(\eta_1 + i\eta_2)^n)$ and $q(\eta_1^2 + \eta_2^2, \Re(\eta_1 + i\eta_2)^n)$, and writing

$$\begin{aligned} P &= p(\eta_1^2 + \eta_2^2, \Re(\eta_1 + i\eta_2)^n) + \Im(\eta_1 + i\eta_2)^n q(\eta_1^2 + \eta_2^2, \Re(\eta_1 + i\eta_2)^n) \\ &= p(\rho^2, \rho^n \cos(n\phi)) + \rho^n \sin(n\phi) q(\rho^2, \rho^n \cos(n\phi)), \end{aligned}$$

where $\rho^n \sin(n\phi)$ is an *auxiliary* or *secondary* polynomial.

Invariant theory

The invariant theory of finite groups is a well-developed mathematical field which combines elements of combinatorial and modern commutative algebra [161, 162, 163]. We are

interested here in the action of a finite group $\mathcal{G}$ on an m -dimensional vector space $\mathcal{R}^m$, and in particular on the set of invariant polynomials of the form

$$p(\mathbf{x}) = p(\Gamma(R)\mathbf{x}),$$

where $\mathbf{x} = (x_1, x_2, \dots, x_m)$, and $\Gamma(R)$ is the matrix Rep, generated by $R \in \mathcal{G}$ on $\mathcal{R}^m$. The sums and products of such polynomials are also invariants, and form a *ring* $[\mathcal{R}^{\mathcal{G}}]$. The goal here is to understand the structure of the invariant ring of polynomials with complex coefficients, i.e. in $\mathbb{C}$, with emphasis on those characteristics that are useful for computing invariants. We state the following properties of these polynomial invariants without proof:

- (i) The ring of invariants $[\mathcal{R}^{\mathcal{G}}]$ is also a *graded K -algebra*, i.e.

$$\mathbb{R}^G = \mathbb{R}_0^G \oplus \mathbb{R}_1^G \oplus \dots \mathbb{R}_i^G \oplus \dots, \text{ with } \mathbb{R}_i^G \mathbb{R}_j^G \subset \mathbb{R}_{i+j}^G,$$

where $\mathbb{R}_i^G$ contains invariant homogeneous polynomials of degree d_i , and the *gradation* is such that $d_0 \leq d_1 \leq \dots \leq d_m$. We know from a celebrated theorem of Hilbert that K -algebras are *finitely generated*, i.e. can be generated from a finite set of generators, called an *integrity basis*.

- (ii) As a matter of fact, we know that *there exist m , but not $m+1$ algebraically independent homogeneous invariants* Θ_i of degree $d_1 \leq d_2 \leq \dots \leq d_m$. These m invariants generate an algebraic ring over the complex field $\mathbb{C}$ which we denote by $\mathcal{C}[\Theta_1, \Theta_2, \dots, \Theta_m]$. Algebraic independence among polynomials means that no polynomial f exists such that $f(p_1(\mathbf{x}), p_2(\mathbf{x}), \dots) = 0$, unless all coefficients are zero. Notice that for nonzero coefficients $f = 0$ if the polynomials share a common root.

Example 17.17

The group $\mathcal{C}_i$

The group $\mathcal{C}_i = \left\{ \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} \right\}$, has invariant polynomials $\Theta_1 = x^2$, $\Theta_2 = y^2$, $\Theta_3 = xy$. We may choose the polynomial basis as $\{\Theta_1, \Theta_2\}$, since $\Theta_3^2 - \Theta_1\Theta_2 = 0$.

- (iii) A set $\{\Theta_1, \Theta_2, \dots, \Theta_m\}$ of m homogeneous invariant polynomials with positive degree is called a *homogeneous system of parameters* (h.s.o.p.), if $[\mathcal{R}^{\mathcal{G}}]$ is a finitely generated *module*¹ over $\mathbb{C}[\Theta_1, \Theta_2, \dots, \Theta_m]$. As h.s.o.p.s the polynomials Θ_i have no common roots except 0.

¹ A vector space M over a field R is a set of objects (vectors), that can be added, subtracted, and multiplied by scalars (members of the underlying field). Thus M is an Abelian group under addition, and for each $r \in R$ and $\mathbf{x} \in M$ we have an element $r\mathbf{x} \in M$. Scalar multiplication is distributive and associative, and the multiplicative identity of the field acts as an identity on vectors. Formally, $r(\mathbf{x} + \mathbf{y}) = r\mathbf{x} + r\mathbf{y}$; $(r + s)\mathbf{x} = r\mathbf{x} + s\mathbf{x}$; $r(s\mathbf{x}) = (rs)\mathbf{x}$; $1\mathbf{x} = \mathbf{x}$ for all $\mathbf{x}, \mathbf{y} \in M$ and $r, s \in R$. A module is just a vector space over a ring.

- (iv) One possible form of an invariant polynomial expressed in terms of Θ_i is written as

$$I(x) \Big|_{x=1} = \prod_{i=1}^m [1 - \Theta_i x^{d_i}]^{-1} = 1 + \sum_i \Theta_i x^{d_i} + \dots,$$

where d_i is the degree of Θ_i . If we replace every Θ_i in this expansion by unity, we obtain

$$\mathcal{H}(x) = \prod_{i=1}^m \frac{1}{[1 - x^{d_i}]} = 1 + \sum_i x^{d_i} + \dots \quad (17.106)$$

Every factor $(1 - x^{d_i})$ that appears in the denominator on the l.h.s. of (17.106) implies that one of the elements of the integrity basis must be of degree d_i . We also note that the value d_i may be degenerate, and hence the coefficient of x^{d_i} in the expansion on the r.h.s. of (17.106) is just the number of linearly independent invariant polynomials of degree d_i . $\mathcal{H}(x)$ in (17.106) is known as the *Hilbert series*.

- (v) The invariant polynomials of finite groups form a ring $\mathbb{R}^G$ that is finitely generated over a subring of h.s.o.p. In such a case, there exists, in addition, a set of homogeneous invariants $\Xi_j \in [\mathbb{R}^G]$, $j = 1, \dots, t$ of degree e_j such that

$$\mathbb{R}^G = \bigoplus_{j=1}^t \Xi_j \mathcal{C}[\Theta_1, \Theta_2, \dots, \Theta_m] = \left(\bigoplus_{j=1}^t \Xi_j \right) \mathcal{C}[\Theta_1, \Theta_2, \dots, \Theta_m], \quad (17.107)$$

with $\Xi_1 = 1$, i.e. $e_1 = 0$. Such rings are called Cohen–Macaulay rings.

We find that any invariant in $\mathbb{R}^G$ may be uniquely written as a linear combination of the Ξ_i with polynomials in the Θ_i as coefficients. Usually, the Θ_i are called *primary* or *basic* invariants, and the Ξ_j , *secondary* or *auxiliary* invariants.

This definition implies that any invariant can be written as a polynomial in $\Theta_1, \Theta_2, \dots, \Theta_m$, or as such a polynomial plus Ξ_j times such a polynomial plus $\dots$. Or, loosely speaking, it tells us that in the construction of an arbitrary invariant, $\Theta_1, \Theta_2, \dots, \Theta_m$ are “free” invariants that can be used as often as needed, while the Ξ_j s are “transient” invariants and can each be used once, at most.

Equations (17.106) and (17.107) suggest that the Molien function may be written as

$$\begin{aligned} \mathcal{M}(x) &= \frac{1}{g} \sum_{R \in G} \frac{1}{\det[\mathbb{I} - x \Gamma(R)]} \\ &= \left(\sum_j x^{e_j} \right) \mathcal{H}(x) = \frac{\sum_j x^{e_j}}{\prod_{i=1}^m (1 - x^{d_i})} = \frac{N(x)}{D(x)}. \end{aligned} \quad (17.108)$$

Multiplying (17.108) by $(1 - x)^m$, and using the identity

$$\frac{1 - x^n}{1 - x} = \sum_{j=0}^{n-1} x^j,$$

we get

$$\begin{aligned} \frac{1}{g} \sum_{R \in G} \frac{(1 - x)^m}{\det[\mathbb{I} - x \Gamma(R)]} &= \left(\sum_j x^{e_j} \right) \prod_{i=1}^m \frac{(1 - x)}{(1 - x^{d_i})} \\ &= \frac{\sum_j x^{e_j}}{\prod_{i=1}^m (\sum_{l=0}^{d_i-1} x^l)}. \end{aligned} \quad (17.109)$$

The only term on the l.h.s. that has a pole of order m at $x = 1$ is the term $(1 - x)^{-m}$ corresponding to E , hence the only surviving term in the summation on the l.h.s. of (17.109) is 1, and setting the number of secondary invariants as t , we get

$$t g = \prod_{i=1}^m d_i. \quad (17.110)$$

Example 17.18

The group C_i of Example 17.13

The invariant polynomials $\Theta_1 = x^2$, $\Theta_2 = y^2$, $\Theta_3 = xy$ may form a Cohen–Macaulay polynomial basis with $d_1 = d_2 = e_2 = 2$. Any invariant can be described as

$$\mathbb{C}[x^2, y^2] \oplus xy \mathbb{C}[x^2, y^2],$$

i.e. as a polynomial in x^2 and y^2 plus xy times another such polynomial. For example,

$$(x + y)^4 = (x^2)^2 + (y^2)^2 + 6(x^2)(y^2) + xy(4x^2 + 4y^2).$$

The structure of the corresponding Molien function, given by

$$\mathcal{M}(x) = \frac{1}{2} \left[\frac{1}{(1-x)^2} + \frac{1}{(1+x)^2} \right] = \frac{1+x^2}{(1-x^2)^2},$$

mirrors the above polynomial invariants, namely, the denominator suggests Θ_1 and Θ_2 of degree 2, and the numerator $\Xi_1 = 1$ and Ξ_2 of degree 2.

Example 17.19

The three-dimensional cyclic group of order 4

$$\left\{ \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \right\}.$$

Its Molien function is

$$\begin{aligned} \mathcal{M}(x) &= \frac{1}{4} \left[\frac{1}{(1-x)^3} + \frac{2}{(1+x)(1+x^2)} + \frac{1}{(1+x)^2(1-x)} \right] \\ &= \frac{1-x+x^2+x^3}{(1+x)^2(1+x^2)(1-x)^3} = \frac{1-x+x^2+x^3}{(1-x^2)^2(1+x^2)(1-x)} \\ &= \frac{(1-x+x^2+x^3)(1+x)}{(1-x^2)^2(1-x^4)} = \frac{1+2x^3+x^4}{(1-x^2)^2(1-x^4)}. \end{aligned}$$

Its denominator suggests an h.s.o.p. set of three Θ_i s, two of degree 2 and one of degree 4. We choose

$$\Theta_1 = x^2 + y^2, \quad \Theta_2 = z^2, \quad \Theta_3 = x^4 + y^4.$$

The number of secondary invariants is $2 \times 2 \times 4/4 = 4$, which we may identify with the aid of the numerator to have $e_2 = e_3 = 3$, and $e_4 = 4$. Using the projection operator $\mathcal{P}_1$ we obtain

$$\Xi_1 = 1, \quad \Xi_2 = xyz, \quad \Xi_3 = x^2y - xy^2, \quad \Xi_4 = x^3y - xy^3.$$

Example 17.20

The group $\mathbf{G} = \mathcal{Z}_4 = \{\mathbf{E}, \mathbf{M}, \mathbf{M}^2, \mathbf{M}^3\}$

With $M = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$, the Molien series of G is given by

$$\begin{aligned} \mathcal{M} &= \frac{1}{4} \left[\frac{1}{(1-x)^2} + \frac{2}{1+x^2} + \frac{1}{(1+x)^2} \right] \\ &= \frac{1+x^4}{(1-x^2)(1-x^4)} \Leftrightarrow \text{Molien function} \\ &= 1 + x^2 + 3x^4 + 3x^6 + 5x^8 + 5x^{10} + O(x^{12}) \Leftrightarrow \text{Molien series.} \end{aligned}$$

We can proceed to determine the algebraically independent and auxiliary invariants in two ways. First, the structure of the Molien function suggests that there may be two independent invariants,

$$\Theta_1 \in R_2^{\mathcal{G}} \rightarrow (1-x^2), \quad \Theta_2 \in R_4^{\mathcal{G}} \rightarrow (1-x^4),$$

and two auxiliary invariants,

$$1 \rightarrow 1, \quad \eta \in R_4^{\mathcal{G}} \rightarrow x^4,$$

such that invariants $f \in R^{\mathcal{G}}$ can be written uniquely in the form $p(\Theta_1, \Theta_2) + \eta \cdot q(\Theta_1, \Theta_2)$, where p and q belong to $\mathbf{C}[x_1, x_2]$. More succinctly, we could write this condition as

$$R^{\mathcal{G}} = \mathbf{C}[\Theta_1, \Theta_2] \oplus \eta \cdot \mathbf{C}[\Theta_1, \Theta_2] = \mathbf{C}[\Theta_1, \Theta_2] (1 \oplus \eta),$$

the sum $\oplus$ being a vector space direct sum (or a $\mathbf{C}$ -module direct sum). Examining the Molien function, it is easy to construct the integrity basis as

$$\Theta_1 = x_1^2 + x_2^2, \quad \Theta_2 = x_1^2 x_2^2, \quad \eta = x_1^3 x_2 - x_1 x_2^3.$$

Alternatively, we use the coefficients of the Molien series to construct

$$\begin{aligned} R_0^{\mathcal{G}} &= \{1\}, \\ R_2^{\mathcal{G}} &= \{x_1^2 + x_2^2\}, \\ R_4^{\mathcal{G}} &= \{x_1^4 + x_2^4, x_1^2 x_2^2, x_1^3 x_2 - x_1 x_2^3\}. \end{aligned}$$

Since the number of independent invariants is 2, we choose them as the algebraically independent polynomials $\Theta_1 = x_1^2 + x_2^2$ and $\Theta_2 = x_1^4 + x_2^4$, with $\mathcal{M}_p(x) = 1/(1-x^2)(1-x^4)$. Next, we find the degrees of the auxiliary invariants by

$$\mathcal{M}_a(x) = \frac{\mathcal{M}(x)}{\mathcal{M}_p(x)} = 1 + x^4,$$

which reveals that there are two auxiliary invariants, one with degree 0, and the other with degree 4. But, since $x_1^2 x_2^2 = \Theta_1^2 - \Theta_2$, we choose $\eta = x_1^3 x_2 - x_1 x_2^3$. Consequently, any invariant may be expressed uniquely in the following form:

$$1 \cdot p(x_1^2 + x_2^2, x_1^4 + x_2^4) + (x_1^3 x_2 - x_1 x_2^3) q(x_1^2 + x_2^2, x_1^4 + x_2^4).$$

Pseudoreflexion groups

A pseudoreflexion group, $\mathcal{G}_p$ acting on a space $\mathcal{R}^m$ of dimension m is generated by set of $r(m \times m)$ matrices, $\Gamma(R_p)$, each having $m-1$ unity eigenvalues, while the m th eigenvalue is an n th root of unity, if the pseudoreflexion has a cycle n , namely,

$$\det[\lambda \mathbb{I} - \Gamma(R_p)] = (\lambda - 1)^{m-1}(\lambda - \rho), \quad \rho^n = 1.$$

For $n = 2$ the operation is just a simple reflection.

A pseudoreflexion group is not a property of the abstract group, it is defined by its matrix Rep engendered on the space $\mathcal{R}^m$, for example the group $\mathcal{D}_6$ is a reflection group when engendered on the two-dimensional hexagon, yet the three-dimensional Rep of $\mathcal{D}_6$ is not.

The ring of invariants of a pseudoreflexion group is just $\mathbb{C}[\Theta_1, \Theta_2, \dots, \Theta_m]$, i.e. only $\Xi_1 = 1$ is allowed. Its Molien function is given by

$$\mathcal{M}(x) = \frac{1}{g_p} \sum_{R \in \mathcal{G}_p} \frac{1}{\det[\mathbb{I} - x \Gamma(R)]} = \prod_{i=1}^m \frac{1}{(1 - x^{d_i})}, \quad (17.111)$$

and with $t = 1$ in (17.110) we obtain

$$\prod_{i=1}^m d_i = g_p. \quad (17.112)$$

We find in the middle expression of (17.111) that the only term that has a pole of order m at $x = 1$ is the term $(1-x)^{-m}$ corresponding to E . Pseudoreflexions have terms of the form $(1-x)^{1-m}(1-\rho x)^{-1}$, where $\rho = \det \Gamma(R_p)$. Thus, the first two terms in the Laurent expansion of $\mathcal{M}(x)$ are

$$\mathcal{M}(x) = \frac{1}{g} \left[\frac{1}{(1-x)^m} + \frac{1}{(1-x)^{m-1}} \sum_{R_p} \frac{1}{1-\rho x} + \dots \right],$$

but since every pseudoreflexion R_p must have its inverse R_p^{-1} in $\mathcal{G}_p$, we find that

$$\frac{1}{1-\rho} + \frac{1}{1-\rho^{-1}} = \frac{1}{1-\rho} - \frac{\rho}{1-\rho} = 1.$$

Hence, the Laurent series becomes

$$\mathcal{M}(x) = \frac{1}{g_p} \left[\frac{1}{(1-x)^m} + \frac{r}{2} \frac{1}{(1-x)^{m-1}} + \cdots \right], \quad (17.113)$$

where r is the number of pseudoreflections. Taking the Laurent expansion of the r.h.s. of (17.111) about $x = 1$, we get

$$\prod_{i=1}^m \frac{1}{(1-x^{d_i})} \Big|_{x=1} = \frac{1}{\prod_i d_i} \frac{1}{(1-x)^m} + \frac{(\sum_i d_i) - m}{2 \prod_i d_i} \frac{1}{(1-x)^{m-1}} + O((1-x)^{2-m}).$$

Comparing the last expression with (17.113) we obtain

$$r = \left(\sum_i d_i \right) - m. \quad (17.114)$$

Example 17.21

Integrity basis for the two-dimensional matrix Reps of m , $2mm$, $4mm$ engendered on the OP space (η_1, η_2)

- (i) The group $1m = \left\{ \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \right\}$ has the Molien function

$$\mathcal{M}(x) = \frac{1}{2} \left[\frac{1}{(1-x)^2} + \frac{1}{(1-x)(1+x)} \right] = \frac{1}{(1-x)(1-x^2)}$$

with one invariant of degree 1, $\eta_1 + \eta_2$, and a degree-2 invariant $\eta_1^2 + \eta_2^2$.

- (ii) The group

$$2mm = \left\{ \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}, \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix} \right\}$$

has the Molien function

$$\mathcal{M}(x) = \frac{1}{4} \left[\frac{1}{(1-x)^2} + \frac{1}{(1+x)^2} + \frac{2}{(1-x)(1+x)} \right] = \frac{1}{(1-x^2)^2},$$

showing two degree-2 invariants, which can be written as $\eta_1^2 + \eta_2^2$ and $\eta_1 \eta_2$.

- (ii) The group $4mm = 2mm + \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \otimes 2mm$ has the Molien function

$$\begin{aligned} \mathcal{M}(x) &= \frac{1}{8} \left[\frac{1}{(1-x)^2} + \frac{1}{(1+x)^2} + \frac{2}{1+x^2} + \frac{4}{(1-x)(1+x)} \right] \\ &= \frac{1}{(1-x^2)(1-x^4)} = 1 + x^2 + 2x^4 + \cdots, \end{aligned}$$

which shows that it has an IB comprising of one degree-2 and one degree-4 invariant, which can be written as $\eta_1^2 + \eta_2^2$ and $\eta_1^4 + \eta_2^4$. The expansion shows that there are two degree-4 invariant polynomials which we choose as $\eta_1^4 + \eta_2^4$ and $\eta_1^2 \eta_2^2$.

Table 17.10. *Integrity basis.*

Image	Invariant polynomials	Image	Invariant polynomials
$\mathcal{C}_n$	$\rho^2; \rho^n \cos(n\phi); \rho^n \sin(n\phi)$	$\mathcal{C}_{nv}$	$\rho^2; \rho^n \cos(n\phi)$
$\mathcal{T}$	$\rho^2 = \sum_{j=1}^3 \eta_j^2; B_2 = \prod_{j=1}^3 \eta_j$ $B_3 = \sum_{j=1}^3 \eta_j^4$ $B_4 = (\eta_1^2 - \eta_2^2)(\eta_2^2 - \eta_3^2)(\eta_3^2 - \eta_1^2)$	$\mathcal{T}_h$	$\rho^2; B_3; B_4; B_5 = \prod_{j=1}^3 \eta_j^2$
$\mathcal{O}$	$\rho^2; B_3; B_5; B_2 \cdot B_4$	$\mathcal{O}_h$	$\rho^2; B_3; B_5$
$\mathcal{Y}$	$\rho^2;$ $B_6 = (a\eta_1^2 - \eta_2^2)(a\eta_2^2 - \eta_3^2)(a\eta_3^2 - \eta_1^2)$ $B_7 = B_3 \cdot (b\eta_1^2 - \eta_2^2)(b\eta_2^2 - \eta_3^2)$ $\quad \times (b\eta_3^2 - \eta_1^2)$ $B_8 = B_2 \cdot f(\eta_1, \eta_2, \eta_3)f(\eta_3, \eta_1, \eta_2)$ $\quad \times f(\eta_2, \eta_3, \eta_1)$	$\mathcal{Y}_h$	$\rho^2; B_6 B_7$
$\mathcal{T}_d$	$\rho^2; B_2; B_3$		

$$a = (3 + \sqrt{5})/2; b = (7 + 3\sqrt{5})/2$$

$$f(\eta_1, \eta_2, \eta_3) = b\eta_1^4 + \frac{1}{b}\eta_2^4 + \eta_3^4 - \eta_1^2\eta_2^2 - 2\eta_3^2 \left(\frac{1 + \sqrt{5}}{2} \eta_1 + \frac{2}{1 + \sqrt{5}} \eta_2 \right)$$

All these groups are reflection generated and their integrity bases comprise primary invariants only.

In three-dimensions, the maximal discrete subgroups of $\mathcal{O}(3)$ generated by reflections are $\mathcal{C}_{nv}$, $\mathcal{D}_{nh}$, $\mathcal{T}_d$, $\mathcal{O}_h$, $\mathcal{Y}$; all the other subgroups of $\mathcal{O}(3)$ are normal subgroups of these groups with Abelian quotient groups.

17.3.2 Group action and OP image groups

The action of elements of a group on a vector space engenders a matrix Rep of the group. Here we are interested in the action of the elements of $\mathbb{S}_0$ on the OP basis set that engenders an active matrix Irrep $(^{*\mathbf{k},\lambda})\Gamma$.

The kernel group

We recall from Section 17.2.7 that some subset K of operations of $\mathbb{S}_0$ is mapped by $(^{*\mathbf{k},\lambda})\Gamma$ onto the identity matrix of the Irrep, namely,

$$(^{*}\mathbf{k},\lambda)\Gamma(K) = \mathbb{I};$$

and constitutes the *kernel* of the Irrep $(^{*\mathbf{k},\lambda})\Gamma$. The set K forms a group called the *kernel group* $\mathbb{K}$. The kernel group is a normal subgroup of $\mathbb{S}_0$, $\mathbb{K} \prec \mathbb{S}_0$, since, for any $R \in \mathbb{S}_0$ and

$K \in \mathbb{K}$, we have

$$({}^{*\mathbf{k},\lambda})\mathbf{\Gamma}(R)({}^{*\mathbf{k},\lambda})\mathbf{\Gamma}(K)({}^{*\mathbf{k},\lambda})\mathbf{\Gamma}^{-1}(R) = \mathbb{I} = ({}^{*\mathbf{k},\lambda})\mathbf{\Gamma}(K') \implies RKR^{-1} = K'.$$

It should be stressed that the stars of wavevectors allowed in strictly crystalline-to-crystalline transitions are either $\mathbf{0}$ or lie at some high-symmetry points on the BZ boundary; such vectors have the form

$$\mathbf{k} = \sum_i q_i \mathbf{b}_i,$$

where the q_i s take rational numbers with denominators of 2, 3, or 4. The corresponding kernel translation group $\mathbb{T}_{*\mathbf{k}}$ has infinite order, so that

$$\mathbb{T} = \sum_{j=1}^l (E|\mathbf{t}_j) \mathbb{T}_{*\mathbf{k}},$$

where $l \leq 12$. $\mathbb{K}$ has an infinite order, since $\mathbb{T}_{*\mathbf{k}} \prec \mathbb{K}$ is its translation subgroup.

The image group

Since $\mathbb{K} \prec \mathbb{S}_0$, we write the left-coset expansion

$$\mathbb{S}_0 = \sum_{j=1}^{i_0} R_{cj} \mathbb{K} = \sum_{j=1}^{i_0} \mathbb{K} R_{cj},$$

and notice that all the elements of the coset $R_{cj} \mathbb{K}$ are represented by the matrix $({}^{*\mathbf{k},\lambda})\mathbf{\Gamma}(R_{cj})$, since $({}^{*\mathbf{k},\lambda})\mathbf{\Gamma}(\mathbb{K}) = \mathbb{I}$. The quotient group

$$\mathbb{Q} = \frac{\mathbb{S}_0}{\mathbb{K}}$$

is then isomorphic to the group of distinct matrices of the Irrep $({}^{*\mathbf{k},\lambda})\mathbf{\Gamma}$; we call this matrix group the *image* group $\mathcal{I}_0$ of $\mathbb{S}_0$ in $({}^{*\mathbf{k},\lambda})\mathbf{\Gamma}$. The order of $\mathcal{I}_0$, i_0 , is finite despite the infinite order of $\mathbb{S}_0$. Moreover, $\mathcal{I}_0$ is a real and unitary Rep, and hence represented by orthogonal matrices, defined in the d -dimensional space of the OP. In other words,

$$\mathcal{I}_0 \subset \mathcal{O}(d).$$

Example 17.22

The kernel and image groups associated with the $\bar{\Gamma}$, $\bar{X}$, and $\bar{M}$ points of the two-dimensional space-group $p4mm$

- (i) **The $\bar{\Gamma}$ -point** (${}^{*\mathbf{k}} = \mathbf{0}$) The group of the wavevector $\mathbb{G}_{\bar{\Gamma}} = P4mm$, with Irreps of coset representatives given in Table 17.11. The first four Irreps are one-dimensional and support a one-dimensional order parameter. It is obvious that for $({}^1)\Gamma$ the kernel $\mathbb{K} = p4mm$, and the image is just $\mathcal{I}_0 = \mathcal{C}_1$. It is also obvious that this Irrep is the identity Irrep of $p4mm$, which does not lead to a phase transition and should be excluded.

As for $({}^2)\Gamma$, the kernel $\mathbb{K} = p4$ and since

$$p4mm = \mathbb{K} + \sigma_v \mathbb{K},$$

Table 17.11. *The character table for the Irreps of*
 $\mathcal{P}_{\mathbf{k}} = 4mm(\mathcal{C}_{4v})$.

		E	C_2	$2C_4$	$2\sigma_v$	$2\sigma_d$
$(1)\bar{M}$	$(1)\bar{\Gamma}$	1	1	1	1	1
$(2)\bar{M}$	$(2)\bar{\Gamma}$	1	1	1	-1	-1
$(3)\bar{M}$	$(3)\bar{\Gamma}$	1	1	-1	1	-1
$(4)\bar{M}$	$(4)\bar{\Gamma}$	1	1	-1	-1	1
$(5)\bar{M}$	$(5)\bar{\Gamma}$	2	-2	0	0	0

the image group is just the quotient group

$$\mathbb{Q} = (E, \sigma_v) = \mathcal{I}_0,$$

so that

$$\mathbf{\Gamma}(\mathcal{I}_0) = 1, -1.$$

This image group is also shared by $(3)\Gamma$ and $(4)\Gamma$, but with kernel group $p2mm$.

Finally, $(5)\Gamma$ is the 2D vector Irrep corresponding to $\mathcal{I}_0 = 4mm$.

(ii) **The $\bar{X}$ -point** ($\star\mathbf{k} = (\pi/a, 0), (0, \pi/a)$) The point-group of the wavevector is

$$\mathcal{G}_{\bar{X}} = 2mm$$

with 1D Irreps, Table 17.12.

The ground representation is two-dimensional, and given by

$$D(\mathcal{G}_{\bar{X}}) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad D(R \notin \mathcal{G}_{\bar{X}}) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.$$

The induced Irreps of $p4mm$ at $\bar{X}$ are shown in Table 17.13, with OP-space dimension 2.

Moreover, the kernel translation group is

$$\mathbb{T}_{\star\bar{X}} = (m_1a, m_2a), \quad m_1, m_2 \text{ even},$$

so that

$$\mathbb{T} = \mathbb{T}_{\star\bar{X}} + (E|(a, 0)) \mathbb{T}_{\star\bar{X}} + (E|(0, a)) \mathbb{T}_{\star\bar{X}} + (E|(a, a)) \mathbb{T}_{\star\bar{X}}.$$

(iii) **The $\bar{M}$ -point** ($\star\mathbf{k} = (\pi/a, \pi/a)$) $\star\bar{M}$ has one branch, the kernel translation group is

$$\begin{aligned} \mathbb{T}_{\bar{M}} &= (m_1a, m_2a), \quad m_1 + m_2 = 2n \\ &= (ma, (2n - m)a), \end{aligned}$$

and

$$\mathbb{T} = ((E|\mathbf{0}), (E|(0, a))) \mathbb{T}_{\bar{M}}.$$

Table 17.12. *The character table for the Irreps of $\mathcal{P}_{\bar{X}} = 2mm (\mathcal{C}_{2v})$.*

	E	C_2	σ_x	σ_y
$^{(1)}X$	1	1	1	1
$^{(2)}X$	1	1	-1	-1
$^{(3)}X$	1	-1	1	-1
$^{(4)}X$	1	-1	-1	1

Table 17.13. *Irreps $^*\bar{X}$ for the space-group $p4mm$.*

	E	C_4 C_4^3	C_2	σ_x σ_y	σ_{xy} $\sigma_{\bar{x}\bar{y}}$	$\mathbb{K}$	$\mathcal{I}_0$
$^{(1)} (^*\bar{X})$	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$	$2mm$	$m_{\bar{x}\bar{y}}$
$^{(2)} (^*\bar{X})$	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix}$	$\begin{bmatrix} 0 & -1 \\ -1 & 0 \end{bmatrix}$	2	$2m_d m_d$
$^{(3)} (^*\bar{X})$	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix}$	$\begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$	$\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$	1	4mm
$^{(4)} (^*\bar{X})$	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix}$	$\begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix}$	$\begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} 0 & -1 \\ -1 & 0 \end{bmatrix}$	1	4mm

The point-group of the wavevector is

$$\mathcal{P}_{\bar{M}} = \mathcal{C}_{4v}.$$

Example 17.23

Construction of $\Delta\Phi$ for the space-group $p4mm$

We retain terms up to fourth degree in the expansion of $\Delta\Phi$.

(i) **The $\bar{\Gamma}$ -point**

- (a) The 1D Irreps $^{(2)}\Gamma$, $^{(3)}\Gamma$, $^{(4)}\Gamma$ have an integrity basis η^2 , and the $\Delta\Phi$ can be written as

$$\Delta\Phi = \frac{1}{2}a_0(T - T_c)\eta^2 + \frac{1}{4}b\eta^4.$$

- (b) For the 2D Irrep $^{(5)}\Gamma$, $\mathcal{I}_0 = 4mm$. We find from the corresponding Molien function (Example 17.21),

$$\mathcal{M}(x) = \frac{1}{(1-x^2)(1-x^4)} = 1 + x^2 + 2x^4 + \dots,$$

that there are two independent polynomials of degree 4; choosing $\eta_1^4 + \eta_2^4$, we may then derive a second linearly independent fourth-degree invariant from $(\eta_1^2 + \eta_2^2)^2$ as $\eta_1^2\eta_2^2$, and write $\Delta\Phi$ as

$$\Delta\Phi(\eta_1, \eta_2) = \frac{1}{2}a_0(T - T_c)(\eta_1^2 + \eta_2^2) + \frac{1}{4}b(\eta_1^4 + \eta_2^4) + \frac{1}{4}c\eta_1^2\eta_2^2$$

(ii) **The $\bar{X}$ -point**

$^{(1)}(*\bar{X})$: $\mathcal{I}_0 = 1m$

$$\mathcal{M}(x) = \frac{1}{(1-x)(1-x^2)} = 1 + x + 2x^2 + 2x^3 + 3x^4 + \dots$$

From the integrity bases $\eta_1 + \eta_2$ and $\eta_1^2 + \eta_2^2$, we find that the former is not actually an invariant of the translation group since

$$(E|\mathbf{t})(\eta_1 + \eta_2) = e^{(\pi/a, 0) \cdot \mathbf{t}} \eta_1 + e^{(0, \pi/a) \cdot \mathbf{t}} \eta_2$$

and should be discarded. Consequently, its square $(\eta_1 + \eta_2)^2$, which yields an independent second-degree polynomial $\eta_1\eta_2$, and its cube $(\eta_1 + \eta_2)^3$, which together with $(\eta_1 + \eta_2)(\eta_1^2 + \eta_2^2)$ produces the two independent cubic invariant polynomials $\eta_1^3 + \eta_2^3$ and $\eta_1^2\eta_2 + \eta_1\eta_2^2$, should also be discarded. We are then left with the second-degree polynomial $\eta_1^2 + \eta_2^2$, which yields two independent fourth-degree polynomial invariants $\eta_1^4 + \eta_2^4$ and $\eta_1^2\eta_2^2$. The third independent invariant of degree 4, predicted by the Molien function expansion, has to be dropped, since it can only be constructed from $(\eta_1 + \eta_2)^4$, as $\eta_1^3\eta_2 + \eta_1\eta_2^3$.

$^{(2)}(*\bar{X})$: $\mathcal{I}_0 = 2mm$

$$\mathcal{M}(x) = \frac{1}{(1-x^2)^2} = 1 + 2x^2 + 3x^4 + \dots$$

On the basis of the arguments given above, we have to discard $\eta_1\eta_2$ as a second-degree invariant, and we also find that there are only two independent fourth-degree polynomial invariants $\eta_1^4 + \eta_2^4$ and $\eta_1^2\eta_2^2$.

$^{(3)}(*\bar{X})$, $^{(4)}(*\bar{X})$: $\mathcal{I}_0 = 4mm$, which was presented above. Thus, we find that all the $\bar{X}$ -point images share the $\Delta\Phi$ expansion

$$\Delta\Phi(\eta_1, \eta_2) = \frac{1}{2}a_0(T - T_c)(\eta_1^2 + \eta_2^2) + \frac{1}{4}b(\eta_1^4 + \eta_2^4) + \frac{1}{2}c\eta_1^2\eta_2^2.$$

- (iii) **The $\bar{M}$ -point** The different Irreps of $\bar{M}$ mirror their counterparts at the $\bar{\Gamma}$ -point, since the quadratic and quartic invariants that appear are also invariants of the translation group.

We note that $\mathcal{I}_0$ is an *irreducible group over the space of the OP*, since it does not leave any subspace of that OP vector space invariant. An alternative definition of an irreducible group, with respect to vector space, is that its vector Rep over that space be irreducible.

It is then possible to enumerate the irreducible groups for any $\mathcal{O}(d)$ associated with a d -component OP.

For $d = 2$, $\mathcal{O}(2)$ has the irreducible subgroup $\mathcal{SO}(2)$, and the irreducible subgroup classes $\mathcal{C}_n$ and $\mathcal{C}_{nv}$.

For $d = 3$, $\mathcal{O}(3)$, in addition to $\mathcal{SO}(3)$, we have the seven irreducible group classes: $\mathcal{T}$, $\mathcal{T}_h$, $\mathcal{T}_d$, $\mathcal{O}$, $\mathcal{O}_h$, $\mathcal{V}$, $\mathcal{V}_h$.

The method of the normal subgroup series We have explained how the concept of kernel and image groups fits into the fabric of the Landau free energy synthesis, and helps to define the vector space of the OP. The idea that the kernel group must be a normal subgroup of the parent group, since its elements are represented by the identity matrix, suggests another procedure for constructing the required integrity basis.

We start with the observation that a polynomial P , defined in the image space, invariant under the operations of the image group $\mathcal{I}_0$, must also be invariant under the operations of the parent group. Our task is then reduced to determining the integrity basis of $\mathcal{I}_0$. This method then involves the identification, if possible, of a descending series of normal subgroups of $\mathcal{I}_0$, namely,

$$\mathcal{I}_0 \succ \mathcal{G}_1 \succ \mathcal{G}_2 \succ \cdots \succ \mathcal{G}_n \succ 1(E),$$

where $\mathcal{G}_{i+1}$ is a normal subgroup of $\mathcal{G}_i$. The factor groups $\frac{\mathcal{G}_i}{\mathcal{G}_{i+1}}$ are called factor groups of a *normal series*. We now describe a procedure for the construction of the integrity basis of $\mathcal{I}_0$ through successive steps, starting from the group 1 or $\mathcal{G}_n$, where the basic invariants of $\mathcal{G}_i$ are to be determined from those of $\mathcal{G}_{i+1}$.

For the sake of clarity we describe the method with the aid of an example, and follow by stating some rules.

Example 17.24

The case of A-15 compounds

As we showed in Example 17.11, for A-15 compounds, space-group $Pm3n(\mathcal{O}_h^3)$ has the two-dimensional Irrep $\Gamma_{12}(E_g)$ at $\mathbf{k} = \mathbf{0}$, OP (η_1, η_2) , with $\mathbb{K} = \{E, 3U, I, 3\sigma\}$, and

$$\mathcal{I}_0 = \left(\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \begin{pmatrix} \omega & 0 \\ 0 & \omega^2 \end{pmatrix}, \begin{pmatrix} \omega^2 & 0 \\ 0 & \omega \end{pmatrix}, \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \begin{pmatrix} 0 & \omega \\ \omega^2 & 0 \end{pmatrix}, \begin{pmatrix} 0 & \omega^2 \\ \omega & 0 \end{pmatrix} \right),$$

which is isomorphic to $\mathcal{C}_{3v}$. $\mathcal{C}_{3v}$ has the normal point-group

$$\mathcal{C}_3 = \left\{ \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \begin{pmatrix} \omega & 0 \\ 0 & \omega^2 \end{pmatrix}, \begin{pmatrix} \omega^2 & 0 \\ 0 & \omega \end{pmatrix} \right\},$$

$$\mathcal{C}_{3v} = \mathcal{C}_3 \oplus \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \mathcal{C}_3 = \mathcal{C}_3 \oplus A\mathcal{C}_3$$

of index 2; $A = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$. The normal series is

$$\mathcal{C}_{3v} \succ \mathcal{C}_3 \succ E.$$

Since Noether's theorem limits the maximum polynomial degree to 3, the order of $\mathcal{C}_3$, we find the following three possible invariants: $\mathcal{J}'_1 = \eta_1^3$, $\mathcal{J}'_2 = \eta_2^3$, $\mathcal{J}'_3 = \eta_1\eta_2$. Operating by the coset representative A , we get

$$A\mathcal{J}'_1 = \mathcal{J}'_2, A\mathcal{J}'_2 = \mathcal{J}'_1, A\mathcal{J}'_3 = \mathcal{J}'_3,$$

which shows that $\mathcal{J}'_3$ is invariant under $\mathcal{C}_{3v}$. The interchange of subscript indices under the action of A suggests that we may obtain invariants of $\mathcal{C}_{3v}$ by the following possible combinations

$$\begin{aligned} \mathcal{J}'_1 + A\mathcal{J}'_1 &= \mathcal{J}'_2 + A\mathcal{J}'_2 = \mathcal{J}'_1 + \mathcal{J}'_2, & \mathcal{J}'_1 A\mathcal{J}'_1 &= \mathcal{J}'_2 A\mathcal{J}'_2 = \mathcal{J}'_1 \mathcal{J}'_2, \\ \mathcal{J}'_1 A\mathcal{J}'_2 + A\mathcal{J}'_1 \mathcal{J}'_2 &= \mathcal{J}'_1{}^2 + \mathcal{J}'_2{}^2. \end{aligned}$$

In fact, we can only have two independent invariant polynomials, which we choose as $\mathcal{J}_1 = \mathcal{J}'_3$, $\mathcal{J}_2 = \mathcal{J}'_1 + \mathcal{J}'_2$; and we find that

$$\mathcal{J}'_1 \mathcal{J}'_2 = \mathcal{J}_1^3, \mathcal{J}'_1{}^2 + \mathcal{J}'_2{}^2 = \mathcal{J}_2^2 - 2\mathcal{J}_1^2.$$

These relations among invariant polynomials of different degrees are coined *syzygies*.

We may construct quadratic, cubic, and quartic monomials from the IB $\mathcal{J}_1 = \eta_1\eta_2$, $\mathcal{J}_2 = \eta_1^3 + \eta_2^3$, namely,

$$\begin{aligned} \Delta\Phi &= a' \eta_1\eta_2 + b' (\eta_1^3 + \eta_2^3) + c' \eta_1^2\eta_2^2 \\ &= a(\xi_1^2 + \xi_2^2) + b(\xi_1^3 - 3\xi_1\xi_2^2) + c(\xi_1^4 + \xi_2^4) \Leftrightarrow \begin{bmatrix} \eta_1 \\ \eta_2 \end{bmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & -i \\ 1 & i \end{pmatrix} \begin{bmatrix} \xi_1 \\ \xi_2 \end{bmatrix}. \end{aligned}$$

As we mentioned in Example 17.11, this free energy expansion does not satisfy the Landau condition, since it supports cubic invariants, and the ensuing transition is not continuous.

From the above example, we surmise the following steps and rules:

- (i) Construct the normal series of $\mathcal{I}_0$, preferably with indices $(g_{i-1}/g_i) \leq 3$.
- (ii) Determine the simple invariants of the lowest normal subgroup $\mathcal{G}_n$, $\mathcal{J}_j^{(n)}$.
- (iii) Operate on these invariants by the coset representative matrices, A_i , $\mathcal{G}_{n-1} = \sum_i A_i \mathcal{G}_n$ and obtain the polynomials $A_i \mathcal{J}_j^{(n)}$.

(a) Rule 1: for index-2 subgroups construct new invariants in the form

$$\mathcal{J}_j^{(n)} + A\mathcal{J}_j^{(n)}; \quad \mathcal{J}_j^{(n)} \times A\mathcal{J}_j^{(n)}; \quad \mathcal{J}_j^{(n)} \times A\mathcal{J}_k^{(n)} + A\mathcal{J}_j^{(n)} \times \mathcal{J}_k^{(n)}$$

(b) Rule 2: for index-3 subgroups construct new invariants in the form

$$\begin{aligned} & \mathcal{J}_j^{(n)} + A_1\mathcal{J}_j^{(n)} + A_2\mathcal{J}_j^{(n)} \\ & \mathcal{J}_j^{(n)} \times A_1\mathcal{J}_j^{(n)} \times A_2\mathcal{J}_j^{(n)} \\ & \mathcal{J}_j^{(n)} \times A_1\mathcal{J}_j^{(n)} + A_1\mathcal{J}_j^{(n)} \times A_2\mathcal{J}_j^{(n)} + A_2\mathcal{J}_j^{(n)} \times \mathcal{J}_j^{(n)} \\ & \mathcal{J}_j^{(n)} \times A_1\mathcal{J}_j^{(n)} \left(\mathcal{J}_j^{(n)} - A_1\mathcal{J}_j^{(n)} \right) + A_1\mathcal{J}_j^{(n)} \times A_2\mathcal{J}_j^{(n)} \left(A_1\mathcal{J}_j^{(n)} - A_2\mathcal{J}_j^{(n)} \right) \\ & \quad + A_2\mathcal{J}_j^{(n)} \times \mathcal{J}_j^{(n)} \left(A_2\mathcal{J}_j^{(n)} - \mathcal{J}_j^{(n)} \right) \\ & \mathcal{J}_j^{(n)} \times \mathcal{J}_k^{(n)} + A_1\mathcal{J}_j^{(n)} \times A_1\mathcal{J}_k^{(n)} + A_2\mathcal{J}_j^{(n)} \times A_2\mathcal{J}_k^{(n)} \\ & \mathcal{J}_j^{(n)} \times A_1\mathcal{J}_j^{(n)} \times A_2\mathcal{J}_k^{(n)} + A_1\mathcal{J}_j^{(n)} \times A_2\mathcal{J}_j^{(n)} \times \mathcal{J}_k^{(n)} + A_2\mathcal{J}_j^{(n)} \times \mathcal{J}_j^{(n)} \times A_1\mathcal{J}_k^{(n)} \\ & \mathcal{J}_j^{(n)} \times A_1\mathcal{J}_k^{(n)} \times A_2\mathcal{J}_k^{(n)} + A_1\mathcal{J}_j^{(n)} \times A_2\mathcal{J}_k^{(n)} \times \mathcal{J}_k^{(n)} + A_2\mathcal{J}_j^{(n)} \times \mathcal{J}_k^{(n)} \times A_1\mathcal{J}_k^{(n)} s \\ & \mathcal{J}_j^{(n)} \left(A_1\mathcal{J}_k^{(n)} - A_2\mathcal{J}_k^{(n)} \right) + A_1\mathcal{J}_j^{(n)} \left(A_2\mathcal{J}_k^{(n)} - \mathcal{J}_1^{(n)} \right) + A_2\mathcal{J}_j^{(n)} \left(\mathcal{J}_k^{(n)} - A_2\mathcal{J}_k^{(n)} \right) \\ & \mathcal{J}_j^{(n)} \times A_1\mathcal{J}_j^{(n)} \left(\mathcal{J}_k^{(n)} - A_1\mathcal{J}_k^{(n)} \right) + A_1\mathcal{J}_j^{(n)} \times A_2\mathcal{J}_j^{(n)} \left(A_1\mathcal{J}_k^{(n)} - A_2\mathcal{J}_k^{(n)} \right) \\ & \quad + A_2\mathcal{J}_j^{(n)} \times \mathcal{J}_j^{(n)} \left(A_2\mathcal{J}_k^{(n)} - \mathcal{J}_k^{(n)} \right) \\ & \mathcal{J}_k^{(n)} \times A_k\mathcal{J}_j^{(n)} \left(\mathcal{J}_j^{(n)} - A_1\mathcal{J}_j^{(n)} \right) + A_1\mathcal{J}_k^{(n)} \times A_2\mathcal{J}_k^{(n)} \left(A_1\mathcal{J}_j^{(n)} - A_2\mathcal{J}_j^{(n)} \right) \\ & \quad + A_2\mathcal{J}_k^{(n)} \times \mathcal{J}_k^{(n)} \left(A_2\mathcal{J}_j^{(n)} - \mathcal{J}_j^{(n)} \right) \end{aligned}$$

OP-space stabilizers, orbits, and strata: isotropy subgroups

We apply the concepts of stabilizers, orbits, and strata to the action of the image group $\mathcal{I}_0$ on the OP-space. Thus:

- (i) A vector $\boldsymbol{\eta}$ in OP-space is left invariant by its stabilizer subgroup.
- (ii) The actions of the remaining operations of $\mathcal{I}_0$ generate the $\boldsymbol{\eta}$ -orbit.
- (iii) The stabilizer subgroups of the remaining members of the $\boldsymbol{\eta}$ -orbit are obtained by conjugation.
- (iv) The orbits with common stabilizers form a stratum.

When such stabilizer subgroups are combined with the kernel group of the Irrep $(^{*\mathbf{k},\lambda})\Gamma$, we obtain the corresponding *isotropy* subgroups of $\mathbb{S}_0$ with respect to $(^{*\mathbf{k},\lambda})\Gamma$.

The kernel subgroup is the common intersection of all possible isotropy subgroups associated with the Irrep $(^{*\mathbf{k},\lambda})\Gamma$.

Each isotropy subgroup defines a possible low-symmetry phase. Thus, it follows that the value of the lowest minimum of $\Delta\Phi$ is found on at least one orbit, and that the isotropy groups of those points are proper subgroups of $\mathbb{S}_0$.

17.3.3 Finding the minima of the Landau free energy

Now that we have described several methods for the construction of a Landau free energy invariant under the operations of the covering group, we are set to discuss methods for its minimization.

Again, it is instructive to start the discussion with a typical example. We consider the minimization of $\Delta\Phi$ for a system with $p4mm$ space-group symmetry, and sort out the corresponding isotropy groups.

Example 17.25

Minima of $\Delta\Phi(\eta_1, \eta_2)$ and their corresponding isotropy subgroups in $p4mm$

As we demonstrated in Example 17.23, the Γ -, X - and M -points share the same $\Delta\Phi$ expansion. Rewriting the expression for $\Delta\Phi$ derived in Example 17.23 as

$$\Delta\Phi = \frac{1}{2}a_0(T - T_c)\xi^2 + \frac{1}{4}b\xi^4 + \frac{1}{4}(c - 2b)\xi^4\zeta_1^2\zeta_2^2,$$

with $\zeta_1^2 + \zeta_2^2 = 1$, and then setting

$$\zeta_1 = \cos\phi, \quad \zeta_2 = \sin\phi,$$

we obtain

$$\Delta\Phi = \frac{1}{2}a_0(T - T_c)\xi^2 + \frac{1}{4}b\xi^4 + \frac{1}{16}(c - 2b)\xi^4\sin^2(2\phi).$$

We differentiate first with respect to ϕ and obtain the extrema condition

$$\phi = \pm \frac{n\pi}{4}, \quad n = 0, 1, 2, 3$$

with minima at

$$\left. \begin{aligned} \phi = 0, \pm\pi &\Rightarrow \zeta_1 = \pm 1, \zeta_2 = 0; \delta\rho = \pm\xi\zeta_1 \\ \phi = \pm\frac{\pi}{2} &\Rightarrow \zeta_1 = 0, \zeta_2 = \pm 1; \delta\rho = \pm\xi\zeta_2 \end{aligned} \right\} \quad \begin{aligned} \xi &= \pm \sqrt{\frac{a_0}{b}}(T_c - T)^{1/2}, \\ b &> 0, \quad c - 2b > 0, \end{aligned}$$

and

$$\left. \begin{aligned} \phi = \pm\frac{\pi}{4} &\Rightarrow \zeta_1 = \pm\zeta_2 = \frac{1}{\sqrt{2}} \\ \phi = \pm\frac{3\pi}{4} &\Rightarrow \zeta_1 = \mp\zeta_2 = -\frac{1}{\sqrt{2}} \end{aligned} \right\} \quad \begin{aligned} \xi &= \pm \sqrt{\frac{4a_0}{2b+c}}(T_c - T)^{1/2}, \\ 2b + c &> 0, \quad 2b - c > 0, \\ \delta\rho &= \pm\xi(\zeta_1 \pm \zeta_2). \end{aligned}$$

Isotropy subgroups

In analyzing the isotropy subgroups of $p4mm$ we must distinguish between the three symmetry points considered here. Before discussing the isotropy subgroups we determine, with the aid of the relations

$$\begin{aligned} (E|\mathbf{t})\zeta_1 &= (-1)^{m_1}\zeta_1, \\ (E|\mathbf{t})\zeta_2 &= (-1)^{m_2}\zeta_2, \end{aligned}$$

the kernel translation groups associated with the different minima we obtained above. We find that:

- (i) $\delta\rho_1 = \pm\xi\zeta_1$ is invariant for m_1 even and arbitrary m_2 , which doubles the unit cell in the 1-direction,
- (ii) $\delta\rho_2 = \pm\xi\zeta_2$ is invariant for m_2 even and arbitrary m_1 , which doubles the unit cell in the 2-direction,
- (iii) $\delta\rho_3^\pm = \xi(\zeta_1 \pm \zeta_2)$ is invariant for m_1, m_2 even, and the unit cell is doubled along both the 1- and 2-directions.

With the aid of these translation invariance relations we now determine the isotropy subgroups as follows:

1. $(^1(\star\bar{X}))$ with kernel point-subgroup is $2mm$.

- i. $\delta\rho_1$ and $\delta\rho_2$: Combining this point-group with the translation groups of $\delta\rho_1$ and $\delta\rho_2$ we find that systems having either of these order parameters correspond to the space-group pmm , with point-group symmetry elements $E, C_2, \sigma_1, \sigma_2$. This space-group is neither t -equal nor k -equal to the high-symmetry space-group $p4mm$.
- ii. We find that the OP described by $\delta\rho_3^+$ is invariant under the action of all $(^1(\star\bar{X}))$ matrices; and when we attach to it $\mathbb{T}_{\bar{X}}$ we obtain the k -equal space-group $p4mm$, with $\mathbf{a}'_1 = 2\mathbf{a}_1, \mathbf{a}'_2 = 2\mathbf{a}_2$.
- iii. The OP $\delta\rho_3^-$ is odd under the action of the symmetry $C_4, C_4^3, \sigma_{xy}, \sigma_{\bar{x}y}$, but remains invariant if we augment these point-group elements with the, now, nonprimitive translation $\mathbf{a}_1 + \mathbf{a}_2$, and we obtain the coset representatives of the space-group

$$(E|\mathbf{0}), (C_2|\mathbf{0}), (\sigma_x|\mathbf{0}), (\sigma_y|\mathbf{0}), (C_4|\boldsymbol{\tau}), (C_4^3|\boldsymbol{\tau}), (\sigma_{xy}|\boldsymbol{\tau}), (\sigma_{\bar{x}y}|\boldsymbol{\tau}),$$

with $\boldsymbol{\tau} = \frac{1}{2}(\mathbf{a}'_1 + \mathbf{a}'_2)$, and isogony $4mm$. Hence, it should be equivalent to one of the two standard 2D space-groups $p4mm$ and $p4gm$ with generators $(C_4|\mathbf{0}), (\sigma_x|\mathbf{0})$ and $(C_4|\mathbf{0}), (\sigma_x|\frac{1}{2}\frac{1}{2})$, respectively. We start by examining the former with the aid of (17.66)–(17.68). The isogonal point-group isomorphism suggests a similarity transformation of the form $(E|\mathbf{v})$. Using (17.68) with $\mathbf{v} = (v_1, v_2)$, $\mathbf{a}_1 + \mathbf{a}_2 = (1/2)(\mathbf{a}'_1 + \mathbf{a}'_2)$ and $\boldsymbol{\tau}^c = \mathbf{0}$ for $p4mm$, we obtain

$$C_4, C_4^3, \sigma_{xy}, \sigma_{\bar{x}y} \Rightarrow v_1 + v_2 = \pm(1/2) + m_1,$$

$$v_1 - v_2 = \mp(1/2) + m_2,$$

$$C_2, \sigma_x, \sigma_y \Rightarrow 2v_j = m_j, j = 1, 2,$$

which is satisfied by $v_1 = 0, v_2 = 1/2$. Thus, our space-subgroup is k -equal to $p4mm$ as shown in Figure 17.13.

2. $(^2(\star\bar{X}))$ with kernel 2

- i. $\delta\rho_1$ and $\delta\rho_2$: Since operations $\sigma_{x,y}$ do not exchange OP components but merely multiply them by a negative sign, we can construct the space-group representatives for both $\delta\rho_1$ and $\delta\rho_2$ as $(E|\mathbf{0}), (C_2|\mathbf{0}), (\sigma_x|\mathbf{a}_{1,2}), (\sigma_y|\mathbf{a}_{1,2})$ with isogony of $2mm$. The primitive vectors maintain the p structure; thus, we have to pick

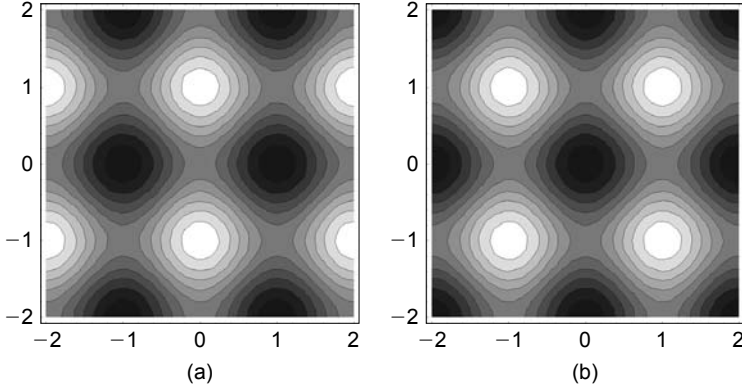


Fig. 17.13. $\delta\rho^-$: (a) origin at $(0,0)$, (b) origin at $(1/2,0)$.

the equivalent $\mathbb{S}^s$ from among pmm , pmg , pgg . Since in 2D there are no screw axes, then we have to choose pgg as the equivalent standard space-group.

- ii. $\delta\rho_3^+$ and $\delta\rho_3^-$: Under the action of $^{(2)}(\bar{*}\bar{X})$, $\delta\rho_3^+$ and $\delta\rho_3^-$ are invariant with respect to the space-groups

$$\{(E|\mathbf{0}), (C_2|\mathbf{0}), (C_4|\mathbf{0}), (C_4^3|\mathbf{0}), (\sigma_x|\boldsymbol{\tau}), (\sigma_y|\boldsymbol{\tau}), (\sigma_{xy}|\boldsymbol{\tau}), (\sigma_{\bar{x}y}|\boldsymbol{\tau})\},$$

and

$$\{(E|\mathbf{0}), (C_2|\mathbf{0}), (C_4|\boldsymbol{\tau}), (C_4^3|\boldsymbol{\tau}), (\sigma_x|\boldsymbol{\tau}), (\sigma_y|\boldsymbol{\tau}), (\sigma_{xy}|\mathbf{0}), (\sigma_{\bar{x}y}|\mathbf{0})\},$$

respectively, with $\boldsymbol{\tau} = \mathbf{a}_1 + \mathbf{a}_2 = \frac{1}{2}(\mathbf{a}'_1 + \mathbf{a}'_2)$. The former space-group is identical with $p4g$, as can be confirmed with the aid of (17.68). However, it is more important to use (17.68) to show that the latter space-group is equivalent to $p4g$, namely,

$$\begin{aligned} C_4 &\Rightarrow v_1 + v_2 = (1/2) + m_1, \\ v_1 - v_2 &= -(1/2) + m_2, \\ \sigma_x &\Rightarrow 2v_1 = m_1, \end{aligned}$$

which is satisfied by $v_1 = 0$, $v_2 = 1/2$, and we find that $\delta\rho^\pm \Rightarrow p4g$.

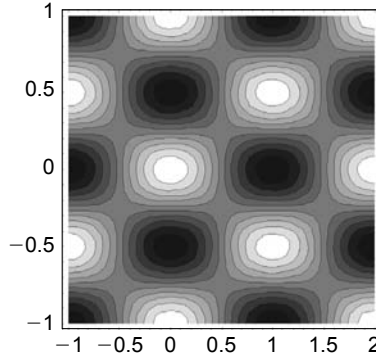
3. $^{(3)}(\bar{*}\bar{X})$, $^{(4)}(\bar{*}\bar{X})$.

- i. $\delta\rho_1$ and $\delta\rho_2$: Under the action of $^{(3)}(\bar{*}\bar{X})$, $\delta\rho_1$ remains invariant with respect to $\mathbb{S} = (E|\mathbf{0}), (C_2|\frac{1}{2}\mathbf{a}'_1), (\sigma_x|\frac{1}{2}\mathbf{a}'_1), (\sigma_y|\mathbf{0})$, with isogony $2mm$ hence, it is equivalent to pmm , pmg , pgg . We check pmm first, and find

$$\begin{aligned} C_2, \sigma_x &\Rightarrow 2v_1 = (1/2) + m_1, \\ C_2, \sigma_y &\Rightarrow 2v_2 = m_2, \end{aligned}$$

giving $v_1 = 1/4$, $v_2 = 0$.

- ii. $\delta\rho_3^+$ and $\delta\rho_3^-$: Under the action of $^{(4)}(\bar{*}\bar{X})$, these two OPs are invariant with

Fig. 17.14. $\delta\rho_1$.

respect to the space-groups

$$\{(E|\mathbf{0}), (C_2|\boldsymbol{\tau}), (\sigma_{xy}|\mathbf{0}), (\sigma_{\bar{x}y}|\boldsymbol{\tau})\}$$

and

$$\{(E|\mathbf{0}), (C_2|\boldsymbol{\tau}), (\sigma_{xy}|\boldsymbol{\tau}), (\sigma_{\bar{x}y}|\mathbf{0})\},$$

respectively. Using (17.68) for $p4mm$, we get

$$\begin{aligned} C_2 &\Rightarrow 2v_1 = (1/2) + m_1, & \sigma_{xy} &\Rightarrow v_1 + v_2 = (1/2) + m_1, \\ 2v_2 &= (1/2) + m_2, & \sigma_{\bar{x}y} &\Rightarrow v_1 - v_2 = m_1, \end{aligned}$$

$$v_1 = v_2 = 1/4.$$

The method of Gufan and Kim

This method gives a recipe for finding the minima of the Landau free energy Φ and associated orbits. It relies on the identification of the finite number of invariant polynomials defining the integrity basis of the image group $\mathcal{I}_0$ [193, 194, 195].

It starts by determining the possible extrema of Φ with the aid of symmetry properties. This is achieved by defining

$$\Phi = \Phi(B_1, \dots, B_r), \quad (17.115)$$

where $B_m(\eta_1, \dots, \eta_n)$ is a homogeneous polynomial in the components $\{\eta_i\}$ of the OP, of degree α_m . It is convenient to express the polynomial B_m as

$$B_m(\eta_1, \dots, \eta_n) = \rho^{\alpha_m} D_m(\gamma_1, \dots, \gamma_n), \quad (17.116)$$

with $B_1 = \rho^2$ being the second-degree term.

Since Φ is invariant under the operations of $\mathcal{I}_0$, the set of derivatives $\{\partial\Phi/\partial\eta_i\} \equiv \nabla\Phi(\boldsymbol{\eta})$ transforms like the vector Rep of $\mathcal{I}_0$, just like the vector $\boldsymbol{\eta}$ in the OP space.

Next, we consider a line of points sharing a nontrivial stabilizer $\mathcal{I} \subset \mathcal{I}_0$, of index i_0/i . Then the corresponding stratum comprises i_0/i lines, including this line. We denote the direction of each line-component of the stratum by $\hat{\gamma}_l$, $l = 1, \dots, i_0/i$, and the corresponding stabilizer $\mathcal{I}_l$. Any point on the line l is given by

$$\boldsymbol{\eta}_l = \rho \hat{\gamma}_l.$$

The very existence of the set of conjugate stabilizers $\{\mathcal{I}_l\}$ requires that Φ exhibit a periodicity of i_0/i with respect to the angular variable associated with the conjugation, and hence extrema at each line-component of the stratum. This, in turn, necessitates the vanishing of the gradient components perpendicular to the line. Consequently, we find that $\nabla \Phi(\rho \hat{\gamma}_l)$ is parallel to $\hat{\gamma}_l$. It then follows that for a vector $\boldsymbol{\eta}_l$, invariant under the operations of its stabilizer $\mathcal{I}_l \subset \mathcal{I}_0$, $\nabla \Phi(\rho \boldsymbol{\gamma}_l)$ is also invariant under $\mathcal{I}_l$. If we choose $\hat{\gamma}_l$ to be one of the basis vectors in OP space, and focus on the temperatures $T < T_c$, then we obtain the following scenario:

- (a) A maximum must exist at the origin.
- (b) The extrema of Φ in the neighborhood of the line $\hat{\gamma}_l$, containing fourth- or higher-degree polynomials, are confined along the line. Their locations depend on the coefficients of the polynomial expansion, which are usually temperature dependent.
- (c) There exist i_0/i equivalent extrema, for each extremum found along the $\hat{\gamma}_l$ -direction.

A similar argument can be given for planar strata. Thus, we can state that:

The gradient of any invariant must be tangent to the stratum

To generalize these ideas, we write Φ as

$$\Phi = \mathcal{L}(\rho^2, D_2, \dots, D_r), \quad (17.117)$$

then the extrema of Φ are determined by setting

$$\frac{\partial \Phi}{\partial \rho} = 2\rho \frac{\partial \mathcal{L}}{\partial \rho^2} = 0, \quad (17.118)$$

$$\frac{\partial \Phi}{\partial \gamma_i} = \sum_{m=2}^r \frac{\partial \mathcal{L}}{\partial D_m} \frac{\partial D_m}{\partial \gamma_i} = 0. \quad (17.119)$$

According to the above argument, $\partial D_m / \partial \gamma_i$ satisfy the condition

$$\left. \frac{\partial D_m}{\partial \gamma_i} \right|_{\hat{\gamma}_l} = 0,$$

along the directions $\hat{\gamma}_l$. The problem then reduces to a function of one variable ρ , from which the extrema, $\rho_{\text{ext}}(T)$, can be determined from (17.118), which can be recast as

$$\frac{\partial \mathcal{L}}{\partial \rho^2} = \frac{1}{2\rho} \frac{\partial \Phi}{\partial \rho} \Big|_{\hat{\gamma}_l}. \quad (17.120)$$

Nontrivial isotropy group types can be identified for two-dimensional OP space with image groups $\mathcal{I}_0 = C_{mv}$ as (E, σ_v) for m odd, and $(E, \sigma_v), (E, \sigma_{v'})$ for m even.

Example 17.26

Nontrivial strata for $\mathcal{I}_0 = \mathcal{C}_{mv}$

The Landau free energy is written as

$$\begin{aligned}\Phi &= \mathcal{L}(\rho^2, D_2 = \cos(m\phi)) \\ &= \frac{a}{2}\rho^2 + \frac{b}{4}\rho^4 + \frac{c}{4}\rho^4 \cos(4\phi) \Rightarrow \mathcal{C}_{4v}, \\ &= \frac{a}{2}\rho^2 + \frac{b}{4}\rho^4 + \frac{c}{6}\rho^6 + \frac{d}{6}\rho^6 \cos(6\phi) \Rightarrow \mathcal{C}_{6v},\end{aligned}$$

where (γ_1, γ_2) are replaced by ϕ . Notice that for $\mathcal{C}_{6v}$ expansion to fourth degree leaves $\mathcal{L}$ direction independent. Moreover, we omitted $\mathcal{C}_{3v}$ since the corresponding Φ violates the Landau condition. The extrema are found at

$$\sin(m\phi) = 0 \Rightarrow \phi = k\pi/m, \quad k = 0, \dots, m-1,$$

giving $D_2 = \pm 1$, and stabilizer, or isotropy group, types (E, σ_v) and $(E, \sigma_{v'})$. The corresponding Φ s and the extrema for $T < T_c$, $a < 0$, obtained with the aid of (17.105), are

$$\begin{aligned}\mathcal{C}_{4v} \Rightarrow \Phi &= \frac{a}{2}\rho^2 + \frac{b \pm c}{4}\rho^4, \\ \rho_{\text{ext}}^2 &= -\frac{a}{b'}, \quad b' = b \pm c > 0, \\ \mathcal{C}_{6v} \Rightarrow \Phi &= \frac{a}{2}\rho^2 + \frac{b}{4}\rho^4 + \frac{c \pm d}{6}\rho^6, \\ \rho_{\text{ext}}^2 &= \frac{-b + \sqrt{b^2 - 4ac'}}{2c'}, \quad c' = c \pm d > 0, \quad -4ac' > 0.\end{aligned}$$

The minima are sorted out, from among the extrema, with the aid of the second derivatives

$$\left. \frac{\partial^2 \Phi}{\partial \rho^2} \right|_{\rho_{\min}, \hat{\gamma}_l} = 4\rho_{\min}^2 \left. \frac{\partial^2 \mathcal{L}}{\partial (\rho^2)^2} \right|_{\rho_{\min}, \hat{\gamma}_l}, \quad (17.121)$$

$$\left. \frac{\partial^2 \Phi}{\partial \rho \partial \gamma_i} \right|_{\rho_{\min}, \hat{\gamma}_l} = 2\rho_{\min} \sum_{m=2}^r \left. \frac{\partial^2 \mathcal{L}}{\partial (\rho^2) \partial D_m} \frac{\partial D_m}{\partial \gamma_i} \right|_{\rho_{\min}, \hat{\gamma}_l} = 0, \quad (17.122)$$

$$\left. \frac{\partial^2 \Phi}{\partial \gamma_k \partial \gamma_i} \right|_{\rho_{\min}, \hat{\gamma}_l} = \sum_{m=2}^r \left. \frac{\partial \mathcal{L}}{\partial D_m} \frac{\partial^2 D_m}{\partial \gamma_i \partial \gamma_j} \right|_{\rho_{\min}, \hat{\gamma}_l}, \quad (17.123)$$

where in (17.23) the terms $\sum_{m,m'} \left. \frac{\partial^2 \mathcal{L}}{\partial D_m \partial D_{m'}} \frac{\partial D_m}{\partial \gamma_i} \frac{\partial D_{m'}}{\partial \gamma_j} \right|_{\rho_{\min}, \hat{\gamma}_l}$ vanish identically.

*Example 17.27***Minima of Example 17.12**

With $D_2 = \cos(m\phi)$ we get $\partial^2 D_2 / \partial \phi^2 = -m^2 \cos(m\phi)$. Expressions for the second derivatives are given in the table below for $\mathcal{C}_{4v}$ and $\mathcal{C}_{6v}$, with the aid of (17.106) and (17.108).

	$\partial^2 \Phi / \partial \rho^2 _{\rho_{\text{ext}}}$	$\partial \mathcal{L} / \partial D_2$
$\mathcal{C}_{4v}$	$-2a > 0$	c
$\mathcal{C}_{6v}$	$\frac{\sqrt{b^2 - 4ac'}(-b + \sqrt{b^2 - 4ac'})}{2c'} > 0$	d

Thus, we find that, for $\mathcal{C}_{4v}$, alternating maxima and minima occur with increasing values of k ; maxima or minima occur at even values if $c > 0$ or $c < 0$, respectively. For $\mathcal{C}_{6v}$ minima may occur either for the (E, σ) stratum or for the (E, σ') stratum, with maxima occurring at the other stratum.

Notice that the set of equivalent minima, as the ones determined in the above example, form an orbit of $\mathcal{I}_0$. Thus, by identifying all the nontrivial stabilizers and their corresponding strata, we can determine the orbits of all the different minima of Φ . However, determining the absolute minima is another endeavor, which has been addressed by Kim.

Absolute minima and the method of Kim

Kim [195] studied the mapping from the surface of the unit sphere defining the γ -space to the different D_m s of the integrity basis, namely

$$\gamma \Rightarrow D_m(\gamma). \quad (17.124)$$

In such mapping, each $\mathcal{I}_0$ generated γ -orbit is represented by a single point in D_m -space. Thus, for an integrity basis comprising r polynomials, invariant under $\mathcal{I}_0$, we can define an $r - 1$ -dimensional space where we define the mapped domain as the set of points with coordinates $[D_2(\gamma), D_3(\gamma), \dots, D_r(\gamma)]$. It is then clear, from the property that the gradient of any invariant must be tangent to the stratum, that the surface boundary of this domain represents the mapping of the extrema of Φ . On such a surface, we identify cusps as corresponding to maximal subgroup symmetry directions, since at such points we have the largest set of vanishing $\partial D_m / \partial \gamma_i$. Similarly, we identify curves with the next highest subsymmetries where the tangential condition means

$$\frac{\partial D_m / \partial \gamma_i}{\partial D_{m'} / \partial \gamma_i} = \text{constant, for } i = 1, \dots, n.$$

Example 17.28 **$\mathcal{I}_0$ s of Example 17.12**

In this example we have a one-dimensional space defined by D_2 . In the space, the mapping (17.109) defines the segment domain $-1 \leq D_2 \leq +1$, with cusps at ± 1 corresponding to the orbits of maximal-isotropy groups.

*Example 17.29***Kim's example for the three-dimensional vector Rep of $\mathcal{I}_0 = \mathcal{O}_h, \mathcal{O}$, and $\mathcal{T}_h$.**

In this example the most general Φ can be written, using Table 17.9, as

$$\begin{aligned}\Phi &= \frac{a}{2} \rho^2 + \frac{1}{4} \rho^4 [b_1 + b_2 D_3(\gamma)] + \frac{1}{6} \rho^6 [c_1 + c_2 D_3(\gamma) + c_3 D_6(\gamma)] + \cdots \\ &= \frac{a}{2} \rho^2 + \frac{1}{4} B \rho^4 + \frac{1}{6} C \rho^6 + \cdots,\end{aligned}$$

where $D_6(\gamma) = \sum_i \gamma_i^6$, and we set $C > 0$ for stability. In this case we have a two-dimensional space defined by D_3 and D_6 .

To minimize Φ we set

$$\begin{aligned}\frac{\partial \Phi}{\partial \rho} &= \rho (a + B \rho^2 + C \rho^4) = 0, \\ \frac{\partial \Phi}{\partial D_3} &= \frac{b_2}{4} \rho^4 + \frac{c_2}{6} \rho^6 = 0, \\ \frac{\partial \Phi}{\partial D_6} &= \frac{c_3}{6} \rho^6 = 0,\end{aligned}$$

where the last relation cannot be satisfied, since $\rho \neq 0$ for $T < T_c$. The second relation gives $\rho_{\text{ext}}^2 = -3b_2/2c_2$, provided $b_2 c_2 < 0$. However, it represents an inflection point since $\partial^2 \Phi / \partial D_3 = 0$.

Thus, we should look for a boundary value of (D_3, D_6) that yields a minimum of Φ . Fixing the direction γ , we obtain from the first relation

$$\rho_{\text{ext}}^2 = \frac{-B + \sqrt{B^2 - 4aC}}{2B}, \text{ with } B^2 - 4aC > 0,$$

with cusps at ± 1 corresponding to the orbits of maximal-isotropy groups.

Exercises

17.1 Minimize the Landau free energy for each of the three cases obtained in Example 17.4.

17.2 Consider systems that belong to the Bravais class $P4mm$:

- Determine the points in the Brillouin zone that satisfy the Lishitz condition.
- Derive the corresponding $\mathbb{P}_k$.

- 17.3 Consider a crystal with cubic symmetry. It was shown in Table 13.8 that the two elastic strain components

$$\eta \propto 2\varepsilon_{33} - \varepsilon_{11} - \varepsilon_{22}, \quad \xi \propto \varepsilon_{11} - \varepsilon_{22},$$

form a basis for the cubic Irrep Γ_{12} .

Show that third-degree invariants of this Irrep do not vanish; and hence, these two strain components cannot drive a second-order phase transition to a t -equal tetragonal structure [164].

- 17.4 Determine the integrity basis of the three-dimensional Rep of the dihedral point-group $\mathcal{D}_6$, with Rep matrix generators

$$C_2 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}; \quad C_6 = \begin{pmatrix} 1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

- 17.4 Gadolinium molybdate, $\text{Gd}_2(\text{Mo}_4)_3$, undergoes a phase transition from a $P\bar{4}2_1m$ to a $Pba2$ space-group symmetry at 160 °C. It involves the point-group change $\bar{4}2m \Rightarrow mm2$. It also involves a reduction in translational symmetry from a P -tetragonal $\mathbb{T}_0$ with basis $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ (along 4-fold symmetry axis), to another P -tetragonal $\mathbb{T}$ with $\mathbf{a}'_1 = \mathbf{a}_1 - \mathbf{a}_2, \mathbf{a}'_2 = \mathbf{a}_1 + \mathbf{a}_2, \mathbf{a}'_3 = \mathbf{a}_3$, with $\mathbb{T}_0 : \mathbb{T} = 2$, giving $\mathbb{S}_0 : \mathbb{S} = 4$.

- Identify $^*\mathbf{k}$.
 - Derive the Irreps of $^*\mathbf{k}$.
 - Determine the corresponding kernel and image groups.
 - Enumerate the possible low-symmetry space-groups, and identify the Irrep corresponding to the phase transition in $\text{Gd}_2(\text{Mo}_4)_3$.
 - Use the integrity basis for $\mathbf{C}_4$ to construct $\Delta\Phi$.
 - We notice that P_3 of the electric polarization tensor and ε_{12} the shear component of the strain tensor are invariant under the point-group operations of $Pba2$. This suggests that the emerging low-symmetry phase can support ferroelectricity and a shear distortion. Write down a $\Delta\Phi'$ in these variables as secondary OPs (SOP), as well as $\Delta\Phi_c$, the terms coupling the primary and secondary OPs.
 - Describe the procedure of obtaining the minima of $\Delta\Phi$.
- 17.5 Determine the possible magnetic arrangement associated with the point-group $4mm, \underline{4mm}, \underline{4mm}, \underline{4mm}$.

18

Incommensurate systems and quasi-crystals

18.1 Introduction

So far we have mainly considered the symmetries of condensed matter systems with regular periodicity in one-, two-, and three-dimensional space (1D, 2D, and 3D). We demonstrated that manifestations of such periodicities are lattice structures in real Euclidean space, and that when a lattice is decorated with an atomic basis we obtain a crystal. Moreover, we showed that there is a finite number of crystal structures, and that each crystal type has a compatible space-group symmetry, comprising point-group and translation operations. In 2D, we classified the lattices into 5 distinct types, with 17 crystallographic space-groups involving 10 point-groups, while in 3D we were able to identify 14 lattices, 230 monochromatic Fedorov space-groups with 32 point-groups, or 1058 Shubnikov dichromatic space-groups with 58 point-groups. We exhaustively discussed the effect of the lattice structures and their underlying symmetries on the different physical properties of material systems.

However, over the past three decades we have witnessed the emergence of systems that do not exhibit periodic structures, yet display well-defined long-range order, manifest in well-defined *diffraction patterns comprising of sharp Bragg peaks*. These systems have been named *quasi-periodic* (QP) [165, 166, 167, 168, 169, 170, 171, 172, 173, 174, 175]. The lack of periodicity in QP systems in 2D and 3D leads to the lifting of related constraints imposed on the regular lattices. For example, it was found that certain QP structures admit the packing of two types of cells, pentagonal and icosahedral. This evidence defies previously accepted notions that long-range order was incompatible with both pentagonal and icosahedral packing, let alone that only one type of cell was admissible in crystal packing.

It is then necessary to reconsider our previously established concept of crystal symmetries, which have been based on the old paradigm that such symmetries have to conform with invariance under the operations of compatible space-groups in their respective d -dimensional (dD) Euclidean space, $d \leq 3$. Such operations involve rigid motion combining translations, rotations, and reflections that leave a physical system invariant. But this is no longer valid for QP systems, which lack the prerequisite of periodicity. Yet QP systems clearly possess some kind of symmetry. We are, therefore, compelled to revise and expand the underlying principles to include more general ideas that capture the notion of symmetry in QP systems.

18.1.1 Diffraction patterns of QP systems: rank and indexing dimension

In the case of normal crystals, or crystallographic (CG) systems in dD , we can assign d integer values (Miller indices) to label the observable reflections. The Miller indices are just the integers associated with the lattice of $\mathbf{G}$ -vectors determined by the diffraction pattern over the familiar reciprocal lattice, dual to a lattice of physical real space translations that leave the density $\rho(\mathbf{r})$ invariant. Since quasi-periodic systems lose periodicity in at least one dimension, it is not possible to describe them in physical dD -space as easily as crystallographic counterparts. Thus, it becomes more difficult to find mathematical formalisms for the interpretation and analysis of diffraction data. However, it was found that integer indices can be assigned to the diffraction intensities of QP systems, when $N = d + n$ linearly independent vectors are used. Integral linear combinations of these N basis vectors generate a lattice that contains the diffraction points as a subset. The smallest number of vectors required to generate the lattice is called its *rank*. Thus, dD incommensurate systems with n modulation vectors have reciprocal lattices of rank $d + n$, polygonal QCs require five vectors and icosahedral QCs, six. We can call them generalized Miller indices. We should be aware that for QP systems the lattice associated with the diffraction pattern has no dual partner in real space: we are stuck in Fourier space!

Thus, what sets CG lattices in d -dimensions apart from their QP counterparts, is that:

- All their points are integral linear combination of just d vectors.
- The physical space periodicity of crystallographic systems guarantees a minimum distance between diffraction points in Fourier space.

By contrast, the lack of periodicity in quasi-crystallographic (QCG) systems is manifest in a *dense* lattice associated with QCG diffraction, i.e. there is no minimum distance between its points. It is the fact that the diffraction intensity is only visible on a finite number of lattice points that renders the discernibility of the corresponding diffraction points.

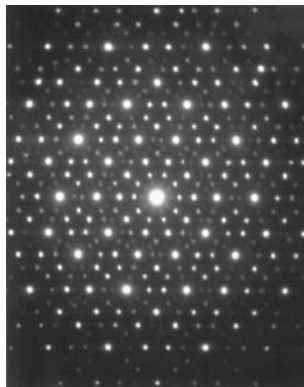


Fig. 18.1. Diffraction pattern of an icosahedral quasi-crystal.

Noncrystallographic point-groups and indexing dimension

The lack of a minimum distance between lattice points leads to a relaxation of the constraint on admissible point-groups. Thus, we may observe diffraction patterns with non-crystallographic point-group symmetries, which are the hallmark of QC systems. Hermann [46] determined the number of dimensions necessary for the existence of an n -fold rotation symmetry while preserving translation symmetry. The crystallographic point-groups have indexing dimension equal to d , the dimension of physical space; while for noncrystallographic point-groups it is larger than d . For example, icosahedral symmetry is allowed in no less than 6D, while noncrystallographic polygonal symmetry may occur in 5D. We then find that each point-group defines the number of basis vectors required to construct a lattice with the corresponding symmetry. We call this number the *indexing dimension* of the point-group. We then regard as QCG lattices only those whose rank equals the indexing dimension of its point-group; they are said to have a *minimum rank*. Lattices with a rank bigger than symmetry requires, should be viewed as superpositions.

We develop a classification scheme only for crystallographic and quasi-crystallographic lattices. A lattice with nonminimal rank can be viewed as the direct sum of two or more lattices of minimal rank. In the crystallographic case such a direct sum is not viewed as a crystallographic lattice, but as a set of points appropriate for characterizing an incommensurately modulated structure. We impose the same organizing principle in the quasi-crystallographic case, reserving the term “quasi-crystal” for structures whose lattices have minimal rank, and regarding more complicated structures as incommensurately modulated quasi-crystals, which are most simply regarded as direct sums of ordinary ones. Hereafter when we use the term “lattice” we always mean crystallographic or quasi-crystallographic lattices. The absence of a minimum distance between points, however, sometimes presents candidates for QCG lattices that actually do not qualify as basic lattices even when the point-group is CG. Consider, for example, the set of all integral linear combinations of two orthogonal unit vectors and another pair that are $\sqrt{2}$ the norm of the first. This is a lattice, closed under addition and subtraction, which clearly has square symmetry and is not equivalent to the ordinary square lattice. It is not counted as a CG lattice because it is clearly a superposition of two incommensurate square lattices, and is better regarded not as a fundamental CG object, but an incommensurately modulated (ICM) structure.

18.1.2 Describing the symmetry of QP systems

There are two distinct approaches to the extension of symmetry concepts to include QP systems. The first is based on treating the quasi-periodicity as a projection onto a lower-dimensional Euclidean space of the lattice points of a perfectly periodic lattice which exists in a higher-dimensional Euclidean space. Or, as Mermin [17] puts it “a lower-dimensional slice of periodic higher-dimensional structures”. Upon the discovery of incommensurately modulated (ICM) systems, which constitute one type of QP systems, in the 1970s, it was found that the positions of the Bragg peaks in their diffraction pattern can only be constructed with the aid of *integral linear combinations of a finite set of $N > d$ basis lattice vectors*. This prompted de Wolff [176, 177], and Janssen and Janner [178] to propose that the extra primitive vectors may be regarded as projections of primitive vectors in a

higher-dimension space, and this was originally used to describe and classify the symmetry of simple ICM systems, before the advent of quasi-crystals. Here, the symmetry of the system is given by the space-group that leaves the crystal in the high-dimension space, or *superspace*, invariant. We refer to this space-group as the *superspace-group*. The additional dimensions introduced to give the symmetry group of an ICM phase actually represent the independent phase of the modulation waves.

The idea of symmetry in a higher-dimension space was not new; for example, it had been previously known that the states of the hydrogen atom manifest $\mathcal{O}(4)$ symmetry, and that nonrigid molecules reflect point-group symmetries in dimensions higher than 3.

The second approach was originally suggested by Bienenstock and Ewald in 1962 [51], long before the discovery of QP systems. It was adopted, refined, and reformulated for QP systems by Mermin and coworkers. This approach relocates the primary description of the symmetry of a QP structure to its reciprocal space pattern. It allows for a unified description of both periodic and quasi-periodic structures, and for a common classification of the space-group scheme in physical reciprocal space.

18.1.3 Types of quasi-periodic systems

Incommensurately modulated periodic structures

These are the simplest QP crystals. Such a structure can be considered as a perfectly periodic lattice that undergoes a periodic perturbative modulation that is incommensurate with its own periodicity. The underlying perfect crystal is referred to as the *basic structure*, and its lattice denoted by $\mathcal{L}_B$. The modulation may involve one or more incommensurate wavevectors; accordingly, this number defines the dimensionality of the modulation, i.e. we talk of an nD modulated system, if it involves n modulation wavevectors. The nature of the modulation may involve atomic displacements, spin orientations, or substitutional atomic species.

As illustrated in Figure 18.2, the manifest diffraction pattern of an ICM structure consists of a set of bright “main Bragg reflections”, corresponding to the reciprocal lattice

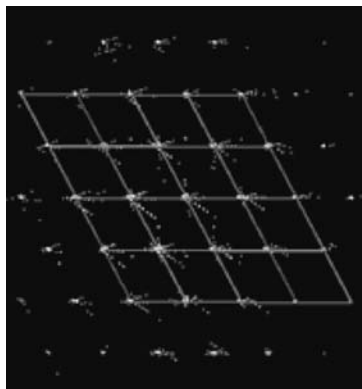


Fig. 18.2. Diffraction pattern of an incommensurate crystal.

of the basic structure, together with a set of weaker Bragg reflections, called *satellites*, which mediate the space between the main reflections, and have the periodicity of the modulation. The basic structure thus presents a natural starting point for constructing the QP wavevector basis set.

We consider the following examples in order to elucidate these ideas.

Example 18.1

One-dimensional displacively modulated structure

We consider the case of a periodic lattice (basic structure) subject to a simple one-dimensional displacive modulation. For pedagogical reasons we confine our presentation to a system in 2D physical space, in order to capture all the essential ingredients of the formalism without sacrificing simplicity. We should emphasize that all the arguments presented apply equally to the case of 3D incommensurate systems. In the basic crystal, the position of the j th atom in the unit cell, defined by a lattice vector $\mathbf{t} = \sum_{i=1}^2 n_i \mathbf{a}_i$, is given by

$$\mathbf{r}(\mathbf{t}, j) = \mathbf{t} + \mathbf{r}_j,$$

with structure factor

$$\mathcal{S}(\mathbf{G}) = \sum_j f_j \exp[i\mathbf{G} \cdot \mathbf{r}_j],$$

where f_j is an atomic scattering factor, and $\mathbf{G}$ is a reciprocal lattice vector, i.e. an integer multiple of the reciprocal basis set $\mathbf{b}_i$,

$$\mathbf{G} = \sum_{i=1}^2 h_i \mathbf{b}_i, \quad h_i \text{ integer.}$$

In the modulated structure the atomic positions become

$$\mathbf{r}(\mathbf{t}, j) = \mathbf{t} + \mathbf{r}_j + \Theta_j(\mathbf{t} \cdot \mathbf{q}), \quad \Theta_j(x + 2\pi) = \Theta_j(x). \quad (18.1)$$

Notice that for one-dimensional modulation, only one wavevector

$$\mathbf{q} = \sigma_1 \mathbf{b}_1 + \sigma_2 \mathbf{b}_2$$

is manifest. Because the modulated structure is *incommensurate*, at least one component of $\mathbf{q}$ is irrational, i.e.

at least one of the coefficients, σ_1, σ_2 , is an irrational number.

The corresponding structure factor is given by

$$\begin{aligned}
 S(\mathbf{K}) &= \sum_{\mathbf{t}j} f_j \exp[i\mathbf{K} \cdot \mathbf{r}(\mathbf{t}, j)] \\
 &= \sum_j f_j \exp[i\mathbf{K} \cdot \mathbf{r}_j] \sum_{\mathbf{t}} \exp[i\mathbf{K} \cdot (\mathbf{t} + \boldsymbol{\Theta}_j(\mathbf{t} \cdot \mathbf{q}))] \\
 &= \sum_m \delta(\mathbf{K} - \mathbf{G} - m\mathbf{q}) \sum_j f_j \exp[i\mathbf{K} \cdot \mathbf{r}_j] \Phi_j(\mathbf{G} + m\mathbf{q}).
 \end{aligned}$$

The diffraction peaks at wavevectors $\mathbf{G}$, i.e. $m = 0$, constitute the *main Bragg reflections*, while the components at $\mathbf{G} + m\mathbf{q}$, $m \neq 0$, are the *satellite Bragg reflections*, alluded to above. The wavevectors $\mathbf{G}$ constitute the reciprocal basic lattice $\mathfrak{L}_{\mathbf{B}}^*$. The Bragg reflections of the density function,

$$\rho(\mathbf{r}) = \sum_{\mathbf{h}} \rho(\mathbf{h}) e^{i\mathbf{h} \cdot \mathbf{r}},$$

then appear at wavevectors given by

$$\mathbf{h} = h_1 \mathbf{b}_1 + h_2 \mathbf{b}_2 + m\mathbf{q} = h_1 \mathbf{b}_1 + h_2 \mathbf{b}_2 + h_3 \mathbf{b}_3,$$

where

$$\mathbf{b}_3 = \mathbf{q} = \begin{pmatrix} \sigma_1 & \sigma_2 \end{pmatrix} \begin{pmatrix} \mathbf{b}_1 \\ \mathbf{b}_2 \end{pmatrix}.$$

The extended set of basis vectors $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{q} \equiv \mathbf{b}_3$ is integrally independent, in the sense that $\mathbf{h} = \mathbf{0}$, if and only if all $h_i = 0$. The rank of the quasi-lattice is 3, while the physical space dimension is 2.

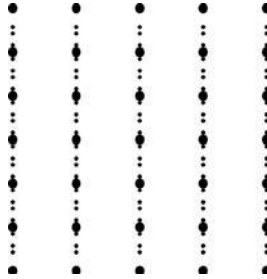


Fig. 18.3. A single-domain diffraction pattern of a 1D-modulated incommensurate crystal, having a square basic structure, and $\mathbf{q} = 1/\sqrt{3} \mathbf{b}_2$, $-2 \leq h_3 \leq 2$.

In general, a diffraction pattern $\mathfrak{D}$ of rank n in dD Euclidean space is described by wavevectors

$$\mathbf{h} = \sum_{i=1}^n h_i \mathbf{b}_i,$$

where $\mathbf{h}$ is the diffraction vector in the dD space, $\mathbf{b}_i$ ($i = 1, 2, \dots, n > d$) are the basis vectors. Such a description allows us to index the diffraction vectors with generalized Miller indices $h_1, h_2, \dots, h_n$. This implies that the location of diffraction spots is related to an n -dimensional lattice, as we will describe below.

According to our above discussion, the diffraction image of the ICM structure should display a very conspicuous 2D reciprocal-lattice $\mathfrak{L}_B^*$ among the points $\mathfrak{D}$, demarked by $m = h_3 = 0$; whereas the satellite Bragg peaks have $h_3 \neq 0$.

Composite incommensurate crystals

The second type of quasi-periodic systems is termed *incommensurate composite crystals*. These may be viewed as two interpenetrating crystals each with a perfect periodicity, but the two periodicities bear an incommensurate relation to each other.

Quasi-crystals

The last type cannot be described by superimposed modulations, their rank equals the indexing dimension of their point-group, and they are identified as *quasi-crystals*.

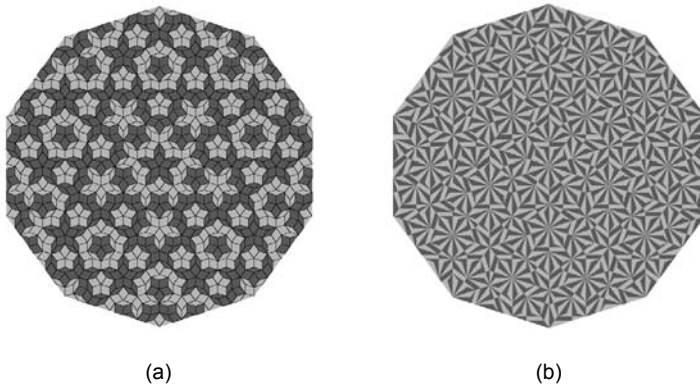


Fig. 18.4. Decagonal tiling. (a) A 10-fold rotation and a horizontal mirror reflection must be accompanied by the exchange of dark and light gray to produce a tiling indistinguishable from the original one, whereas the vertical mirror does not require the exchange of colors. (b) Both horizontal and vertical mirrors require the exchange of colors but the 10-fold rotation does not. The two tilings have different color point-groups.

We develop a classification scheme only for crystallographic and quasi-crystallographic lattices. A lattice with nonminimal rank can be viewed as the direct sum (i.e. the set of all sums of pairs of vectors, one from each lattice) of two or more lattices of minimal rank. In the crystallographic case such a direct sum is not viewed as a crystallographic lattice, but as a set of points appropriate for characterizing an incommensurately modulated structure. We impose the same organizing principle in the quasi-crystallographic case, reserving the term “quasi-crystal” for structures whose lattices have minimal rank, and regarding more complicated structures as incommensurately modulated quasi-crystals, which are most simply regarded as direct sums of ordinary ones. Hereafter when we use the term “lattice” we will always mean crystallographic or quasi-crystallographic lattices. Typical two-dimensional quasi-crystal structures are shown in Figure 18.4.

18.2 The concept of higher-dimensional spaces: superspaces and superlattices

In 1974, de Wolff [176] argued that, since the diffraction pattern of a crystal is the Fourier spectrum of its density function, be it electron, atom, or spin, it should be possible to regard the diffraction spots as the projection of the ND reciprocal-lattice points onto dD space. The diffraction spots then suggest a periodic structure in ND space. Thus, we have $N > d$ vectors spanning an ND reciprocal space, and, consequently, a dual ND direct space, in which a periodic structure can be constructed that gives rise to the diffraction pattern obtained. From the properties of the Fourier transformation, the intersection of electron density at the subspace normal to some direction is obtained from the diffraction pattern projected onto the subspace along that direction. The irrational gradient intersection of the periodic electron density leads to an aperiodic structure in the intersection. Thus, the modulated structure that has lost a period along some direction can be expressed as an irrational dD intersection of a periodic structure in ND space. The symmetry of such a crystal in nD space will be given by the space-group in nD space.

Superspace crystallography classifies the symmetry of aperiodic crystals by extending them to periodic crystals in a higher-dimension space, which possess crystallographic space-groups. The key steps are embedding the aperiodic crystal in more than 3D and applying the higher-dimensional symmetry classification of periodic systems.

We have seen that in order to interpret the structure of QP diffraction patterns we had to introduce $N > d$ basis vectors and label the diffraction spots with N corresponding *generalized Miller indices*. An N -component basis is suggestive of a crystallographic system in N -dimensions.

18.2.1 Projection from higher dimensions: pedagogy

We consider here a 2D square net and its projection onto a 1D subspace, *the physical space*, incommensurately inclined with respect to the square lattice. For such an IC inclination, the projection onto the 1D line is *dense*.

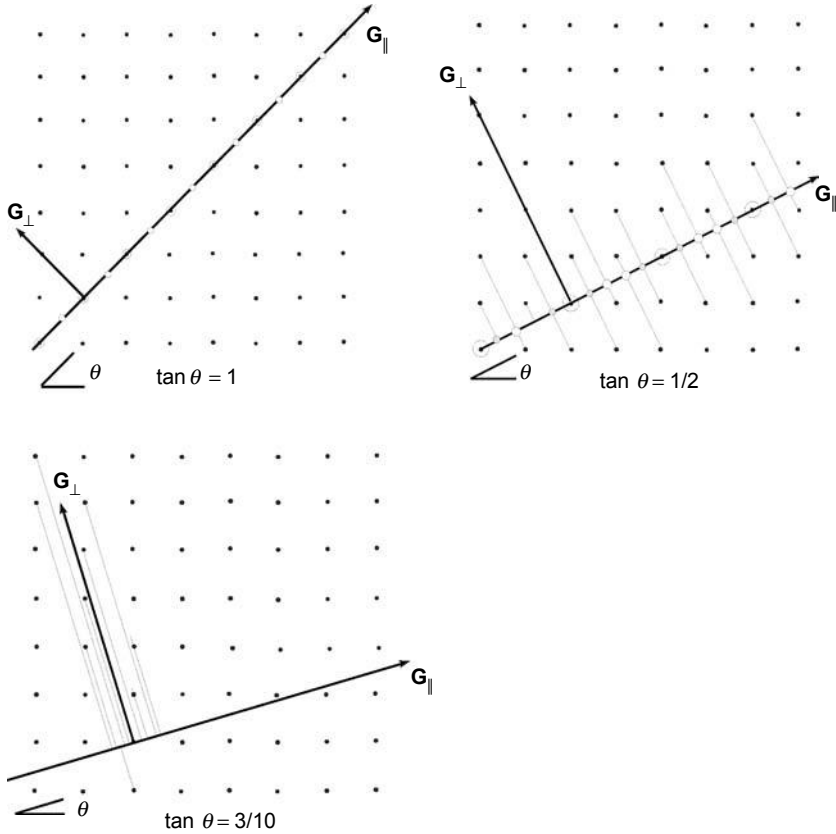


Fig. 18.5. Increase in density of projected points as inclination approaches incommensurability.

In order to elucidate the idea of a dense lattice, we show in Figure 18.5 a 2D Fourier-superspace square net, defined by 2D $\mathbf{G}$ vectors, and its projection onto the physical 1D Fourier subspace at points defining the corresponding $\mathbf{G}_{\parallel}$ lattice, for three different inclinations of the physical space axis with respect to the square net. It is obvious that the density of projected points increases as the inclination tends to incommensurability, where it diverges.

Another aspect that characterizes such a projection is the correlation between the degree of proximity of lattice points on the physical axis with wide separation in the orthogonal direction: The closer two projected points, $\mathbf{G}_{\parallel}^1$ and $\mathbf{G}_{\parallel}^2$, located in physical space, are, the greater is the projected separation along the orthogonal axis $\mathbf{G}_{\perp}^2 - \mathbf{G}_{\perp}^1$ of their corresponding superlattice points. We can thus relate the limits on resolution in physical space, $\Delta \mathbf{G}_{\parallel}$, to a corresponding limit on the width of the projection strip in orthogonal space, $\Delta \mathbf{G}_{\perp}$.

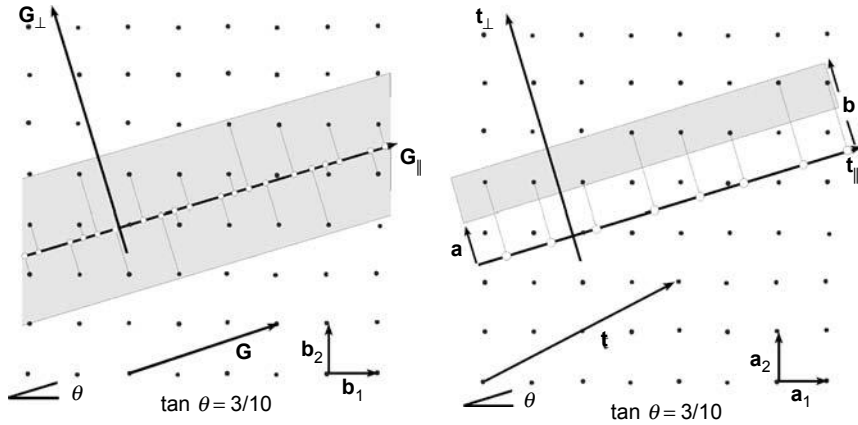


Fig. 18.6. (a) Resolution in Fourier space, (b) direct space structure.

Now, if we examine the character of the observed QC diffraction patterns in the light of the above argument, we find that:

- (i) If contributions to the diffraction intensity from all superspace lattice points were of comparable magnitude, then the dense nature of projected points should produce a streaky diffraction that permeates the whole of physical Fourier space.
- (ii) The sharp character of the actual diffraction intensities underscores the fact that the projected contributions must be limited to a narrow strip in superspace that straddles the real space axis, as depicted in Figure 18.6(a).
- (iii) A necessary condition for such a scenario is that the projected intensity of a superspace lattice point $\mathbf{G} = (\mathbf{G}_{\parallel}, \mathbf{G}_{\perp})$ must decrease with $|\mathbf{G}_{\perp}|$.
- (iv) The detailed mode of decay of intensities with increasing $|\mathbf{G}_{\perp}|$ is determined by the structure of the QC system.
- (v) Under such a scenario, the contributions to the discrete quasi-periodic distribution of projected lattice points in the corresponding real, or direct, physical space are restricted to a strip in direct superspace, for example bounded by $a \leq x_{\perp} \leq b$, as shown in Figure 18.6(b).

Pursuing the example of Figure 18.6, we find that the crystallographic property of the superspace lattices requires that

$$\exp[i\mathbf{G} \cdot \mathbf{t}] = 1,$$

where $\mathbf{t}$ is a direct lattice translation vector. Moreover, when the physical axes in Fourier and direct spaces are taken parallel, as in Figure 18.6, we get $\mathbf{G} \cdot \mathbf{t} = G_{\parallel}t_{\parallel} + G_{\perp}t_{\perp}$, or

$$\exp[iG_{\parallel}t_{\parallel}] = \exp[-iG_{\perp}t_{\perp}],$$

which we use to determine the structure factor, namely

$$S(G_{\parallel}) = \sum_{\mathbf{t}} e^{iG_{\parallel} t_{\parallel}} = \sum_{\mathbf{t}} e^{-iG_{\perp} t_{\perp}}.$$

For a superlattice of infinite extension, and an IC inclination, the distribution of values of $t_{\perp}$ in the strip $a \leq x_{\perp} \leq b$ covers all values from a to b , and we get

$$S(G_{\parallel}) \simeq \int_a^b dt_{\perp} e^{-iG_{\perp} t_{\perp}} \propto \frac{\sin[(b-a)G_{\parallel}/2]}{(b-a)G_{\parallel}/2}.$$

The oscillatory character of $S(G_{\parallel})$ is a consequence of the sharp cutoff of the $x_{\perp}$ distribution; a Gaussian form, for example, will produce a more localized and smooth $S(G_{\parallel})$.

Example 18.2

One-dimensional displacively modulated structure (continued)

Since incommensurately modulated structures have a well-defined crystallographic basic structure, it provides a natural pedagogical course for developing the superspace picture. We motivate this idea by further consideration of the relatively simple 1D IMS of Example 18.1.

It is possible to view the diffraction image $\mathfrak{D}$ as comprising of $\mathfrak{L}_{\mathbf{B}}^*$, while the satellite structure as being a perspective of points actually lying in planes parallel to the plane of the diffraction image. These planes are regularly stacked along a direction normal to the plane of the image. In this picture, shown in Figure 18.7, the points occur at intersections of the parallel planes with oblique lines passing through the points of $\mathfrak{L}_{\mathbf{B}}^*$. The mathematical

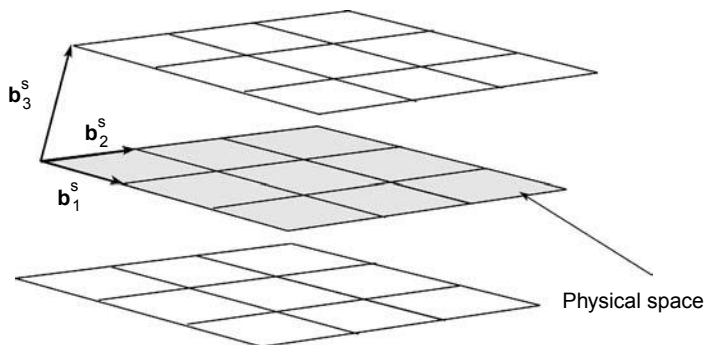
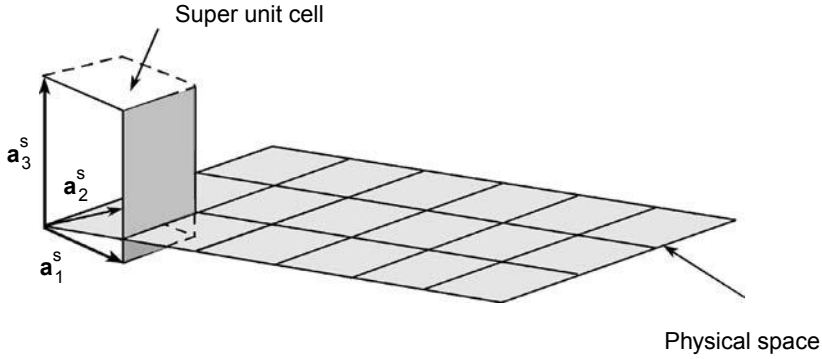


Fig. 18.7. Diffraction superspace $\mathfrak{L}_{\mathbf{s}}^*$.

Fig. 18.8. Real superspace $\mathfrak{L}_s$.

construct of this picture is obtained if we define a new 3D *superlattice* $\mathfrak{L}_s^*$, whose points are defined by the *supervectors*

$$\mathbf{h}_s = h_1 \mathbf{b}_1^s + h_2 \mathbf{b}_2^s + h_3 \mathbf{b}_3^s, \quad (18.2)$$

where

$$\begin{pmatrix} \mathbf{b}_1^s \\ \mathbf{b}_2^s \\ \mathbf{b}_3^s \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ \sigma_1 & \sigma_2 & 1 \end{pmatrix} \begin{pmatrix} \mathbf{b}_1 \\ \mathbf{b}_2 \\ \mathbf{e}_3 \end{pmatrix}; \quad (18.3)$$

$\mathbf{e}_3$ is a vector normal to the plane of $\mathfrak{D}$ whose length defines the interplane separation, which, for convenience, will be set to be a unit vector. $\mathfrak{L}_s^*$ is indeed *crystallographic*, it has 3D periodicity and can be associated with a 3D space-group.

This formalism allows us to construct a 3D real-space lattice $\mathfrak{L}_s$, dual to $\mathfrak{L}_s^*$, i.e. its primitive vectors are defined by the duality conditions $\mathbf{a}_i^s \cdot \mathbf{b}_j^s = \delta_{ij}$. Keeping in mind that for the 2D basic lattice we have

$$\mathbf{a}_i = \frac{\mathbf{b}_j}{|\mathbf{b}_1 \times \mathbf{b}_2|} \times \frac{(\mathbf{b}_i \times \mathbf{b}_j)}{|\mathbf{b}_1 \times \mathbf{b}_2|} = \frac{\mathbf{b}_j \times \hat{\mathbf{e}}_3}{|\mathbf{b}_1 \times \mathbf{b}_2|},$$

we get

$$\begin{aligned} \mathbf{a}_1^s &= \frac{\mathbf{b}_2^s \times \mathbf{b}_3^s}{\mathbf{b}_1^s \cdot (\mathbf{b}_2^s \times \mathbf{b}_3^s)} = \frac{\mathbf{b}_2 \times (\mathbf{b}_3 + \hat{\mathbf{e}}_3)}{\mathbf{b}_1 \cdot (\mathbf{b}_2 \times (\mathbf{b}_3 + \hat{\mathbf{e}}_3))} \\ &= \frac{\mathbf{b}_2 \times (\mathbf{b}_3 + \hat{\mathbf{e}}_3)}{(\mathbf{b}_3 + \hat{\mathbf{e}}_3) \cdot (\mathbf{b}_1 \times \mathbf{b}_2)} = \frac{\mathbf{b}_2 \times \hat{\mathbf{e}}_3}{|\mathbf{b}_1 \times \mathbf{b}_2|} + \frac{\mathbf{b}_2 \times \mathbf{b}_3}{|\mathbf{b}_1 \times \mathbf{b}_2|} \\ &= \mathbf{a}_1 - \sigma_1 \hat{\mathbf{e}}_3, \\ \mathbf{a}_2^s &= \mathbf{a}_2 - \sigma_2 \hat{\mathbf{e}}_3, \\ \mathbf{a}_3^s &= \hat{\mathbf{e}}_3. \end{aligned}$$

It is easy to see that a lattice vector

$$\begin{aligned}\mathbf{t} &= n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 = n_1 (\mathbf{a}_1^s + \sigma_1 \hat{\mathbf{e}}_3) + n_2 (\mathbf{a}_2^s + \sigma_2 \hat{\mathbf{e}}_3) \\ &= (n_1 \mathbf{a}_1^s + n_2 \mathbf{a}_2^s) + (n_1 \sigma_1 + n_2 \sigma_2) \hat{\mathbf{e}}_3\end{aligned}$$

is a unique projection of a partner supervector. Moreover, if we label the coordinates of a point in the 3D superspace with respect to the primitive base $\mathbf{a}_i^s$ as x_i , we find that x_1 and x_2 are identical to those in the 2D space, since it is just a projection of the 3D superspace. We can define the 2D planar space as

$$\hat{\mathbf{e}}_3 \cdot (x_1 \mathbf{a}_1^s + x_2 \mathbf{a}_2^s + x_3 \mathbf{a}_3^s) = -(x_1 \sigma_1 + x_2 \sigma_2) + x_3 = 0.$$

Now that we have defined the crystallographic 3D superlattice and its *embedding* in relation to the real physical space, we are in a position to determine the structure of the *hyperatoms* in that space and its relation to the actual incommensurate positions of the physical atoms. We start with the real physical space modulation, namely,

$$\mathbf{r}(\mathbf{t}, j) = \mathbf{t} + \mathbf{r}_j + \Theta_j(\mathbf{t} \cdot \mathbf{q}), \quad \Theta_j(x + 2\pi) = \Theta_j(x),$$

and extend it to 3D superspace by introducing a modulation phase τ as

$$\mathbf{r}_s(\mathbf{t}, \tau, j) = [\mathbf{t} + \mathbf{r}_j + \Theta_j(\mathbf{t} \cdot \mathbf{q} + \tau), \tau],$$

which intersects real physical space at $\tau = 0$, the positions of the incommensurately-modulated crystal structure. The hyperatomic lines resulting from fixing $\mathbf{t}$ and varying τ , shown in Figure 18.9, are periodic in real superspace, and the resulting pattern is invariant with respect to translations

$$\mathbf{t}_s = m_1 (\mathbf{a}_1, -\mathbf{q} \cdot \mathbf{a}_1) + m_2 (\mathbf{a}_2, -\mathbf{q} \cdot \mathbf{a}_2) + 2\pi\ell,$$

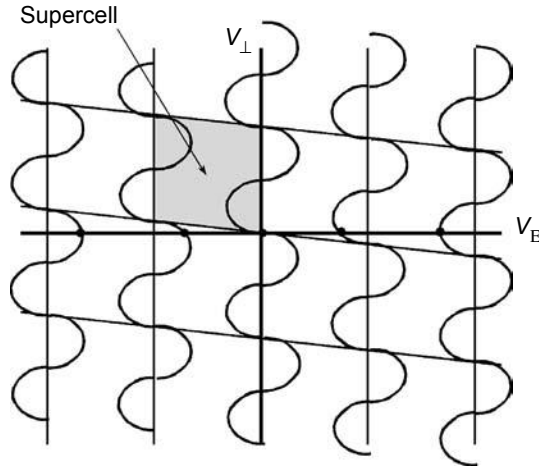


Fig. 18.9. Embedding of quasi-periodic crystal with 1D sinusoidal modulation. The projection onto real space V_E is indicated by solid circles.

with a dual reciprocal-lattice basis

$$(\mathbf{b}_1, 0), (\mathbf{b}_2, 0), (\mathbf{q}, 1),$$

and an arbitrary vector

$$\mathbf{K} = (h\mathbf{b}_1 + k\mathbf{b}_2 + m\mathbf{q}, m).$$

The density function

$$\rho(\mathbf{r}) = \sum_{\mathbf{h}} \rho(h_1 h_2 h_3) e^{i\mathbf{h} \cdot \mathbf{r}} = \sum_{h_1 h_2 h_3} \rho(h_1 h_2 h_3) e^{i(h_1 \mathbf{a}_1 + h_2 \mathbf{a}_2 + h_3 \mathbf{q}) \cdot \mathbf{r}},$$

can be regarded as a restriction to $\tau = 0$ of the density function of three variables

$$\rho(\mathbf{r}, \tau) = \sum_{h_1 h_2 h_3} \rho(h_1 h_2 h_3) e^{i(h_1 \mathbf{a}_1 + h_2 \mathbf{a}_2 + h_3 \mathbf{q}) \cdot \mathbf{r} + h_3 \tau}.$$

Notice that the functions $\rho(\mathbf{r})$ and $\rho(\mathbf{r}, \tau)$ are 2D and 3D Fourier transforms, respectively, of the same set of complex numbers $\rho(h_1 h_2 h_3)$ defined on two different sets of points related by a projection: they are carriers of the same structural information, depicted in spaces of different dimensions.

We now generalize the concepts we developed in Example 18.2 for any d and n . Thus, we define

$$\mathbf{h} = \sum_{i=1}^N h_i \mathbf{b}_i \quad (18.4)$$

with the set

$$\mathbf{b}_{d+j} = \sum_{i=1}^d \sigma_{ji} \mathbf{b}_i, \quad j = 1, \dots, n. \quad (18.5)$$

We construct the Fourier superspace basis vectors $\mathbf{b}_i^s$ as

$$\begin{aligned} \mathbf{b}_i^s &= (\mathbf{b}_i, \mathbf{0}), \quad i = 1, \dots, d, \\ \mathbf{b}_{d+j}^s &= (\mathbf{b}_{d+j}, \mathbf{e}_j), \quad j = 1, \dots, n, \end{aligned} \quad (18.6)$$

that generate the reciprocal superspace lattice $\mathcal{L}_s$. The vectors $\mathbf{e}_j$ are perpendicular to the Fourier physical space, and thus generate an nD space $V_\perp^*$, orthogonal to the physical space $V_\parallel^*$. The $\mathbf{e}_j$ s are chosen to be mutually orthogonal, and since the additional dimensions do not have a physical meaning, we set the lengths of the $\mathbf{e}_j$ s to unity. We recast (18.6) in matrix form

$$\mathbf{B}^s = \begin{pmatrix} \mathbb{I} & \mathbf{0} \\ \boldsymbol{\sigma} & \mathbb{I} \end{pmatrix} \begin{pmatrix} \mathbf{b}_i \\ \mathbf{e}_j \end{pmatrix}$$

where $\mathbf{B}^s = (\mathbf{b}_1^s, \dots, \mathbf{b}_N^s)$, and

$$\det \left| \begin{pmatrix} \mathbb{I} & \mathbf{0} \\ \boldsymbol{\sigma} & \mathbb{I} \end{pmatrix} \right| = 1.$$

This choice of the $\mathbf{e}_j$ s guarantees that they generate a dual direct, or real, lattice in $V_\perp$, with primitive vectors $\mathbf{e}_j$. Making use of this property, together with the duality relations

$$\begin{aligned}\mathbf{a}_i \cdot \mathbf{b}_j &= \delta_{ij}, \\ \mathbf{a}_i^s \cdot \mathbf{b}_j^s &= \delta_{ij},\end{aligned}$$

we write

$$\mathbf{A}^s = \begin{pmatrix} \mathbb{I} & -\tilde{\boldsymbol{\sigma}} \\ \mathbf{0} & \mathbb{I} \end{pmatrix} \begin{pmatrix} \mathbf{a}_i \\ \mathbf{e}_j \end{pmatrix},$$

which may be written in expanded form as

$$\begin{aligned}\mathbf{a}_i^s &= \left(\mathbf{a}_i, -\sum_{j=1}^n \sigma_{ji} \mathbf{e}_j \right), \quad i = 1, \dots, d, \\ \mathbf{a}_{d+j}^s &= (\mathbf{0}, \mathbf{e}_j), \quad j = 1, \dots, n.\end{aligned}\tag{18.7}$$

Hence, $\mathfrak{L}_s$ is determined by the $\mathbf{a}_i$ s, spanning the real physical lattice $\mathfrak{L}$, by the $\mathbf{e}_j$ s, spanning a lattice $\mathfrak{L}_\perp$ in an n D space orthogonal to the d D physical space and the matrix $\boldsymbol{\sigma}$. This procedure establishes the construction of the dual superspace lattices $\mathfrak{L}_s$ and $\mathfrak{L}_s^*$.

In order to construct the superspace crystal, we make use of the measured Fourier intensities, or form factors $\rho(\mathbf{h})$. Since there is a one-to-one correspondence between the physical space indexing on the $\mathbf{b}_i$ s and the $\mathbf{b}_i^s$ s, $i = 1, \dots, N$, this task is quite straightforward, and we readily obtain the form factors in the Fourier superspace as

$$\rho_s(\mathbf{K}) = \rho(\mathbf{h}), \quad \mathbf{K} \in \mathfrak{L}_s^*, \quad \mathbf{h} \in \mathfrak{L}^*.$$

The real superspace density function $\rho_s(\mathbf{r}_s)$ is then obtained as the isomorphic mapping

$$\rho(\mathbf{r}) = \sum_{\mathbf{h}} \rho(\mathbf{h}) e^{i\mathbf{h} \cdot \mathbf{r}} \quad \Rightarrow \quad \rho_s(\mathbf{r}_s) = \sum_{\mathbf{K}} \rho_s(\mathbf{K}) e^{i\mathbf{K} \cdot \mathbf{r}_s}.\tag{18.8}$$

$\rho_s(\mathbf{r}_s)$ is periodic with respect to the superspace lattice $\mathfrak{L}_s$. We are thus able to obtain a periodic structure in N D Euclidean space, from which the d D IMS can be obtained by appropriate projection techniques. Thus, it is only necessary to define a single unit cell of the N D structure. The contents of the N D unit cell consist of *hyperatoms* in analogy to the atoms in the normal unit cell. This enables us to describe the whole unit quasi-crystal structure with a finite set of parameters. If we described it in the original d D Euclidean space, we would be required to define thousands of atomic positions to obtain a representative volume segment of the whole structure.

Intersection in real space corresponds to projection in reciprocal space

Consider an ND Euclidean space $\mathcal{R}^N$ in which V is a dD subspace generated by basis vectors $\mathbf{a}_1, \dots, \mathbf{a}_d$, to which we add $N-d$ vectors to form a basis of $\mathbf{a}_1, \dots, \mathbf{a}_N$ of $\mathcal{R}^N$, with a general vector $\mathbf{r} = \sum_{i=1}^N x_i \mathbf{a}_i$. The reciprocal basis is given by $\mathbf{b}_1, \dots, \mathbf{b}_N$, with vectors $\mathbf{k} = \sum_{i=1}^N h_i \mathbf{b}_i$. The projection of a function $F(\mathbf{k})$ onto V is given by

$$\begin{aligned} g(h_1 \dots h_m) &= \int F(h_1 \dots h_N) dh_{d+1} \dots dh_N \\ &= \int dx_1 \dots dx_N \int f(x_1 \dots x_N) \exp \left[-2\pi i \sum_{j=1}^N h_j x_j \right] \\ &\quad \times dh_{d+1} \dots dh_N \\ &= \int f(x_1, \dots, x_d, 0, 0, \dots, 0) \exp \left[-2\pi i \sum_{j=1}^d h_j x_j \right] \\ &\quad \times dx_1 \dots dx_d, \end{aligned}$$

which is the Fourier transform of the restriction of f to the subspace V . In this sense the projection of the Fourier transform on V is the Fourier transform of the restriction of f to V .

18.2.2 Symmetry and superspace groups*Symmetry of the diffraction image $\mathfrak{D}$*

Since the diffraction image $\mathfrak{D}$ is defined on the quasi-lattice, the point-group that leaves $\mathfrak{D}$ invariant, i.e. the Laue group $\mathcal{P}_L$, is a subgroup of the quasi-lattice holohedry. Its elements have representative matrices in $GL(N, \mathbb{Z})$ generated by

$$R \mathbf{b}_i = \sum_{j=1}^N \Gamma(R^{-1})_{ij} \mathbf{b}_j, \quad N = d + n.$$

Elements of the Laue group of an IM system must map main reflections onto main reflections and satellites onto satellites, consequently, $\mathcal{P}_L$ is also a subgroup of the holohedry of the basic lattice.

Because $\Gamma(R)$ is a Rep of a finite group, it is equivalent to a fully reducible Rep and also to an orthogonal one, namely

$$\Gamma(R) = \Gamma_{\parallel}(R) \oplus \Gamma_{\perp}(R).$$

This means that both $\Gamma_{\parallel}(R)$ and $\Gamma_{\perp}(R)$ are Reps of $R \in \mathcal{P}_L$ of dimensions d and n , respectively.

Superspace point-groups

We explore the properties of the ND crystallographic point-groups, $\mathcal{P}_N$ that are admitted in the symmetry of the superspace lattices [179, 180]. Since the spaces $V_{\parallel}$ and $V_{\perp}$ are restricted to remain mutually exclusive at all times, no rotation or reflection operations that interchange coordinates between the two spaces are to be admitted when describing the symmetry of $\mathfrak{L}_s$. We thus conclude that $\mathcal{P}_N \subset \mathcal{P}_d \otimes \mathcal{P}_n$, where $\mathcal{P}_d$ and $\mathcal{P}_n$ are crystallographic point-groups in dD and nD , respectively. Hence, we write an allowed point-group operation as $R = (R_{\parallel}, R_{\perp}) \in \mathcal{P}_N$. Operating on the basis vectors of $\mathfrak{L}_s$, $\mathfrak{L}_{\parallel}$, and $\mathfrak{L}_{\perp}$, we obtain

$$\begin{aligned} R \mathbf{A}_s &= \mathbf{A}_s \Gamma(R), \\ R_{\parallel} \mathbf{A}_{\parallel} &= \mathbf{A}_{\parallel} \Gamma_{\parallel}(R), & \mathbf{A}_{\parallel} &= (\mathbf{a}_1, \dots, \mathbf{a}_d) \\ R_{\perp} \mathbf{A}_{\perp} &= \mathbf{A}_{\perp} \Gamma_{\perp}(R), & \mathbf{A}_{\perp} &= (\hat{\mathbf{e}}_1, \dots, \hat{\mathbf{e}}_n) \end{aligned}$$

where $\Gamma(R) \in GL(N, \mathbb{Z})$, $\Gamma_{\parallel}(R) \in GL(d, \mathbb{Z})$ and $\Gamma_{\perp}(R) \in GL(n, \mathbb{Z})$. But,

$$\begin{aligned} R \mathbf{A}_s &= R \begin{pmatrix} \mathbb{I} & -\tilde{\boldsymbol{\sigma}} \\ \mathbf{0} & \mathbb{I} \end{pmatrix} \begin{pmatrix} \mathbf{a}_i \\ \hat{\mathbf{e}}_j \end{pmatrix} = \begin{pmatrix} \mathbf{a}_i & \hat{\mathbf{e}}_j \end{pmatrix} \begin{pmatrix} \Gamma_{\parallel}(R) & \mathbf{0} \\ -\Gamma_{\perp}(R) \boldsymbol{\sigma} & \Gamma_{\perp}(R) \end{pmatrix} \\ &= \mathbf{A}_s \begin{pmatrix} \mathbb{I} & \mathbf{0} \\ \boldsymbol{\sigma} & \mathbb{I} \end{pmatrix} \begin{pmatrix} \Gamma_{\parallel}(R) & \mathbf{0} \\ -\Gamma_{\perp}(R) \boldsymbol{\sigma} & \Gamma_{\perp}(R) \end{pmatrix} = \mathbf{A}_s \begin{pmatrix} \Gamma_{\parallel}(R) & \mathbf{0} \\ \Gamma_M(R) & \Gamma_{\perp}(R) \end{pmatrix}, \end{aligned} \quad (18.9)$$

where

$$\Gamma_M(R) = \boldsymbol{\sigma} \Gamma(R_{\parallel}) - \Gamma(R_{\perp}) \boldsymbol{\sigma}. \quad (18.10)$$

Since Γ_M must have integer entries, (18.10) imposes severe restrictions on $\boldsymbol{\sigma}$, which has rational and irrational entries.

Example 18.3

The γ -phase of Na_2CO_3 , a case of 1D incommensurate modulation

The $\hat{\mathbf{e}}_3$ -axis can be transformed according to $\Gamma(R_{\perp}) = \pm 1$, so that $\Gamma(R_{\perp}) \boldsymbol{\sigma} = \varepsilon \mathbf{q}$, $\varepsilon = \pm 1$. Thus, we require that

$$\boldsymbol{\sigma} \Gamma_{\parallel}(R) = \Gamma_{\parallel}(R) \mathbf{q} = \varepsilon \mathbf{q} + \mathbf{G}, \quad \forall R_{\parallel} \in \mathcal{P}_d,$$

which renders

$$\Gamma_M(R) = (m_1, \dots, m_d) \Rightarrow \mathbf{G} = \sum_{i=1}^d m_i \mathbf{b}_i.$$

Now, the main reflection in the diffraction pattern of the γ -phase of Na_2CO_3 corresponds to a C-centered monoclinic lattice and the modulation wavevector is

$$\mathbf{q} = \sigma_1 \mathbf{b}_1 + \sigma_3 \mathbf{b}_3,$$

the monoclinic point-group is $\mathcal{P}_b = 2/m$, with an arithmetic Rep

$$\begin{aligned}\Gamma(C_2^y) &= \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}; & \Gamma(\sigma_y) &= \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}. \\ \Gamma_{\parallel}(C_2^y)\mathbf{q} &= \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}\mathbf{q} = -\mathbf{q}, & \Gamma_{\perp}(C_2^y)\mathbf{q} &= -\mathbf{q} \Rightarrow \Gamma_M(C_2^y) = \mathbf{0}, \\ \Gamma_{\parallel}(\sigma_y)\mathbf{q} &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\mathbf{q} = \mathbf{q}, & \Gamma_{\perp}(\sigma_y)\mathbf{q} &= \mathbf{q} \Rightarrow \Gamma_M(\sigma_y) = \mathbf{0}.\end{aligned}$$

The basis vectors of the 4D reciprocal and real superspace are:

$$\begin{aligned}\mathbf{b}_1^s &= (\mathbf{b}_1, \mathbf{0}), \mathbf{b}_2^s = (\mathbf{b}_2, \mathbf{0}), \mathbf{b}_3^s = (\mathbf{b}_3, \mathbf{0}), \mathbf{b}_4^s = (\mathbf{q}, \mathbf{1}), \\ \mathbf{a}_1^s &= (\mathbf{a}_1, -2\pi\sigma_1), \mathbf{a}_2^s = (\mathbf{a}_2, -2\pi\sigma_2), \mathbf{a}_3^s = (\mathbf{a}_3, -2\pi\sigma_3), \mathbf{a}_4^s = (\mathbf{0}, 2\pi).\end{aligned}$$

Superspace-groups

As we have remarked above, the density function $\rho_s(\mathbf{r}_s)$ is invariant under the lattice translations $\mathbf{t}_s \in \mathfrak{L}_s$, as well as under elements $(R|\boldsymbol{\tau}_s) \equiv ((R_{\parallel}|\boldsymbol{\tau}_{\parallel}), (R_{\perp}|\boldsymbol{\tau}_{\perp}))$, where

$$(R|\boldsymbol{\tau}_s)\mathbf{r}_s = R_{\parallel}\mathbf{r}_{\parallel} + \boldsymbol{\tau}_{\parallel}, R_{\perp}\mathbf{r}_{\perp} + \boldsymbol{\tau}_{\perp}, \quad (18.11)$$

such that

$$\rho_s((R|\boldsymbol{\tau}_s)\mathbf{r}_s) = \rho_s(\mathbf{r}_s). \quad (18.12)$$

The combined operations, $(R|\boldsymbol{\tau}_s + \mathbf{t}_s)$, constitute the *superspace-group* $\mathbb{S}_s$ of the embedded crystal in ND . Because of the existence of the basic structure, the group $\mathbb{S}_{\parallel} \ni (R_{\parallel}|\boldsymbol{\tau}_{\parallel})$ is equivalent to one of the dD space-groups, namely, the 17 two-dimensional or the 230 three-dimensional space-groups.

Nature of the nonprimitive translations in $\mathfrak{L}_{\perp}$ In order to elucidate the idea of the symmetry of nonprimitive translations, we consider an $N = 2$ displacively modulated system, i.e. with $d = n = 1$. In this case, the position of an atom κ in primitive cell ℓa , where a is the basis of the basic structure, is given by

$$u(\kappa, \ell, x_{\perp}) = U_{\kappa}(q(\ell a + x_{\kappa}) + x_{\perp}), \quad \text{with } U_{\kappa}(\alpha + 1) = U_{\kappa}(\alpha), \quad (18.13)$$

$x_{\perp}$ is the extra-coordinate, x_{κ} is the position of the κ th atom in the primitive cell, and q is the modulation wavevector. Although the translational symmetry, $t = ja$, is lost upon modulation, it can be regained by replacing $x_{\perp}$ by $x_{\perp} - qt$. Remembering that the addition of any integer p to $x_{\perp}$ will leave U_{κ} invariant, we find that the translation group of the 2D superspace lattice is the set $\{(ja, -qja + p)\}$, such that

$$x'_{\parallel} = x_{\parallel} + ja, \quad x'_{\perp} = x_{\perp} - qja + p. \quad (18.14)$$

A general symmetry operation can then be written as

$$x'_{\parallel} = v x_{\parallel} + j a, \quad x'_{\perp} = \varepsilon x_{\perp} - q j a + p, \quad (18.15)$$

where $v = \pm 1$, $\varepsilon = \pm 1$ are the only allowed homogeneous operations in 1D. We now show that the condition $v = \varepsilon$ must be satisfied. We start with the translation operation $(1, -q) \bmod a$, and generate the following sequence:

$$\begin{aligned} (v, \varepsilon) (1, -q) \bmod a &\rightarrow (v, -\varepsilon q) \bmod a \\ v (v, -\varepsilon q) \bmod a &\rightarrow (1, -v\varepsilon q) \bmod a \\ (-1, q) \bmod a (1, -v\varepsilon q) \bmod a &\rightarrow (0, (1 - v\varepsilon)q) \bmod a. \end{aligned}$$

The last operation is of the form $(0, p)$, with p an integer. Since q is irrational, this can only be satisfied if $v\varepsilon = 1$, or $v = \varepsilon$.

We now generalize these results for $d > 1$, $n = 1$; then (18.13) becomes

$$\mathbf{u}(\kappa, \mathbf{t}_{\ell}, x_{\perp}) = \mathbf{U}_{\kappa}(\mathbf{q} \cdot (\mathbf{t}_{\ell} + \mathbf{x}_{\kappa}) + x_{\perp}), \quad \text{with } \mathbf{U}_{\kappa}(\alpha + 1) = \mathbf{U}_{\kappa}(\alpha), \quad (18.16)$$

with $\mathbf{t}_{\ell} = \sum_{i=1}^d l_i \mathbf{a}_i$. The group symmetry translations become

$$\mathbf{x}'_{\parallel} = \mathbf{x}_{\parallel} + \mathbf{t}, \quad x'_{\perp} = x_{\perp} - \mathbf{q} \cdot \mathbf{t} + p \rightarrow (\mathbf{t}, -\mathbf{q} \cdot \mathbf{t} + p). \quad (18.17)$$

The general symmetry operation takes the form

$$x'_{\parallel} = R \mathbf{x}_{\parallel} + \mathbf{t}, \quad x'_{\perp} = \varepsilon x_{\perp} - \mathbf{q} \cdot \mathbf{t} + p. \quad (18.18)$$

Example 18.4

One-dimensional displacive modulation in potassium selenate, K_2SeO_4

In this section we analyze the structure of K_2SeO_4 , which has an incommensurable modulated phase between 93 and 128 K, using the superspace-group concept [181]. Relevant aspects of its lattice dynamics and the phase transition were discussed in Chapters 15 and 17, respectively.

The modulation is of the displacive type, having a basic structure with an orthorhombic lattice $\mathfrak{L}_b$ and a space-group symmetry $Pnam$ (see Section 15.3.4). There are four formula units per unit cell: in each formula the four O atoms form a tetrahedron with the Se atom located at its center. The K atoms are located at (c) Wyckoff positions.

The modulation is described in the rigid SeO_4 approximation and involves 12 displacive modulation waves $f_j(\mathbf{r})$ ($j = 1, 2, \dots, 12$) and four rotative ones $R_j(\mathbf{r})$ ($j = 1, 2, 3, 4$). The satellites due to this modulation are characterized by wavevectors $\mathbf{q}_{\delta}$ and $\mathbf{q}_{2\delta}$ with

$$\mathbf{q}_{\delta} = \frac{1}{3}(1 - \delta)\mathbf{b}_1, \quad \text{and } \mathbf{q}_{2\delta} = \mathbf{b}_1 - 2\mathbf{q}_{\delta}.$$

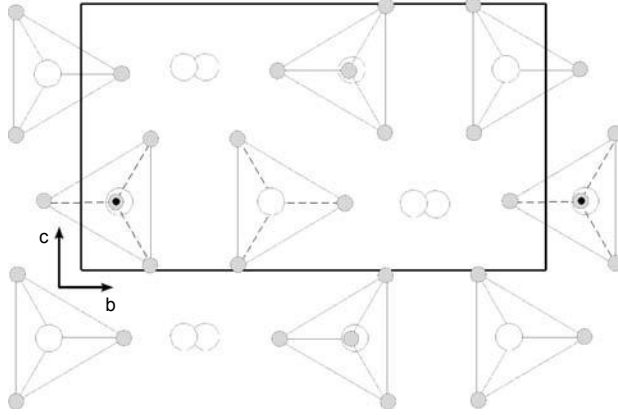


Fig. 18.10. Projection of the unit cell of K_2SeO_4 along the $[100]$ direction. Se, solid black circles; O, solid gray circles; and K, white circles. Hidden atoms are not shown.

With respect to the basis $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ of $\mathfrak{L}_b$ the vector $\mathbf{q}_\delta$ has components

$$q_1 = \frac{1}{3}(1 - \delta), \quad q_2 = q_3 = 0.$$

The dimension of $V_\perp$ is $n = 1$. As coordinate system in superspace we choose the basis $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$, and $\hat{\mathbf{e}}$, where $\hat{\mathbf{e}}$ is a vector in $V_\perp$. Then a primitive basis for the lattice in superspace is

$$(1, 0, 0, -q_1), \quad (0, 1, 0, 0), \quad (0, 0, 1, 0), \quad \text{and} \quad (0, 0, 0, 1).$$

The Bravais class of this lattice is $P_{\overline{1}11}^{\text{Pmmm}}$ (see [182, 183]). The holohedry of this lattice is generated by the superspace point-group transformations

$$(\sigma_x, \varepsilon = -1), \quad (\sigma_y, \varepsilon = 1), \quad \text{and} \quad (\sigma_z, \varepsilon = 1).$$

Elements of the superspace-group $\mathbb{S}_s$ have to fulfill conditions (18.16), (18.17), and (18.18). The first one is satisfied if $\mathbb{S}_\parallel \subset Pnam$. For the invariance conditions (18.17) and (18.18) one uses the fact that the total displacement transforms according to the Σ_2 Irrep. The procedure of deriving the superspace-group directly from that information has already been discussed in [178]. The point-group of $\mathbf{q}_\delta$ has elements $1, \sigma_y, \sigma_z, 2_x$ with characters $1, -1, -1, 1$ respectively, in the Σ_2 Irrep. For these elements $\mathbf{G} = \mathbf{0}$; hence for $R = (\sigma_y, 1)$ and $R = (\sigma_z, 1)$, (18.17) and (18.18) reduce to

$$\begin{aligned} f_j(\mathbf{q}) &= -f_j(\mathbf{q}) e^{-iq_\perp \tau_\perp}, \\ \mathbf{R}_j(\mathbf{q}) &= -\mathbf{R}_j(\mathbf{q}) e^{-iq_\perp \tau_\perp}, \end{aligned} \quad (18.19)$$

where $\mathbf{q} = \mathbf{q}_\delta$. Accordingly, $q_\perp = \hat{\mathbf{e}}$ and (18.19) is satisfied for $\tau_\perp = 1/2\hat{\mathbf{e}}$. This leads to the following set of nonprimitive translations:

$$\begin{aligned}\tau(\sigma_y, 1) &= \left(\frac{1}{2}, \frac{1}{2}, 0, \frac{1 - q_1}{2} \right), \\ \tau(\sigma_z, 1) &= \left(0, 0, \frac{1}{2}, \frac{1}{2} \right).\end{aligned}\tag{18.20}$$

Finally, we consider $R_\parallel = -1$, which implies $R_\perp = -1$. For this case also, $\mathbf{q} = \mathbf{q}_\delta$, and one gets $\mathbf{G} = \mathbf{0}$. Since the total displacement transforms according to a one-dimensional corepresentation, it follows that the $\mathbf{q}_\delta$ components of the modulation vector fields obey the relations

$$\begin{aligned}f_j(\mathbf{q}) &= -e^{i\varphi} f_j(\mathbf{q}) e^{-iq_\perp \tau_\perp}, \\ \mathbf{R}_j(\mathbf{q}) &= -e^{i\varphi} \mathbf{R}_j(\mathbf{q}) e^{-iq_\perp \tau_\perp}.\end{aligned}\tag{18.21}$$

Hence there is an element $\tau_\perp = \tau_\perp(\bar{1}, \bar{1})$ solving (18.21). Such a non primitive translation is, however, equivalent to zero, and can be transformed away by a shift of the origin (taken along the x -direction to keep (18.20) unchanged). Consequently, the superspace-group for K_2SeO_4 in the incommensurate crystal phase is

$$P_{\bar{1}\bar{1}\bar{1}}^{\text{Pnam}}.$$

This group is generated by the translations $(1, 0, 0, -q_1), (0, 1, 0, 0), (0, 0, 1, 0)$ and $(0, 0, 0, 1)$ and by the following superspace-group elements:

$$\begin{aligned}((\sigma_x, \bar{1})|\tau_s(\sigma_x, \bar{1})) &: (x, y, z, x_\perp) \rightarrow (-x + 1/2, y + 1/2, z + 1/2, -x_\perp - \sigma_1/2), \\ ((\sigma_y, 1)|\tau_s(\sigma_y, 1)) &: (x, y, z, x_\perp) \rightarrow (x + 1/2, -y + 1/2, z, x_\perp + 1/2 - \sigma_1/2), \\ ((\sigma_z, 1)|\tau_s(\sigma_z, 1)) &: (x, y, z, x_\perp) \rightarrow (x, y, -z + 1/2, x_\perp + 1/2).\end{aligned}$$

As de Wolff has pointed out, the systematic extinctions due to the superspace-group $P_{\bar{1}\bar{1}\bar{1}}^{\text{Pnam}}$ are only approximately observed. The assignment of the modulation to a Σ_2 Irrep (as assumed here) has therefore to be considered with some caution.

Phason excitations As we discussed in Chapter 15, crystalline structures have the property that their energy remains invariant under arbitrary rigid translations; and a manifestation of this property is the presence of zero-energy acoustic modes at $\mathbf{q} = \mathbf{0}$. The same principle applies to supercrystalline structures, and we find that their energies remain invariant under arbitrary rigid translations. Consequently, the energy of the embedded incommensurate structure should also be invariant against such displacements: they simply correspond to a shift of origin.

Using the simple example of the 1D incommensurately modulated structure of Figure 18.9, we find that a rigid displacement along the real line V_E describes a uniform displacement of the system. On the other hand, a shift along $V_\perp$ involves some internal

rearrangement of the atoms, which may also be viewed as changes in the phase modulation $\mathbf{q}_2 \cdot \mathbf{r}_i$; such displacements represent excitation modes that have been appropriately labeled *phason excitations*.

18.3 Quasi-crystal symmetry: the notion of indistinguishability and the classification of space-groups

We have learned in Chapter 10 that the symmetry of periodic systems in d -dimensions entails that the density $\rho(\mathbf{r})$ remains invariant under the operations of the defining space-group, namely translation invariance under the subgroup of translations,

$$\rho(\mathbf{r} + \mathbf{t}) = \rho(\mathbf{r}),$$

as well as under the composite operations $(R|\boldsymbol{\tau})$. This invariance is manifest in the existence of a sharp diffraction pattern, well defined on a dual lattice that shares the same point-group symmetry and whose basis translation vectors, $\mathbf{b}_i$, bear a definite relation to those of the periodic system, $\mathbf{a}_i$, namely,

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi \delta_{ij}.$$

We also showed, in Section 10.5, that each space-group operation $(R|\boldsymbol{\tau})$ can be defined on the dual lattice points $\mathbf{G}$ by a set of phases $\phi_R(\mathbf{G})$. We can then classify a space-group's Fourier-space according to the corresponding set of phases that is consistent with the action of its symmetry operations on the lattice.

Mermin and coworkers [165, 166, 167, 168, 169, 170, 171, 172] suggested that these definitions can be substantially generalized. In the expanded landscape, where we are no longer tied down by periodicity or rigid rotations in real space, the concept of space-group symmetries becomes a very special case.

18.3.1 Quasi-periodic systems and the concept of indistinguishability

In contrast to periodic systems, the densities of QP systems, in general, lack global translational symmetry and direct-space lattices, as well as the real-space symmetries discussed above. The lack of rotational symmetry is a consequence of the fact that if a system possesses more than one point whereby it can be brought into coincidence with itself when operated upon by an n -fold rotation ($n > 2$), it has to be periodic. However, QP systems possess some peculiar symmetry, which can be summed-up by the following quote [171]

Certain rotations take a QP system into one which looks very much like the original unrotated one. This is because the two systems contain the same statistical distribution of “bounded substructures” of arbitrary size: We find that any bounded region in the rotated QP system can be found in the unrotated one, but the larger the region in one system the further away its counterpart in the other system.

This interesting property of *mesoscopic homogeneity*, as coined by Mermin, germinates the idea of *indistinguishability*, and leads to establishing a unified scheme for classifying the symmetries of crystals, quasi-crystals, and incommensurate systems.

The concept of indistinguishability

Mermin and coworkers [171] introduced the idea of indistinguishability for QP systems as an alternative to invariance for periodic systems. Here, two densities that are statistically the same in the above sense, though not necessarily identical, are termed *indistinguishable*. We formulate this condition, mathematically, by defining positionally averaged n -point autocorrelation functions, $\forall n$, as

$$c(\mathbf{r}_1, \dots, \mathbf{r}_n) = \lim_{V \rightarrow \infty} \frac{1}{V} \int d\mathbf{r} \rho(\mathbf{r}_1 - \mathbf{r}) \dots \rho(\mathbf{r}_n - \mathbf{r}). \quad (18.19)$$

Then, the condition of indistinguishability between two densities ρ and ρ' can be expressed as

$$c(\mathbf{r}_1, \dots, \mathbf{r}_n) = c'(\mathbf{r}_1, \dots, \mathbf{r}_n), \quad (18.20)$$

for every n th-order autocorrelation function c and c' , respectively, in the heirarchy defined by (18.19).

This definition of indistinguishability allows us to identify the symmetry operations associated with QP systems, namely, the operations that leave the system indistinguishable, by preserving all positionally averaged autocorrelation functions.

Density function on the Fourier-space lattice, and its autocorrelations

As we mentioned in the introduction, diffraction experiments demonstrate that the density function of QP systems in Fourier space, $\rho(\mathbf{K})$, exhibits Bragg peaks that appear on a regular lattice Λ^* , defined by a dense infinitely countable set of vectors $\mathbf{K}$. The real-space partner, $\rho(\mathbf{r})$, can be expressed as

$$\rho(\mathbf{r}) = \sum_{\mathbf{K}} \rho(\mathbf{K}) e^{i\mathbf{K} \cdot \mathbf{r}}, \quad (18.21)$$

with the proviso

$$\rho(-\mathbf{K}) = \rho^*(\mathbf{K}), \quad (18.22)$$

since the density is a real function. Taking the Fourier transform of (18.19), we find that the surviving components in the Fourier transform of the autocorrelation function $c(\mathbf{r}_1, \dots, \mathbf{r}_n)$ have the form

$$\begin{aligned} C(\mathbf{K}_1, \dots, \mathbf{K}_n) &= \frac{1}{n} \prod_{i=1}^n \rho(\mathbf{K}_i) \int d\mathbf{r} \exp \left[i \sum_{i=1}^n \mathbf{K}_i \cdot \mathbf{r} \right] \\ &= \delta \left(\sum_{i=1}^n \mathbf{K}_i \right) \prod_{i=1}^n \rho(\mathbf{K}_i), \end{aligned} \quad (18.23)$$

and the Fourier-space form of (18.20) can be expressed as

$$\rho(\mathbf{K}_1) \dots \rho(\mathbf{K}_n) = \rho'(\mathbf{K}_1) \dots \rho'(\mathbf{K}_n), \quad (18.24)$$

whenever

$$\sum_{i=1}^n \mathbf{K}_i = 0. \quad (18.25)$$

The linear gauge function In the case of $C(\mathbf{K}_1, \mathbf{K}_2)$ with $\mathbf{K}_2 = -\mathbf{K}_1$, (18.22) implies that

$$|\rho|^2 = |\rho'|^2, \quad (18.26)$$

and, therefore, the Fourier coefficients themselves differ only by a real phase

$$\begin{aligned} \rho'(\mathbf{K}) &= e^{2\pi i \chi(\mathbf{K})} \rho(\mathbf{K}), \\ \chi(-\mathbf{K}) &= -\chi(\mathbf{K}) \pmod{1} \\ &\equiv -\chi(\mathbf{K}). \end{aligned} \quad (18.27)$$

Mermin coined the function $\chi(\mathbf{K})$ as the *gauge function*, in analogy to the gauge functions of electrodynamics; it can alter the phase of a wavefunction without altering observable properties.

Extending our analysis to $C(\mathbf{K}_1, \mathbf{K}_2, \mathbf{K}_3)$, we obtain, using (18.24) and (18.27),

$$\begin{aligned} \rho(\mathbf{K}_1) \rho(\mathbf{K}_2) \rho(\mathbf{K}_3) &= \exp[2\pi i (\chi(\mathbf{K}_1) + \chi(\mathbf{K}_2) + \chi(\mathbf{K}_3))] \\ &\quad \times \rho(\mathbf{K}_1) \rho(\mathbf{K}_2) \rho(\mathbf{K}_3), \end{aligned} \quad (18.28)$$

$$\chi(\mathbf{K}_1) + \chi(\mathbf{K}_2) + \chi(\mathbf{K}_3) = \chi(\mathbf{K}_1) + \chi(\mathbf{K}_2) - \chi(\mathbf{K}_1 + \mathbf{K}_2) \equiv 0,$$

or

$$\chi(\mathbf{K}_1 + \mathbf{K}_2) \equiv \chi(\mathbf{K}_1) + \chi(\mathbf{K}_2). \quad (18.29)$$

Condition (18.29) allows us to satisfy all orders of (18.24). Thus, *two densities are indistinguishable if and only if their Fourier coefficients are related by a linear gauge function as defined in (18.27).*

Point-groups and phase functions

By analogy to invariance under symmetry operations in the case of periodic systems, we now identify the symmetry operations associated with a QP system as those that leave the system indistinguishable, i.e. for a point symmetry operation R , all conditions (12.68), namely,

$$\phi_{R_1 R_2}(\mathbf{G}) \equiv \phi_{R_1}(R_2 \mathbf{G}) + \phi_{R_2}(\mathbf{G}),$$

must be satisfied by $\rho(R^{-1}\mathbf{r})$ and $\rho(\mathbf{r})$. We have shown above that this is just equivalent to condition (18.27), and we obtain

$$\rho(R\mathbf{K}) = e^{2\pi i\phi_R(\mathbf{K})} \rho(\mathbf{K}). \quad (18.30)$$

Mermin termed the gauge functions associated with the point-group $\mathcal{G}$, namely $\phi_R(\mathbf{K})$, *phase functions*.

In terms of the phase functions, the constraint equation (18.24) becomes

$$\phi_R(\mathbf{K}_1) + \phi_R(\mathbf{K}_2) + \cdots + \phi_R(\mathbf{K}_m) \equiv 0 \quad (18.31)$$

whenever

$$\mathbf{K}_1 + \mathbf{K}_2 + \cdots + \mathbf{K}_m = 0, \quad \mathbf{K}_i \in \mathfrak{D},$$

where $\equiv$ denotes equality to within an integer, i.e. modulo one.

Next, we consider the action of two symmetry operations $R_1, R_2 \in \mathcal{G}$. We find that because of the associativity of the operations,

$$\rho([R_1 R_2]\mathbf{K}) = \rho(R_1[R_2\mathbf{K}]),$$

these, together with (18.29), show that the phase functions associated with the group elements of $\mathcal{G}$ must satisfy the *group compatibility condition*

$$\phi_{R_i R_j}(\mathbf{K}) \equiv \phi_{R_i}(R_j\mathbf{K}) + \Phi_{R_j}(\mathbf{K}); \quad \forall R_i, R_j \in \mathcal{G}. \quad (18.32)$$

Gauge-equivalent phase functions

We now explore the possibility of having two sets of equivalent phase functions associated with a point-group $\mathcal{G}$. We proceed by considering two indistinguishable systems with densities ρ and ρ' , such that

$$\rho'(\mathbf{K}) = e^{2\pi i\chi(\mathbf{K})} \rho(\mathbf{K}).$$

Since such systems should also be indistinguishable under the operations of the point-group $\mathcal{G}$, we have

$$\rho(R\mathbf{K}) = e^{2\pi i\phi_R(\mathbf{K})} \rho(\mathbf{K}),$$

$$\rho'(R\mathbf{K}) = e^{2\pi i\phi'_R(\mathbf{K})} \rho'(\mathbf{K}).$$

We then find, with the aid of (18.25), that

$$\begin{aligned} \rho'(R\mathbf{K}) &= e^{2\pi i\phi'_R(\mathbf{K})} \rho'(\mathbf{K}) = e^{2\pi i(\phi'_R(\mathbf{K}) + \chi(\mathbf{K}))} \rho(\mathbf{K}) \\ &= e^{2\pi i\chi(R\mathbf{K})} \rho(R\mathbf{K}) = e^{2\pi i(\phi_R(\mathbf{K}) + \chi(R\mathbf{K}))} \rho(\mathbf{K}), \end{aligned}$$

which leads to the equivalence condition

$$\begin{aligned}\phi'_R(\mathbf{K}) &\equiv \phi_R(\mathbf{K}) + \chi(R\mathbf{K}) - \chi(\mathbf{K}) \\ &= \phi_R(\mathbf{K}) + \chi([R - \mathbb{I}]\mathbf{K}),\end{aligned}\tag{18.33}$$

where we used (18.26) and (18.27). Two sets of phase functions that bear such relations, with respect to a given gauge function χ , are called *gauge-equivalent*, and the relations are called *gauge transformations*.

Extinction and gauge-invariant phases

When $R\mathbf{K} = \mathbf{K}$

- (i) Equation (18.33) stipulates the invariance of $\phi_R(\mathbf{K})$ under arbitrary gauge transformations, i.e.

$$\phi'_R(\mathbf{K}) \equiv \phi_R(\mathbf{K})$$

- (ii) Equation (18.30) requires that

$$\rho(\mathbf{K}) = 0, \quad \text{if} \quad \phi_R(\mathbf{K}) \bmod 1 \neq 0.$$

Thus, the noninteger parts of the phase functions determine sets of wavevectors at which the Fourier coefficients of the density necessarily vanish.

Or, alternatively, the Bragg peaks associated with lattice vectors in the invariant subspace of a point-group operation R will be extinguished if

$$\phi_R(\mathbf{K}) \bmod 1 \neq 0.$$

This condition is manifest in the phenomenon of missing Bragg peaks in diffraction patterns and is known as the phenomenon of *extinctions*.

We classify point-group operations associated with invariant subspaces as follows:

- (1) A lattice wavevector $\mathbf{K}$ is left invariant by a reflection σ , namely $\sigma\mathbf{K} = \mathbf{K}$, if it lies in the mirror plane. Since $\sigma^2 = E$, we obtain

$$\phi_{\sigma^2}(\mathbf{K}) \equiv \phi_{\sigma}(\sigma\mathbf{K}) + \phi_{\sigma}(\mathbf{K}) = 2\phi_{\sigma}(\mathbf{K}) \equiv 0, \quad \Rightarrow \quad \phi_{\sigma}(\mathbf{K}) \equiv 0, \quad 1/2. \tag{18.34}$$

For $\phi_{\sigma}(\mathbf{K}) \equiv 1/2$ we have extinction.

- (2) If R is an improper operation other than a pure reflection, it has no invariant lattice subspace.
- (3) For a proper n -fold rotation to satisfy $R_n\mathbf{K} = \mathbf{K}$, $\mathbf{K}$ must lie on the axis of rotation. With the aid of the relation $R_n^n = E$ we obtain

$$\phi_{R_n^n}(\mathbf{K}) \equiv n\phi_{R_n}(\mathbf{K}) \equiv 0 \quad \Rightarrow \quad \phi_{R_n}(\mathbf{K}) \equiv \frac{j}{n}, \quad j = 0, 1, \dots, n-1. \tag{18.35}$$

For $j \neq 0$ we have extinction.

- (4) Further restrictions on the possible values of j arise from other point-group generating relations:

- (a) When the axis of R_n lies in a mirror plane, we have $R_n m R_n = m$, which by the group compatibility relation gives

$$\phi_{R_n \sigma R_n}(\mathbf{K}) \equiv \phi_{R_n \sigma}(R_n \mathbf{K}) + \phi_{R_n}(\mathbf{K}) \equiv 2\phi_{R_n}(\mathbf{K}) + \phi_{\sigma}(\mathbf{K}) \equiv \phi_{\sigma}(\mathbf{K}),$$

or

$$2\phi_{R_n}(\mathbf{K}) \equiv 0 \quad \Rightarrow \quad \phi_{R_n}(\mathbf{K}) \equiv 0, 1/2. \quad (18.36)$$

This restricts n to even values, and $j = 1/2$.

- (b) When $R_n \mathbf{K} = \mathbf{K}$, and its rotation axis is perpendicular to a mirror plane, we have the relation $R_n \sigma = \sigma R_n$, which leads to

$$\phi_{R_n}(\sigma \mathbf{K}) + \phi_{\sigma}(\mathbf{K}) \equiv \phi_{\sigma}(R_n \mathbf{K}) + \phi_{R_n}(\mathbf{K}), \Rightarrow 2\phi_{R_n}(\mathbf{K}) \equiv 0. \quad (18.37)$$

Alternatively, if $\sigma \mathbf{K} = \mathbf{K}$, we have

$$\phi_{\sigma}(\mathbf{K}) \equiv \phi_{\sigma}(R_n \mathbf{K}), \quad (18.38)$$

which imposes the requirement that the pattern of extinctions associated with the glide plane operation should be invariant under R_n .

Thus, if two systems have gauge-equivalent phase functions, then they have the same space-group.

The concepts of scale-equivalence

Scaling Suppose $\mathcal{L}$ is a lattice generated by $\mathfrak{N}$ integrally independent vectors $\mathbf{b}_1, \mathbf{b}_2, \dots, \mathbf{b}_{\mathfrak{N}}$, so that any vector $\mathbf{K}$ in $\mathcal{L}$ can be expressed as

$$\mathbf{K} = \sum_{i=1}^{\mathfrak{N}} n_i \mathbf{b}_i, \quad (18.39)$$

with integral n_i . Let $\mathbf{c}_1, \mathbf{c}_2, \dots, \mathbf{c}_{\mathfrak{N}}$ be any other $\mathfrak{N}$ integrally independent vectors in $\mathcal{L}$. Since the $\mathbf{c}_i$ are in $\mathcal{L}$ they have the form

$$\mathbf{c}_i = \sum_{j=1}^{\mathfrak{N}} M_{ij} \mathbf{b}_j, \quad (18.40)$$

where M is a matrix of integers. The $\mathbf{c}_i$ are integrally independent, so $\sum_{i=1}^{\mathfrak{N}} r_i \mathbf{c}_i$ vanishes for rational numbers r_i if and only if the r_i are all zero. Because the $\mathbf{b}_i$ are also integrally independent, this condition implies that

$$\sum_{i=1}^{\mathfrak{N}} r_i M_{ij}$$

vanishes for all j only if all the r_i vanish, which is precisely the condition that the matrix M has an inverse. We use this inverse to expand the $\mathbf{b}_i$ in terms of the $\mathbf{c}_j$,

$$\mathbf{b}_i = \sum_{j=1}^{\mathfrak{N}} [M^{-1}]_{ij} \mathbf{c}_j. \quad (18.41)$$

The elements of M^{-1} are integers divided by $\det[M]$, so the vectors $\mathbf{B}_i = \det[M] \mathbf{b}_i$ can be expressed as integral linear combinations of the $\mathbf{c}_i$. If $\mathfrak{L}$ is scaled up by a factor of $\det[M]$, then any vector in the rescaled $\mathfrak{L}$ will be an integral linear combination of the $\mathbf{B}_i$, and therefore an integral linear combination of the $\mathbf{c}_i$. Thus:

Any set of $\mathfrak{N}$ integrally independent vectors contained in a lattice of rank $\mathfrak{N}$ can be taken as generating vectors for a scaled version of the lattice.

Scale equivalence Two densities $\rho(\mathbf{r})$ and $\rho(\lambda\mathbf{r})$ that differ only by an overall scale factor, evidently belong to the same space-group type. In the crystallographic case this merely means that the phase functions $\phi_R(\mathbf{K})$ and $\phi_R(\mathbf{K}/\lambda)$ are essentially the same phase functions, characterizing the same space-group on lattices differing by the scale factor λ .

If, however, rescaling by λ leaves the lattice invariant, then $\phi_R(\mathbf{K})$ and $\phi_R(\mathbf{K}/\lambda)$ can also be regarded as two *different* phase functions defined on the *same lattice*. Since they characterize densities differing only by a scale factor, they must still characterize the same space-group. Moreover, since, in general, such phase functions are not gauge-equivalent, we arrive at a second condition for the equivalence of space-groups, **scale equivalence**.

Two phase functions are said to belong to the same quasi-crystallographic space-group type if they are gauge and/or scale equivalent.

Example 18.5

Icosahedral Fourier-space lattices

The icosahedral point-group Y and its Irreps are given in Table 18.1.

$\tau = (1 + \sqrt{5})/2$ is the golden mean, and $\tau_- = (\sqrt{5} - 1)/2$. It is generated by the relations

$$C_5^5 = C_2^2 = (C_2 C_5)^3 = E.$$

Table 18.1. <i>Irreps of Y.</i>					
Irrep	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$
A_g	1	1	1	1	1
F_{1g}	3	τ	$-\tau_-$	0	-1
F_{2g}	3	$-\tau_-$	τ	0	-1
G_g	4	-1	-1	1	0
H_g	5	0	0	-1	1

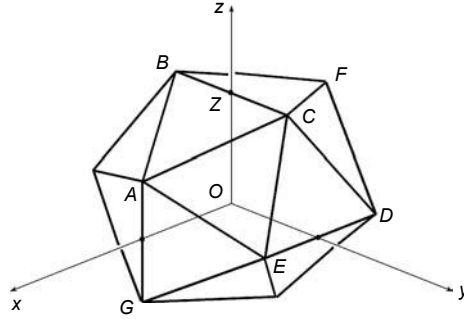


Fig. 18.11. Icosahedron with edge length = 2, and intercept $OZ = \tau$ the golden mean. The icosahedron can then be inscribed in a cube of edge = 2τ .

$Y_h = I \otimes Y$ have five more Irreps with u replacing the subscript g, and where $\chi(IR) = \chi(R)$ for Irreps with subscript g and $\chi(IR) = -\chi(R)$ for Irreps with subscript u.

Figure 18.11 shows an icosahedron with the x -, y -, and z -axes among the 15 two-fold axes, the remaining 12 are lines drawn from the origin O as perpendicular bisectors of the remaining edges. We can identify from the figure the six vectors

$$\begin{aligned} \overline{OA} &= (\tau, 0, 1), \quad \overline{OG} = (\tau, 0, -1), & \overline{OA} + \overline{OG} &= (2\tau, 0, 0), \\ \overline{OE} &= (1, \tau, 0), \quad \overline{OD} = (-1, \tau, 0), & \overline{OD} + \overline{OE} &= (0, 2\tau, 0), \\ \overline{OB} &= (0, -1, \tau), \quad \overline{OC} = (0, 1, \tau), & \overline{OB} + \overline{OC} &= (0, 0, 2\tau), \end{aligned}$$

which can be shown to be linearly integrally independent. Each pair can be permuted by a 2-fold rotation about one of the axes, and yield a vector sum of 2τ directed along the axis of rotation. This property is true for any lattice vector $\mathbf{K}$ and a 2-fold axis i : writing $K_{\parallel}$ as the component of $\mathbf{K}$ along i -axis we have

$$\mathbf{K} + C_2^{(i)} \mathbf{K} = 2 \times K_{\parallel} \hat{\mathbf{e}}_i.$$

Replacing $\overline{OG}$ by $\overline{OF}$, we obtain another integrally independent basis, where the projections on $\overline{OC}$ of the remaining five vectors are positive. A primitive icosahedral lattice (P) comprises integral linear combinations of this basis. A b.c.i. lattice (I) comprises all sets of six integers, which are either all odd or all even. An f.c.i. lattice (F) contains sets whose sum is even.

The P lattice is scale-invariant by τ^3 , while the I and F lattices are scale-invariant by τ .

The concepts of Bravais classes

The concepts of Bravais class, arithmetic crystal class, and space-group type can be defined directly in terms of the rank $\mathfrak{N}$ -lattice $\mathfrak{L}$ of three-dimensional wavevectors, its holohedry $\mathcal{G}_L$, the point-group $\mathcal{G}$ of the QP system, and the associated phases.

Two lattices $\mathfrak{L}$ and $\mathfrak{L}'$ are in the same *Bravais class* if their holohedries $\mathcal{G}_L$ and $\mathcal{G}_{L'}$ are conjugate subgroups of $\mathcal{O}(3)$,

$$\mathcal{G}_{L'} = R\mathcal{G}_L R^{-1}, \quad R \in \mathcal{SO}(3), \quad (18.42)$$

and there exists an invertible linear map f from $\mathfrak{L}'$ to $\mathfrak{L}$ that commutes with their point-groups, i.e. $\forall \mathbf{K} \in \mathfrak{L}$,

$$f(L\mathbf{K}) = L' f(\mathbf{K}), \quad L' = RLR^{-1}, \quad L' \in \mathcal{G}_{L'}, \quad L \in \mathcal{G}_L \quad (18.43)$$

The existence of f ensures that the lattices are isomorphic as Abelian groups and, therefore, in particular, that they have the same rank. That isomorphism is required by (18.42) to preserve the action of the point-groups on their lattices. (It is this proviso that distinguishes the three rank-3 cubic Bravais classes.) Since a point-group operation induces a linear map on $\mathfrak{L}$, we can define a product of linear maps,

$$f \circ L(\mathbf{K}) = L' \circ f(\mathbf{K}) = L'[f(\mathbf{K})], \quad (18.44)$$

in terms of which, condition (18.19) requires that

$$RLR^{-1} = f \circ L \circ f^{-1}. \quad (18.45)$$

New definition of space groups

A new description of a space-group associated with a QP system can be surmised from the above presentation as follows:

- (i) A density function $\rho(\mathbf{K})$ is defined on a lattice $\mathfrak{L}$ of wavevectors. The lattice is invariant under some point-group $\mathcal{G}_L$, while the density is found to be indistinguishable under operations of a subgroup $\mathcal{G}_D \subset \mathcal{G}_L$.
- (ii) A space-group is then identified through a set of phase functions $\phi_R(\mathbf{K})$, one for every $R \in \mathcal{G}$, which satisfy the group compatibility condition (18.32).

In the case of crystallographic groups, $\phi_R(\mathbf{K}) \equiv \mathbf{K} \cdot \mathbf{d}_R$. We may choose $\mathbf{d}_R$ to be the nonprimitive translations.

In this definition of a space-group, we may identify an operator as the set (R, ϕ_R) . In any case, we continue to call this a space-group even though it is no longer a subgroup of the Euclidean group $\mathcal{E}(3)$.

18.4 Two-dimensional lattices, cyclotomic integers, and axial stacking

We now consider 3D Fourier-space lattices, crystallographic and non-crystallographic with a unique axis of high symmetry. We label such lattices as *axial*. Axial lattices can be constructed from corresponding 2D lattices in two ways: either by direct or by staggered stacking of 2D sheets. We therefore start with the analysis of 2D lattices, and introduce some algebraic techniques that are both special and convenient for their representation. Although our interest here is mainly in quasi-crystallographic patterns that have greater than six-fold symmetry, the analytical methods established will also handle crystallographic cases of four- and six-fold symmetry.

18.4.1 The standard lattices: classification of 2D generalized lattices

Following Mermin and coworkers [169], a 2D lattice that possesses N -fold rotational symmetry ($N > 2$) is referred to as an N -lattice. The rotational symmetry of a simple N -lattice can be established according to the following procedure. We apply, repeatedly, a rotation through $2\pi/N$, $R\left(\frac{2\pi}{N}\right)$, to some vector $\mathbf{b}_0$, and produce a set of N vectors, namely,

$$\mathbf{b}_j = R^j\left(\frac{2\pi}{N}\right)\mathbf{b}_0, \quad j = 0, \dots, N-1. \quad (18.46)$$

Next, we construct the simple, or primitive, N -lattice as the set of all vectors obtained from all integral linear combinations of these N vectors, so that a general standard lattice vector $\mathbf{G}$ is given by

$$\mathbf{G} = \sum_{i=0}^{N-1} m_i \mathbf{b}_i.$$

It is evident that this construction ensures that it has N -fold rotational symmetry. This set is referred to as a **standard lattice**; and the set of N vectors $\mathbf{b}_j$ is termed a *symmetric basis*. The excluded case $N = 2$ is pathological in that the definition of the standard lattice only yields a one-dimensional set of points.

Since a lattice containing a vector $\mathbf{G}$ must also contain $-\mathbf{G}$, N must be even. This, in turn, entails the presence of two types of mirror-lines, one set coincides with the N vectors and the other set bisects the angles between them. Thus, the corresponding holohedry must be Nmm , which is true for $N < 46$.

A symmetric basis cannot be integrally independent, since by their definition we have

$$\mathbf{b}_0 + \mathbf{b}_1 + \dots + \mathbf{b}_{N-1} = 0.$$

A general N -fold symmetric lattice is then composed of a set of N -fold standard lattices, each generated by some symmetric basis.

The rank of any N -lattice is at least the rank of the standard N -lattice. This implies that the indexing dimension for two-dimensional point-groups with N -fold rotational symmetry is just the rank of the standard N -lattice.

We consider two N -lattices as equivalent if they differ only by a scale factor and/or a rotation.

It is a deep theorem of algebraic number theory that, for all even integers $2 < N < 46$, any N -lattice is equivalent to the standard N -lattice.

For given $N \geq 46$, the number of inequivalent N -lattices is finite, but grows roughly exponentially with increasing N .

Here, we give a complete analysis of only the simplest possible case: those space-groups associated with diffraction patterns that give rise to standard lattices. We are, nevertheless, thereby giving the complete analysis of two-dimensional quasi-crystallographic space-groups for all lattices with $N < 46$ (and for $N = 48, 50, 54, 60, 66, 70, 84$ and 90 – the only other cases in which all lattices are equivalent to the standard one).

Since N is even and since standard lattices have mirroring, the standard lattice belongs to the holohedry Nmm . It is a surprising fact that for certain $N > 2$ there exist lattices without mirror symmetry. For example, when $N = 46$ there is an enantiomorphic pair of distinct nonstandard lattices belonging to the holohedry N . In the rest of this section we

restrict our attention to standard lattices, though we call attention to those results that are more generally valid, as they emerge.

A link between N -lattices and algebraic number theory emerges when the 2D N vectors are represented in the complex plane, namely,

$$\mathbf{b}_j = e^{2i\pi j/N}.$$

18.4.2 Standard lattices and cyclotomic integers

The construction of the N -fold symmetric basis bears a strong similarity to vectors representing the N th roots of unity, ζ_N^j , $j = 0, \dots, N-1$, in the complex plane; which allows us to first establish the one-to-one correspondence

$$\begin{aligned} \mathbf{b}_j &\rightarrow \exp(2\pi i j/N) = \zeta_N^j, \quad \zeta_N = \exp[2\pi i/N], \\ j &= 0, \dots, N-1, \end{aligned} \tag{18.47}$$

and then to construct the lattice comprising all integral linear combinations of the N vectors ζ_N^j , i.e. the set $\mathbf{Z}_N$, which is clearly an isomorphic representation of the standard N -lattice.

The set of all rational linear combinations of the N roots is called the *cyclotomic field* Q_N , and $\mathbf{Z}_N$ is known as the *cyclotomic integer of degree N* . A general cyclotomic integer μ is given by

$$\mu = \sum_{j=0}^{N-1} m_j \zeta_N^j. \tag{18.48}$$

The word cyclotomic comes from the Greek. Its literal meaning is, “cut the circle into pieces”, and that’s what a cyclotomic basis does.

The adoption of this representation of N -lattices, based on the algebraic notation that uses *cyclotomic* concepts, will prove to be powerful, insightful, and virtually indispensable in deriving the categories of lattices and space-groups.

First, we should note that:

- (i) For N odd, the cyclotomic integers of degree N and $2N$ are identical, since the basis set of all $2N$ th roots of unity comprises the basis set of the N th roots and their negatives, and, by (18.48), $-\zeta_N^j$ is just a trivial integral linear combination of the ζ_N^j , and hence is already in $\mathbf{Z}_N$.
- (ii) The mapping of the standard N -lattice onto the cyclotomic integers of degree N reveals that the indexing dimension of quasi-crystallographic diffraction patterns

with N -fold symmetry, i.e. the rank of the standard N -lattice, is just the number of N th roots of unity that are linearly independent over the integers. It is known as the Euler totient number of N ,¹ commonly denoted $\phi(N)$, and is simply given by

$$\left[\left(\frac{p_1 - 1}{p_1} \right) \left(\frac{p_2 - 1}{p_2} \right) \dots \right] N, \quad (18.49)$$

where all the primes $p_1, p_2, \dots$ that divide N are included. Thus 12 has prime factors 2 and 3, so $\phi(12) = \frac{1}{2} \times \frac{2}{3} \times 12 = 4$ (primes that appear several times are counted only once).

18.4.3 Classification of two-dimensional N -lattices

In order to establish a classification scheme of 2D N -lattices, we have to define the equivalence operation among possible standard lattices of N -fold symmetry. We begin by requiring that for any subset $\mathbf{S}_N$ of $\mathbf{Z}_N$ to be an N -lattice, it must:

- (i) be invariant under rotations through $2\pi/N$, i.e. under multiplication by ζ_N , or, simply dropping the N , by ζ ;
- (ii) be closed under sums and differences of its constituent elements, and hence the product of any element of $\mathbf{S}_N$ by an arbitrary ζ -integer must be in $\mathbf{S}_N$.

Such a subset of $\mathbf{Z}_N$ is called an ideal. The N -lattices are just ideals of $\mathbf{Z}_N$.

A special type of ideal can be obtained by multiplying $\mathbf{Z}_N$ itself by some ζ -integer, say α . $\alpha\mathbf{Z}_N$ is just $\mathbf{Z}_N$ rescaled by $|\alpha|$ and rotated by the phase of α , and is obviously equivalent to $\mathbf{Z}_N$. It is called a *principal ideal*. Conversely, the principal ideals of $\mathbf{Z}_N$ are equivalent to $\mathbf{Z}_N$, so are their corresponding N -lattices.

We generalize these concepts by considering two sets of complex numbers representing N -lattices $\mathbf{S}_N^{(1)}$ and $\mathbf{S}_N^{(2)}$ to be equivalent, if there is a complex number z such that

$$\mathbf{S}_N^{(2)} = z\mathbf{S}_N^{(1)}.$$

Thus, for every $\alpha \in \mathbf{S}_N^{(1)}$, $z\alpha = \beta$ must be in $\mathbf{S}_N^{(2)}$; and by scaling both sides by α , we recast the equivalence condition as

$$\alpha\mathbf{S}_N^{(2)} = z\alpha\mathbf{S}_N^{(1)} = \beta\mathbf{S}_N^{(1)}.$$

Thus, the number of distinct classes of reciprocal lattices with N -fold symmetry is the number of distinct classes of equivalent ideals of $\mathbf{Z}_N$. This number, h_n , is called the class number of the cyclotomic field Q_N .

The existence of a single N -lattice means that *all ideals of $\mathbf{Z}_N$ are principal ideals*. This is true for all N -lattices with $N < 46$.

¹ The Euler number is also the number of integers less than N (including unity) that have no prime factors in common with N .

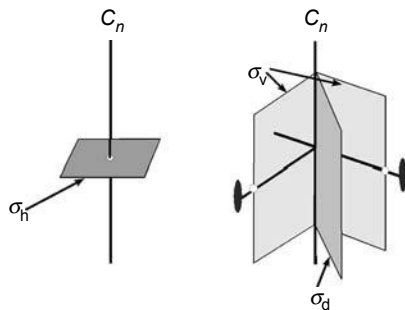


Fig. 18.12. Action of the two sets of inequivalent mirror lines m and m' in the complex plane.

18.4.4 The action of point-groups on cyclotomic integers in the complex plane

In this subsection we show how 2D point-group operations associated with the standard lattices act on their representative cyclotomic integers in the complex plane. This action is represented in terms of simple and familiar operations on the complex plane, namely:

- (i) a rotation by $2\pi/n$ corresponds to multiplication by ζ_n ,
- (ii) a mirror along the real axis corresponds to complex conjugation, and
- (iii) a mirror along the imaginary axis corresponds to complex conjugation followed by inversion (multiplication by -1).

The two mirror operations are shown in Figure 18.12.

For standard lattices n is even, and two sets of mirror planes, shown in Figure 18.13, appear as symmetry elements, each comprising $n/2$ mirror lines. The set m contains the real axis as a mirror line, while the set m' contains the imaginary axis as a mirror line. The presence of either set of mirror planes implies the presence of the other, so there is only a single improper point-group, nm .

Table 18.2 lists the two-dimensional point-groups $\mathcal{G}$ having a principal axis of n -fold symmetry and their actions on cyclotomic integers. Notice that there are two point-groups for even n , nm and n , and the rotational symmetry of the underlying lattice has $N = n$.

When n is odd then $N = 2n$, and three distinct point-groups emerge, $nm1$, $n1m$, and n . The mirror set m appears in $nm1$, while the set m' is manifest in $n1m$:

- (i) As we described above, the real axis is one of the mirror planes in the case of $nm1$, and each of the $4m4$ lines contains a pair of $2n$ th roots of unity. In this case we define the operation m to be the operation of complex conjugation associated with mirroring in the real axis:

$$m\alpha = \alpha^* \quad (n \text{ odd}, \mathcal{G} = nm1). \quad (18.50)$$

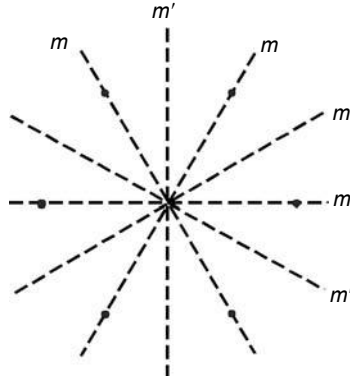


Fig. 18.13. The disposition of the two sets of inequivalent mirror lines for the lattice point-groups nmm .

Table 18.2. *Point groups with N -fold symmetry compatible with lattices of N -fold symmetry.*

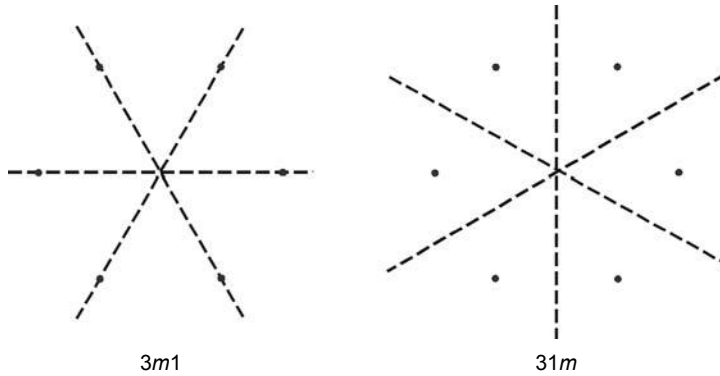
n	Point group	Generators	Lattice
n even	nmm	$\begin{cases} r : \alpha \rightarrow \zeta_n \alpha \\ m : \alpha \rightarrow \alpha^* \end{cases}$	Z_n
	n	$r : \alpha \rightarrow \zeta_n \alpha$	Z_n
n odd	$nm1$	$\begin{cases} r : \alpha \rightarrow \zeta_n \alpha \\ m : \alpha \rightarrow \alpha^* \end{cases}$	Z_{2n}
	$n1m$	$\begin{cases} r : \alpha \rightarrow \zeta_n \alpha \\ m : \alpha \rightarrow -\alpha^* \end{cases}$	Z_{2n}
	n	$r : \alpha \rightarrow \zeta_n \alpha$	Z_{2n}

(ii) Similarly, since the imaginary axis is one of the mirror lines of the m' set, we define the complex plane mirroring operations for the $n1m$ as

$$m\alpha = -\alpha^* \quad (n \text{ odd, } \mathcal{G} = n1m). \tag{18.51}$$

The only crystallographic case of odd n occurs for $N = 6$, $n = 3$, and we have the two distinct subgroups of the symmetry group $\mathcal{G}_L$ of Z_6 , $p3m1$, and $p31m$, shown in Figure 18.14.

In generalizing the relationship between $nm1$ and $n1m$ to the quasi-crystallographic case, one must be careful, since there is no unique symmetric basis. We show in the next subsection that unless the odd integer n is a power of a prime number, these two ways of orienting the point-group nm relative to the lattice Z_2 are in fact indistinguishable.

Fig. 18.14. Disposition of mirror lines for the point-groups $3m1$ and $31m$.

18.4.5 Scale invariance of standard lattices: cyclotomic units

So far we have demonstrated that the set of ζ_N^j , $j = 0, \dots, N-1$ form a symmetric basis for the standard N -lattice. The question then arises as to whether some other set of rotationally N -fold invariant vectors of the N -lattice may serve as a bona fide alternative symmetric basis.

To demonstrate the nature of this invariance, we explore the conditions required to render a set comprising a cyclotomic integer μ and its rotations $\zeta_N^j \mu$ as substitute basis. This set can be viewed as arising from scaling and rotating the ζ_N^j set by $|\mu|$ and by the phase of μ , respectively. However, in order to qualify as basis, this set must generate all the cyclotomic integers contained in $\mathbf{Z}_N$, and in particular the cyclotomic integer 1. Thus, there must be a set of integer coefficients m_j , such that

$$1 = \sum_{j=0}^{N-1} m_j (\zeta_N^j \mu) = \mu \sum_{j=0}^{N-1} m_j \zeta_N^j = \mu \lambda. \quad (18.52)$$

We infer then that in order to construct a symmetric basis from a cyclotomic integer μ it must have a multiplicative inverse among the cyclotomic integers of $\mathbf{Z}_N$: $\mu\lambda = 1$, with

$$\lambda = \sum_{j=0}^{N-1} m_j \zeta_N^j. \quad (18.53)$$

A cyclotomic integer whose inverse is also a cyclotomic integer is called a *unit*.

The preceding scenario demonstrates that any symmetric basis for the cyclotomic integers can be obtained by rescaling the ζ_N s by a unit.

We consider the case where μ and λ are mutual cyclotomic integer inverses, $\mu\lambda = 1$, and take the product of any cyclotomic integer α with μ ; $\mu\alpha$ is then another cyclotomic integer and can be expanded in terms of the ζ_N^j s as

$$\mu\alpha = \sum_{j=0}^{N-1} n_j \zeta_N^j. \quad (18.54)$$

Multiplying this by λ we have

$$\alpha = \lambda \sum_{j=0}^{N-1} n_j \zeta_N^j = \sum_{j=0}^{N-1} n_j \left(\zeta_N^j \lambda \right), \quad (18.55)$$

which explicitly gives α as an integral linear combination of λ and its rotations.

More on cyclotomic units

Kummer used the symbol $\alpha(\zeta_n)$ to denote the cyclotomic integer

$$\alpha = \sum_{j=0}^{n-1} m_j \zeta_n^j,$$

which has the advantage of allowing the definition of *conjugate* cyclotomic integers as $\alpha(\zeta_n^k)$, where every ζ_n is replaced by ζ_n^k , namely

$$\alpha(\zeta_n^k) = \sum_{j=0}^{n-1} m_j \zeta_n^{kj}.$$

For any cyclotomic integer $\alpha(\zeta_n)$, Kummer denoted by $N\alpha(\zeta_n)$ the norm of a cyclotomic integer, which is the product of the $(n-1)$ conjugates of $\alpha(\zeta_n)$, namely,

$$N\alpha(\zeta_n) = \prod_{j=1}^{n-1} \alpha(\zeta_n^j),$$

which is an integer. A cyclotomic unit, such as μ , has a norm of 1. This can be seen if we write

$$N\mu(\zeta_n) = \mu(\zeta_n) \prod_{j=2}^{n-1} \mu(\zeta_n^j) = 1,$$

and hence

$$\mu(\zeta_n)^{-1} = \prod_{j=2}^{n-1} \mu(\zeta_n^j).$$

Let $L = \mathbb{Q}(\zeta_n)$ be a cyclotomic extension of $\mathbb{Q}$ with m chosen to be minimal. Then the ring of integers is given by $Z(\zeta_n)$, and we denote the group of units by $\mathcal{O}_L^\times$. The cyclotomic units are the elements of a subgroup C of $\mathcal{O}_L^\times$ given by

$$\eta = \frac{\zeta_n^r - 1}{\zeta_n^s - 1},$$

with r and s relatively prime to n . We define an integer a such that

$$a \cdot s = r \pmod{n}$$

so that it follows $\zeta_n^r = \zeta_n^{as}$. Using the equation of polynomials:

$$x^{as} - 1 = (x^s - 1) \left(x^{s(a-1)} + x^{s(a-2)} + \cdots + x^s + 1 \right)$$

and we get

$$\begin{aligned} \eta &= \frac{\zeta_n^r - 1}{\zeta_n^s - 1} = \frac{\zeta_n^{as} - 1}{\zeta_n^s - 1} \\ &= \frac{(x^s - 1) \left(x^{s(a-1)} + x^{s(a-2)} + \cdots + x^s + 1 \right)}{\zeta_n^s - 1} \\ &= x^{s(a-1)} + x^{s(a-2)} + \cdots + x^s + 1 = \mathbb{Z}[\zeta]. \end{aligned}$$

If we now interchange the role of r and s we demonstrate that

$$\frac{\zeta_n^s - 1}{\zeta_n^r - 1} \in \mathbb{Z}_n.$$

The only cyclotomic units for crystallographic N -lattices, i.e. $N = 4, 6$, are the ζ_{Ns} . However, for other values of $N > 2$ there are cyclotomic units with magnitudes different from unity. For example, for $N = 5$ the norms of the cyclotomic integers have the form $(A^2 - 5B^2)/4$, where A and B are integers that are either both odd or both even, and an infinite number of cyclotomic units can be determined from the relation

$$A^2 = 4 + 5B^2.$$

Since positive and negative powers of units are also units,² there will then be units of arbitrarily large and small magnitudes.

- (i) When $N/2 = p^s$, for some prime number $p > 1$ and an integer s , it is said to be a prime power. In such a case, we find that all the units of $\mathbf{Z}_N$ lie on rays in the complex plane passing through the N th roots of unity. Therefore, all symmetric bases of $\mathbf{Z}_N$ are related by a *real* scale factor.

Thus, when n is a power of an odd prime, the two subgroups $nm1$ and $n1m$ of $\mathcal{G}_L$ lead to distinguishable actions on the lattice $\mathbf{Z}_{2n}$. (The issue does not arise when n is a power of 2.)

- (ii) If $N/2$ is not a prime power, then the units lie either on the rays passing through the N th roots of unity, or on a second set of rays that bisect the angles between adjacent rays in the first set. (The second set of units has a different scale from the first; in particular, unlike the first, which contains the N th roots of unity, the second contains no points on the unit circle.)

Thus, when $N/2$ is not a prime power, there is a second family of symmetric bases along directions rotated from those in the first set by $1/2(2\pi/N) = \pi/N$.

² This follows directly from the definition of units: if $\alpha\beta = 1$ then $1 = (\alpha\beta)^j = \alpha^j \beta^j$.

In this case it is impossible to distinguish the two types of mirror lines: whether the symmetric basis vectors lie on or between the mirror lines depends on how one chooses to pick those vectors: rotating the lattice $\mathbf{Z}_N$ by $2\pi/2N$ simply gives a scaled version of the (unrotated) lattice $\mathbf{Z}_N$.

As a consequence of this it is only pertinent to distinguish between $nm1$ and $n1m$ when n is a power of an odd prime number; for other odd n there is only the single case nm .

18.4.6 Quasi-crystallographic space-groups in two dimensions

In this section we construct all the two-dimensional quasi-crystallographic space-groups for standard lattices. The procedure is as follows. The elements of various two-dimensional point-groups are all either powers of the rotation C_n (a proper point-group) or products of powers of C_n and a mirror σ (an improper point-group). Thus, a specification of ψ_R for proper point-groups, or ϕ_R , an ϕ_σ for improper point-groups, completely determines the corresponding space-groups since the phase functions for all other point-group elements can be constructed in terms of these two.

The space-groups for the standard lattices are classified by the rotational symmetry n of their point-groups, which is subdivided into two cases (n even and n odd). In Table 18.3 rows with additional entries in the first column are restricted to the cases specified by those entries (p is any odd prime). The last two columns give the values of the phase functions ϕ_r and (when mirrorings are present) ϕ_m on the symmetric basis vectors using the gauge functions developed in the text. (Note, however, that the one nonzero entry is gauge invariant.) When n is less than 23, these are the only 2D quasi-crystallographic space-groups, since when N is less than 46 there are no nonstandard lattices.

Table 18.3. 2D space-groups for standard lattices.

	Point-group	Space-group	Lattice-group	$\phi_r(\zeta_n)$	$\phi_m(\zeta_n)$
n even	n	$\mathbf{Z}_n$	pn	0	—
	nmm	$\mathbf{Z}_n$	$pnmm$	0	0
	$n = 2^s$	nmm	$pngm$	0	$\begin{cases} 1 \\ 2 \end{cases}$
n odd	n	$\mathbf{Z}_{2n}$	pn	0	—
	$n \neq p^s$	nm	pnm	0	0
	$n = p^s$	$nm1$	$pnm1$	0	0
	$n = p^s$	$n1m$	$pn1m$	0	0

The rotation phase function ϕ_{R_n}

Two-dimensional point-groups are characterized by the presence of a high-symmetry n -fold axis normal to the 2D plane. In setting up the phase functions defining 2D space-groups, we choose to set the $\phi_{R_n} = 0$, with the aid of a suitable gauge function χ . Repeated application of the group compatibility condition will then ensure that all $\phi_{R_n^j} = 0$, or that the space-group pn is symmorphic.

Note that in terms of cyclotomic integers, the gauge relation (18.33) between equivalent phase functions assumes the form

$$\Delta\phi_{R_n}(\alpha) \equiv \phi'_{R_n}(\alpha) - \phi_{R_n}(\alpha) \equiv \chi[(R_n - \mathbb{I})\alpha] = \chi[(\zeta_n - 1)\alpha], \quad (18.56)$$

where α is the cyclotomic integer representative of a lattice point. We choose the mapping $\chi[\alpha] \rightarrow \frac{n}{1-\zeta_n} \alpha$ as the gauge, namely,

$$\chi(\alpha) \equiv \frac{1}{n} \phi_{R_n} \left(\frac{n}{1-\zeta_n} \alpha \right),$$

and obtain

$$\begin{aligned} \phi'_{R_n}(\alpha) &\equiv \phi_{R_n}(\alpha) + \frac{1}{n} \phi_{R_n} \left[(\zeta_n - 1)n \frac{\alpha}{1-\zeta_n} \right] \\ &\equiv \phi_{R_n}(\alpha) - \frac{1}{n} \phi_{R_n}(n\alpha) \equiv 0, \end{aligned}$$

where we used the fact that $\phi_{R_n}(n\alpha) = n\phi_{R_n}(\alpha)$, since $n\alpha$ is in the lattice and ϕ is a linear function.

We now show that $\chi[\alpha] \rightarrow \frac{n}{1-\zeta_n} \alpha$ maps one lattice point α into another lattice point. We start with the polynomial factorization

$$z^n - 1 = (z - 1)(z - \zeta_n)(z - \zeta_n^2) \cdots (z - \zeta_n^{n-1}),$$

and dividing both sides by $z - 1$ we obtain

$$z^{n-1} + z^{n-2} + \cdots + z + 1 = (z - \zeta_n)(z - \zeta_n^2) \cdots (z - \zeta_n^{n-1}).$$

Setting z equal to 1 on both sides of the last equation, we find that

$$n/(1 - \zeta_n) = (1 - \zeta_n)(1 - \zeta_n^2) \cdots (1 - \zeta_n^{n-1}),$$

which is a cyclotomic integer, and its multiplication by α demonstrates that $n\alpha/(1 - \zeta_n)$ is also a lattice vector. Notice the fact that $\alpha/(1 - \zeta_n)$ may not, in general, be a cyclotomic integer disallows the operation $\phi_{R_n} \left(\frac{n}{1-\zeta_n} \alpha \right) = n \phi_{R_n} \left(\frac{1}{1-\zeta_n} \alpha \right)$.

Thus, within the class of equivalent phase functions comprising a given 2D space-group, it is always possible to choose a gauge function χ such that the phase function associated with the rotation R_n satisfies $\phi_{R_n}(\alpha) \equiv 0$ for all vectors α in the lattice. (This is one of the major simplifying features of the two-dimensional problem; in three dimensions, phase functions associated with rotations cannot in general be reduced to zero by the proper

choice of gauge.) When the point-group $\mathcal{G}$ is n , there is therefore only one space-group, which we denote by the symbol pn .

Our subsequent analysis will be carried out in such a gauge. In deriving this conclusion we nowhere used the fact that L was a standard lattice, so this conclusion remains more generally valid. If the lattice is nonstandard the space-group symbol will remain the same, except that the “p” (for “primitive”) will be replaced by a specification of the lattice. In discussing the phase functions ϕ_m associated with mirrorings, we find it useful to take advantage of the freedom that remains in choosing a gauge function from among those giving $\phi_r \equiv 0$. Note, therefore, that if Θ is linear on the lattice and assumes values that are integral multiples of $1/n$, then ϕ_r is unaffected by a further gauge transformation of the form

$$\chi'(\alpha) = \Theta \left(\frac{n\alpha}{\zeta_n - 1} \right),$$

since (18.56) gives for the corresponding change in ϕ_r ,

$$\chi'((\zeta_n - 1)\alpha) \equiv \Theta(n\alpha) \equiv n\Theta(\alpha) \equiv 0.$$

The mirror phase function ϕ_m

It is convenient here to work in the gauge where $\phi_{R_n} \equiv 0$. In order to determine mirror phase functions, we use the generating relations for point-groups containing both m and R_n , together with (18.37), namely,

$$\begin{aligned} \sigma^2 = E &\Rightarrow \phi_{\sigma^2}(\alpha) = \phi_{\sigma}(\sigma\alpha) + \phi_{\sigma}(\alpha) = 0 \\ \text{or} &\quad \phi_{\sigma}(\sigma\alpha) = -\phi_{\sigma}(\alpha), \end{aligned} \tag{18.57}$$

$$\begin{aligned} R_n\sigma R_n = \sigma &\Rightarrow \phi_{\sigma}(\alpha) = \phi_{R_n\sigma R_n}(\alpha) \\ &= \phi_{R_n}(\sigma\zeta_n\alpha) + \phi_{\sigma}(\zeta_n\alpha) + \phi_{R_n}(\alpha) \\ &= \phi_{\sigma}(\zeta_n\alpha) \\ \text{or} &\quad \phi_{\sigma}(\zeta_n\alpha) = \phi_{\sigma}(\alpha). \end{aligned} \tag{18.58}$$

In order to put (18.58) into a more useful form, we introduce the following property:

- If $n = kl$, where k and l are integers, then ζ_n^l is the k th root of unity, and hence must satisfy the integral dependence relation

$$\sum_{j=1}^k \zeta_n^j \alpha = 0, \tag{18.59}$$

for any lattice vector α . Using the linearity of ϕ_{σ} , and applying (18.58) repeatedly to (18.59) we arrive at

$$k\phi_{\sigma}(\alpha) = 0 \pmod{1}. \tag{18.60}$$

- When k and l are relatively prime, then, if for some number r both kr and lr are integers, r must be an integer.

Table 18.4. *Classification of 2D space-groups according to ϕ_σ .*

n not a prime power	n odd prime power	n a power of 2
$n = kl, k, l$ relatively prime $k\phi_\sigma(\alpha) \equiv 0, l\phi_\sigma(\alpha) \equiv 0$ $\phi_\sigma(\alpha)$ integer $\rightarrow \phi_\sigma(\alpha) \equiv 0$	$n = p^s, p$ odd prime Rank $(p-1)p^{s-1}$ $p^s = pp^{s-1} \rightarrow p\phi_\sigma(\alpha) \equiv 0$	$n = 2^s$ $2\phi_\sigma(\alpha) \equiv 0$ $\phi_\sigma(\alpha) = 0, 1/2$
n even	n odd	$\phi_\sigma(\alpha) = 0, \rightarrow pnmm$
$\phi \left\{ \begin{smallmatrix} \sigma \\ R_n \end{smallmatrix} \right\}$	$pnm1 \equiv pn1m$	$\phi_\sigma(\alpha) = 1/2 \rightarrow pngn$
$S = S_C = pnmm$	$S = pnm1$ $S = pn1m$	
by rescaling of basis unique pnm	$\zeta_n^0 = 1 \rightarrow \sigma\zeta^0 = \zeta^0$ $(18.57) \rightarrow 2\phi(\zeta_n^0) \equiv 0$ $p, 2$ relatively prime $\phi_\sigma(\zeta_n^0)$ integer $\phi_\sigma(\alpha) \equiv 0$ $pnm1$ unique	Suitable χ yields $\phi \left\{ \begin{smallmatrix} \sigma \\ R_n \end{smallmatrix} \right\} (\alpha) \equiv 0$ $pn1m$ unique

18.4.7 Cubic lattices in n -dimensions

Cubic symmetry requires that if $(x_1, x_2, \dots, x_n)$ is in the translation group $\mathbb{T}$, then so are the vectors with any permutations of these coordinates, as well as the vectors $(\pm x_1, \pm x_2, \dots, \pm x_n)$. If we consider a vector $\mathbf{t}_+$ with component x_i , then there must be a vector $\mathbf{t}_-$ with $-x_i$ component, otherwise identical to the first, and, hence a lattice vector of magnitude $2x_i$ directed along the i -axis must also be in $\mathbb{T}$. If we set the scale such that the shortest vectors along the axes have magnitude 2, we obtain a lattice with unit cell $0 \leq x_i \leq 2$, the standard lattice, and with any general vector having integral coordinates only.

The possibility of constructing distinct centered cubic lattices in n -dimensions reduces to the problem of decorating the unit cell with primitive vectors with components of 0 or 1. Permutation symmetry ensures that for m components of ± 1 , there are

$$\frac{2^m n!}{m! (n-m)!}$$

distinct vectors. $m = 1$ is not allowed, since the shortest vectors along the axes are set equal to 2. The only minimum values of m are 2 or n , as it can be shown that any value $2 < m < n$ will produce vectors with m' 1s and $n - m'$ 0s, and with $m' < m$.

Thus an n D null vector decoration results in a simple cubic lattice. In the case of $m = n$ we obtain a body-centered lattice, and $m = 2$ produces a face-centered lattice which contains only vectors having even numbers of 1s.

For $n \geq 5$ we obtain distinct b.c.c. and f.c.c. lattices, which can be demonstrated by generating the nearest-neighboring sites to the origin in each case. However, for $n = 4$ these two centered lattices become indistinguishable. To show this we follow the argument of Mermin *et al.* [172]. The vectors

$$\hat{\mathbf{e}}_1 = (1, 1, 0, 0), \quad \hat{\mathbf{e}}_2 = (1, -1, 0, 0), \quad \hat{\mathbf{e}}_3 = (0, 0, 1, 1), \quad \hat{\mathbf{e}}_4 = (0, 0, 1, -1)$$

primitively generate a simple cubic lattice since $\hat{\mathbf{e}}_i \cdot \hat{\mathbf{e}}_j = 2\delta_{ij}$, which consists of all vectors (l, m, l', m') with $l + m$ and $l' + m'$ both even. A b.c.c. lattice is obtained by appending to this lattice the translation

$$\frac{1}{2} (\hat{\mathbf{e}}_1 + \hat{\mathbf{e}}_2 + \hat{\mathbf{e}}_3 + \hat{\mathbf{e}}_4) = (1, 0, 1, 0).$$

This augments the original set with vectors having $l + m$ and $l' + m'$ both odd. Thus, the full b.c.c. lattice comprises even sums $l + m + l' + m'$, which is just the f.c.c. lattice.

Bibliography

The following are some suggested general references on group theory:

- S. L. Altmann, *Induced Representations in Crystals and Molecules* (New York: Academic Press, 1977).
- S. Bhagavantam, *Crystal Symmetry and Physical Properties* (New York: Academic Press, 1966).
- C. J. Bradley & A. P. Cracknell, *The Mathematical Theory of Symmetry in Solids* (Oxford: Clarendon Press, 1972).
- G. Burns & A. M. Glazer, *Space Groups for Solid State Scientists* (New York: Academic Press, 1978).
- W. Burnside, *The Theory of Groups of Finite Order* (New York: Dover Publications, 1955).
- J.-Q. Chen, *Group Representation Theory for Physicists* (Singapore: World Scientific, 1989).
- R. A. Evarestov & V. P. Smirnov, *Site Symmetry in Crystals: Theory and Applications*, second edition (Berlin, Heidelberg: Springer-Verlag, 1997).
- M. Hamermesh, *Group Theory and Its Application to Physical Problems* (New York: Dover, 1989).
- T. Inui, Y. Tanabe, & Y. Onodera, *Group Theory and Its Applications in Physics* (Berlin, Heidelberg: Springer-Verlag, 1990).
- L. Jansen & M. Boon, *Theory of Finite Groups. Applications in Physics* (Amsterdam: North Holland, 1967).
- R. S. Knox & A. Gold, *Symmetry in the Solid State* (New York: Benjamin, 1964).
- M. F. C. Ladd, *Symmetry in Molecules and Crystals* (Chichester: Ellis Horwood Limited, 1989).
- M. Lax, *Symmetry Principles in Solid State and Molecular Physics* (New York: Wiley-Interscience, 1974).
- J. S. Lomont, *Applications of Finite Groups* (New York: Academic Press, 1959).
- G. Ya. Lyubarskii, *The Application of Group Theory in Physics* (London: Pergamon Press, 1960).
- W. Ludwig & C. Falter, *Symmetries in Physics*, second edition (Berlin, Heidelberg: Springer-Verlag, 1996).

- R. McWeeny, *Symmetry: An Introduction to Group Theory and Its Applications* (Oxford: Pergamon, 1963).
- P. H. E. Meijer & E. Bauer, *Group Theory: The Application to Quantum Mechanics* (Amsterdam: North-Holland, 1962).
- M. Tinkham, *Group Theory and Quantum Mechanics* (New York: McGraw-Hill, 1964).
- E. P. Wigner, *Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra* (New York: Academic Press, 1959).

References

- [1] Tinkham, M. *Group Theory and Quantum Mechanics* (New York: McGraw-Hill, 1964).
- [2] Wigner, E. *Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra* (New York: Academic Press, 1959).
- [3] Burnside, W. *The Theory of Groups of Finite Order* (New York: Dover, 1955).
- [4] Dixon, J. High speed computation of group characters. *Numerische Mathematik* **10**, 446–450 (1967).
- [5] Flodmark, S. Theory of symmetry projections in applied quantum mechanics. *Phys. Rev.* **132**, 1343–1348 (1963).
- [6] Blokker, E. A theory for the construction of irreducible representations of finite groups. *Int. J. Quantum Chem.* **6**, 925–933 (1972).
- [7] Blokker, E. Symmetry projection of crystal wave functions by means of a computer. *J. Comp. Phys.* **12**, 471–490 (1973).
- [8] Flodmark, S. & Blokker, E. A computer program for calculation of irreducible representations of finite groups. *Int. J. Quantum Chem.* **1S**, 703–711 (1967).
- [9] Flodmark, S. & Blokker, E. Symmetry adaptation of physical states by means of computers. *Group theory and Its Applications* **2**, 199–219 (1971).
- [10] Blokker, E. & Flodmark, S. The arbitrary finite group and its irreducible representations. *Int. J. Quantum Chem.* **4**, 463–472 (1971).
- [11] Blokker, E. & Flodmark, S. A computer program for symmetry adaptation of electronic states in crystals. *Int. J. Quantum Chem.* **5**, 569–578 (1971).
- [12] Altmann, S. *Induced Representations in Crystals and Molecules* (New York: Academic Press, 1977).
- [13] Bradley, C. & Cracknell, A. *The Mathematical Theory of Symmetry in Solids* (Oxford: Clarendon Press, 1972).
- [14] Hamermesh, M. *Group Theory and Its Application to Physical Problems* (New York: Dover, 1989).
- [15] Jansen, L. & Boon, M. *Theory of Finite Groups. Applications in Physics* (Amsterdam: North Holland: 1967).
- [16] Lomont, J. *Applications of Finite Groups* (New York: Academic Press, 1959).
- [17] Ludwig, W. & Falter, C. *Symmetries in Physics*, second edition (Berlin, Heidelberg: Springer-Verlag, 1996).

- [18] Chen, J.-Q. *Group Representation Theory for Physicists* (Singapore: World Scientific, 1989).
- [19] Lyubarskii, G. *The Application of Group Theory in Physics* (London: Pergamon Press, 1960).
- [20] Michel, L. Symmetry, invariants, topology. Basic tools. *Phys. Rep.* **341**, 11–84 (2001).
- [21] Molien, T. Über die invarianten der linearen substitutionsgruppen. *Sitzungsb. Königl. Preuss. Akad. Wiss.* **52**, 1152–1156 (1897).
- [22] Janssen, T. *Crystallographic Groups* (Amsterdam: North Holland/American Elsevier, 1973).
- [23] Bravais, A. Mémoire sur les systèmes formés par des points distribués régulièrement sur un plan ou dans l'espace. *J. Ecole Polytech.* **19**, 1–128 (1850).
- [24] Federov, E. Theorie der kristallstruktur. *Zeit. Kristallogr.* **24**, 209–252 (1895).
- [25] Schoenflies, A. *Kristallsysteme und Kristallstruktur* (Leipzig: Teubner, 1891).
- [26] Bieberbach, L. Über die bewegungsgruppen der euklidischen räume die gruppen mit einem endlichen fundamentalbereich. *Math. Ann.* **72**, 400–412 (1912).
- [27] Burns, G. & Glazer, A. *Space Groups for Solid State Scientists* (New York: Academic Press, 1978).
- [28] Ladd, M. *Symmetry in Molecules and Crystals* (Chichester: Ellis Horwood Limited, 1989).
- [29] Inui, T., Tanabe, Y. & Onodera, Y. *Group Theory and Its Applications in Physics* (Berlin, Heidelberg: Springer-Verlag, 1990).
- [30] Evarestov, R. & Smirnov, V. *Site Symmetry in Crystals: Theory and Applications*, second edition (Berlin, Heidelberg: Springer-Verlag, 1997).
- [31] Michel, L. Fundamental concepts for the study of crystal symmetry. *Rep. Phys.* **341**, 265–336 (2001).
- [32] Pitteri, M. & Zanzotto, G. On the definition and classification of Bravais lattices. *Acta Cryst.* **A52**, 830–838 (1996).
- [33] Bieberbach, L. Über die Bewegungsgruppen des n -dimensionalen euklidischen Raumes mit einem endlichen Fundamentalbereich. *Göttinger Nachr.* 75–84 (1910).
- [34] Burzlaff, H. & Zimmermann, H. On the choice of origins in the description of space groups. *Zeit. Kristallogr.* **153**, 151–179 (1980).
- [35] Gubler, M. Normalizer groups and automorphism groups of symmetry groups. *Zeit. Kristallogr.* **158**, 1–26 (1982).
- [36] Fischer, W. & Koch, E. On the equivalence of point configurations due to Euclidean normalizers (Cheshire groups) of space groups. *Acta Cryst.* **A39**, 907–915 (1983).
- [37] Koch, E. The implications of normalizers on group-subgroup relations between space groups. *Acta Cryst.* **A40**, 593–600 (1984).
- [38] Slater, J. *Symmetry and Energy Bands in Crystals*, Vol. 2 of *Quantum Theory of Molecules and Solids* (New York: McGraw-Hill, 1965).
- [39] Kovalev, O. *Representations of the Crystallographic Space Groups: Irreducible Representations, Induced Representations and Corepresentations* (Gordon and Breach Science Publishers, 1993).
- [40] McWeeny, R. *Symmetry: An Introduction to Group Theory and Its Applications* (Oxford: Pergamon, 1963).

- [41] Warren, J. Further considerations on the symmetry properties of the normal vibrations in a crystal. *Rev. Mod. Phys.* **40**, 38 (1968).
- [42] Koch, E. & Fischer, W. Automorphismengruppen von Raumgruppen und die Zuordnung von Punktlagen zu Konfigurationslagen. *Acta Cryst.* **A31**, 88–95 (1975).
- [43] Engel, P. *Geometric Crystallography: An Axiomatic Introduction to Crystallography* (Dordrecht: D. Reidel, 1986).
- [44] Senechal, M. A simple characterization of the subgroups of space groups. *Acta Cryst.* **A36**, 845–850 (1980).
- [45] Hahn, T. (ed.) *International Tables for Crystallography* (Dordrecht: Kluwer Academic Publishers, 2002).
- [46] Hermann, C. The implications of normalizers on group-subgroup relations between space groups. *Zeit. Kristallogr.* **69**, 533–555 (1929).
- [47] Bertaut, E. & Billiet, Y. On equivalent subgroups and supergroups of the space groups. *Acta Cryst.* **A35**, 733–745 (1979).
- [48] Koch, E. & Fischer, W. Lattice complexes and limiting complexes versus orbit types and non-characteristic orbits: a comparative discussion. *Acta Cryst.* **A41**, 421–426 (1985).
- [49] Wondratschek, H. Extraordinary orbits of space groups. *Zeit. Kristallogr.* **143**, 460–470 (1976).
- [50] Boisen, M. B. Jr., Gibbs, G.V. & Wondratschek, H. Derivation of the normalizers of the space groups. *Acta Cryst.* **A46**, 545–552 (1990).
- [51] Bienenstock, A. & Ewald, P. Symmetry in Fourier space. *Acta Cryst.* **15**, 1253–1261 (1962).
- [52] Mermin, N. Extinctions in scattering from periodic or aperiodic crystals. *Phys. Stat. Sol. (a)* **151**, 275 (1995).
- [53] König, A. & Mermin, N. Screw rotations and glide mirrors: Crystallography in Fourier space. *Proc. Nat. Acad. Sci. USA* **96**, 3502–3506 (1999).
- [54] Herring, C. Character table for two space groups. *J. Franklin Inst.* **233**, 525–543 (1942).
- [55] Sakurai, J.J. *Modern Quantum Mechanics* (Reading, MA: Addison-Wesley, 1995).
- [56] Opechowski, W. The double crystallographic groups. *Physica* **7**, 552–562 (1940).
- [57] Heine, V. *Group Theory in Quantum Mechanics* (New York: Dover, 1993).
- [58] Cracknell, A. *Magnetism in Crystalline Materials*, Vol. 72 of *International Series of Monographs in Natural Philosophy* (Pergamon Press, 1975).
- [59] Jaswon, M. & Rose, M. *Crystal Symmetry: Theory of Colour Crystallography* (Chichester: Ellis Horwood Ltd., 1983).
- [60] Bradley, C. & Davies, B. Magnetic groups and their corepresentations. *Rev. Mod. Phys.* **40**, 359–379 (1968).
- [61] Dimmock, J. *The Mathematics of Physics and Chemistry*, Vol. 2, Chapter 12 (New York: Van Nostrand, 1964).
- [62] Opechowski, W. & Guccione, R. Magnetic symmetry. *Magnetism* **IIA**, 105–165 (1965).
- [63] Opechowski, W. & Dreyfus, T. Classifications of magnetic structures. *Acta Cryst.* **A27**, 470–484 (1971).
- [64] Shubnikov, A. & Belov, N. *Colored Symmetry* (Oxford: Pergamon, 1964).

- [65] Bertaut, E. Representation analysis of magnetic structures. *Acta Cryst.* **A24**, 733–745 (1968).
- [66] Shubnikov, A. & Koptsik, V. *Symmetry in Science and Art* (New York: Plenum, 1974).
- [67] Koptsik, V. *Shubnikov Groups* (Moscow: Moscow University Press, 1966).
- [68] Landau, L., Lifshitz, E. & Pitaevskii, L. *Electrodynamics of Continuous Media*, Vol. 8 of *Course of Theoretical Physics*, second edition (London: Elsevier Butterworth-Heinemann, 1984).
- [69] Litvin, D., Kotsev, J. & Birman, J. Physical applications of crystallographic color groups: Landau theory of phase transitions. *Phys. Rev. B* **26**, 6947–6970 (1982).
- [70] Kotzev, J. N. & Alexandrova, D. Full tables of colour space groups with colour-preserving translations. *Acta Cryst.* **A44**, 1082–1096 (1988).
- [71] Dimmock, J. & Wheeler, R. Symmetry properties of wave-functions in magnetic crystals. *Phys. Rev.* **127**, 391 (1962).
- [72] Cracknell, A. Crystal field theory and the Shubnikov point groups. *Adv. Phys.* **17**, 367–420 (1968).
- [73] Cracknell, A. Group theory and magnetic phenomena in solids. *Rep. Prog. Phys.* **32**, 633–707 (1969).
- [74] Onsager, L. Reciprocal relations in irreversible processes I. *Phys. Rev.* **37**, 405 (1931).
- [75] Onsager, L. Reciprocal relations in irreversible processes II. *Phys. Rev.* **38**, 2265 (1931).
- [76] Callen, H. B. & Welton, T. Irreversibility and general noise. *Phys. Rev.* **83**, 34 (1951).
- [77] Greene, R. & Callen, H. B. On the formalism of thermodynamic fluctuation theory. *Phys. Rev.* **83**, 1231 (1951).
- [78] Callen, H. B. & Greene, R. On a theorem of irreversible thermodynamics. *Phys. Rev.* **86**, 702 (1952).
- [79] Greene, R. & Callen, H. B. On a theorem of irreversible thermodynamics II. *Phys. Rev.* **88**, 1387 (1952).
- [80] Nye, J. *Physical Properties of Crystals* (Oxford: Clarendon Press, 1957).
- [81] Wooster, W. *Tensors and Group Theory for the Physical Properties of Crystals* (Oxford: Oxford University Press, 1973).
- [82] Nowick, A. *Crystal Properties Via Group Theory* (Cambridge: Cambridge University Press, 1995).
- [83] Birss, R. *Symmetry and Magnetism* (Amsterdam: North-Holland Publ. Co., 1964).
- [84] Erdös, P. The determination of the components of a tensor characterizing a crystal. *Hel. Phys. Acta* **37**, 493–509 (1964).
- [85] Bhagavantam, S. *Crystal Symmetry and Physical Properties* (New York: Academic Press, 1966).
- [86] Litvin, D. Tensor fields on crystals. *J. Math. Phys.* **23**, 377–344 (1982).
- [87] Coleman, A. *Induced and Subduce Representations*, 57–116 (New York: Academic Press, 1968).
- [88] Jones, W. & March, N. *Theoretical Solid State Physics* (New York: John Wiley, 1973).

- [89] Callaway, J. *Quantum Theory of the Solid State* (New York: Academic Press, 1985).
- [90] Martin, R. M. *Electronic Structure: Basic Theory and Practical Methods* (Cambridge: Cambridge University Press, 2004).
- [91] Altmann, S. On the symmetries of spherical harmonics. *Proc. Cambridge Philos. Soc.* **53**, 343–367 (1957).
- [92] Altmann, S. & Bradley, C. A note on the calculation of the matrix elements of the rotation group. *Philos. Trans. R. Soc. London*, **255**, 193–198 (1963).
- [93] Cracknell, A. Group theory in solid-state physics is not dead yet alias some recent developments in the use of group theory in solid-state physics. *Adv. Phys.* **23**, 673 (1974).
- [94] Cracknell, A. The symmetry properties of the spin-wave dispersion relations of a ferromagnetic metal. *J. Phys. C: Metal Phys. Suppl.* **2**, S175–S188 (1970).
- [95] Cracknell, A. Time-reversal degeneracy in the band structure of a ferromagnetic metal. *Phys. Rev. B* **1**, 1261–1263 (1970).
- [96] Cracknell, A. Time-reversal degeneracy in the electronic band structure of a magnetic metal. *J. Phys. Cond. Mat.* **2**, 1425–1433 (1969).
- [97] Loudon, R. Theory of infrared and optical spectra of antiferromagnets. *Adv. Phys.* **17**, 243–280 (1968).
- [98] Brinkman, W. & Elliott, R. Space group theory for spin waves. *J. Appl. Phys.* **37**, 1457–1459 (1966).
- [99] Brinkman, W. & Elliott, R. Theory of spin-space groups. *Proc. R. Soc. London* **294**, 343–358 (1966).
- [100] Cracknell, A. The determination of the symmetries of paramagnons, with applications to MnF_2 and NiF_2 . *J. Phys. Cond. Mat.* **2**, 1764–1776 (1969).
- [101] Lax, M. *Symmetry Principles in Solid State and Molecular Physics* (New York: Wiley-Interscience, 1974).
- [102] Maradudin, A. & Vosko, S. Symmetry properties of the normal vibrations in a crystal. *Rev. Mod. Phys.* **40**, 1 (1968).
- [103] Maradudin, A., Montroll, E., Weiss, G. & Ipatova, I. *Theory of lattice dynamics in the harmonic approximation* (Second edition, New York: Academic Press, 1971).
- [104] Birman, J. *Theory of Crystal Space Groups and Lattice Dynamics* (Berlin: Springer-Verlag, 1984).
- [105] Yanagawa, S. *Prog. Theor. Phys.* **10**, 83 (1953).
- [106] Born, M. & Huang, K. *Dynamical Theory of Crystal Lattices* (Oxford: Oxford University Press, 1954).
- [107] Kress, W. & de Wette, F. *Surface Phonons* (Berlin, Heidelberg: Springer-Verlag, 1991).
- [108] Hulpke, E. (ed.) *Helium Atom Scattering from Surfaces* (Berlin, Springer-Verlag, 1992).
- [109] Allen, R. E., Alldredge G. A. & de Wette, F.W. Studies of vibrational surface modes. I. General formulation. *Phys. Rev. B* **4**, 1648–1660 (1971).
- [110] Venkataraman, G. & Sahni, V.C. External vibrations in complex crystals. *Rev. Mod. Phys.* **42**, 409–470 (1970).
- [111] Venkataraman, G., Feldkamp, L. & Sahni, V. *Dynamics of Perfect Crystals* (Cambridge, Massachusetts: MIT Press, 1975).

- [112] Weissbluth, M. *Atoms and Molecules* (New York: Academic Press, 1978).
- [113] Nestor, J. & Spiro, T. Circularly polarized Raman spectroscopy: Direct determination of antisymmetric scattering in the resonance Raman spectrum of ferrocyanochrome. *J. Raman Spectrosc.* **1**, 539–550 (1973).
- [114] Kevan, S. *Angle-resolved Photoemission: Theory and Current Application* (Amsterdam: Elsevier Science Publishers, 1992).
- [115] Adawi, I. Theory of surface photoelectric effect for one and two photons. *Phys. Rev.* **134**, A788 (1964).
- [116] Mahan, G. Theory of photoemission in simple metals. *Phys. Rev. B* **2**, 2334 (1970).
- [117] Liebsch, A. Theory of photoemission from localized adsorbate levels. *Phys. Rev. B* **13**, 544 (1976).
- [118] Niles, D., Rioux, D. & Höchst, H. Polarization selection rules in photoemission from the valence bands of zinc-blende-structure semiconductors. *Phys. Rev. B* **46-I**, 12547 (1992).
- [119] Benbow, R. Dipole selection rules for the hexagonal-close-packed lattice. *Phys. Rev. B* **22**, 3775 (1980).
- [120] Borstel, G., Neumann, M. & Wöhleke, M. Necessity of relativistic dipole selection rules in photoemission. *Phys. Rev. B* **23**, 3121 (1981).
- [121] Wöhleke, M. & Borstel, G. Light-induced electron-spin polarization in cubic crystals. *Phys. Rev. B* **23**, 980 (1981).
- [122] Wöhleke, M. & Borstel, G. Spin-polarization photoelectrons from high-symmetry points of the Brillouin zone. *Phys. Rev. B* **24**, 2321 (1981).
- [123] Lovesey, S. *Theory of Thermal Neutron Scattering: The Use of Neutrons for the Investigation of Condensed Matter* (Oxford: Clarendon Press, 1971).
- [124] Lovesey, S. *Dynamics of Solids and Liquids by Neutron Scattering* (Berlin: Springer-Verlag, 1977).
- [125] Lovesey, S. *Theory of Neutron Scattering from Condensed Matter*, Vol. 1–2 (New York: Oxford University Press, 1984).
- [126] Elliott, R. & Thorpe, M. Group theoretical selection rules in inelastic neutron scattering. *Proc. Phys. Soc.* **91**, 903 (1967).
- [127] Casella, R. & Trevino, S. Group-theoretical selection rules in inelastic neutron scattering within the rigid-molecule model. *Phys. Rev. B* **6**, 4533 (1972).
- [128] Devine, S. & Peckham, G. Group theoretical selection rules for inelastic neutron scattering with application to LiNbO_3 . *J. Phys. C* **4**, 1091 (1971).
- [129] Sieskind, M. Inelastic neutron scattering selection rules of α HgI_2 . *J. de Physique* **39**, 899 (1978).
- [130] Torruella, A. Simplified group-theoretical selection rules in inelastic neutron scattering. *Phys. Rev. B* **14**, 5532 (1976).
- [131] Perez-Mato, J., Aroyo, M., Hlinka, J., Quilichini, M. & Currat, R. Phonon symmetry selection rules for inelastic neutron scattering. *Phys. Rev. Lett.* **81**, 2462–2465 (1998).
- [132] Balcar, E. & Lovesey, S. *Theory of Magnetic Neutron and Photon Scattering* (New York: Oxford University Press, 1989).
- [133] Manson, R. & Celli, V. Inelastic surface scattering of non-penetrating particles. *Surf. Sci* **24**, 495 (1971).

- [134] Cabrera, N., Celli, V., Goodman, F. & Manson, R. Scattering of atoms by solid surfaces. *Surf. Sci* **19**, 67 (1970).
- [135] Garibaldi, U., Levi, A., Spadacini, R. & Tommei, G. Quantum theory of atom-surface scattering: Diffraction and rainbow. *Surf. Sci.* **48**, 649 (1975).
- [136] Levi, A. C. *Nuovo Cimento B* **54**, 357 (1979).
- [137] Levi, A. & Suhl, H. Quantum theory of atom-surface scattering: Debye-Waller factor. *Surf. Sci.* **88**, 221 (1979).
- [138] El-Batanouny, M., Murthy, G., Willis, C. R., Kais, S. & Staemmler, V. Feasibility of measuring surface electron spin dynamics by inelastic scattering of metastable helium atoms. *Phys. Rev. B* **58**, 7391–7402 (1998).
- [139] Marynowski, M., Franzen, W., El-Batanouny, M. & Staemmler, V. Observation of an extraordinary antiferromagnetic transition on the NiO(100) surface by metastable helium atom diffraction. *Phys. Rev. B* **60**, 6053–6067 (1999).
- [140] Gell-Mann, M. & Goldberger, M. L. The formal theory of scattering. *Phys. Rev* **91**, 398–408 (1953).
- [141] Jackson, J. & Mott, N. Energy exchange between inert gas atoms and a solid surface. *Proc. R. Soc. London* **137**, A703–717 (1932).
- [142] Schiff, L. *Quantum Mechanics* (New York: McGraw-Hill, 1970).
- [143] Garibaldi, U., Levi, A., Spadacini, R. & Tommei, G. E. Correlation functions in atom scattering from surfaces. *Surf. Sci.* **38**, 269 (1973).
- [144] Callen, H. B. *Thermodynamics and an Introduction to Thermostatistics* (New York: John Wiley, 1985).
- [145] Landau, L. & Lifshitz, E. *Statistical Physics: Part 1*, Vol. 5 of *Course of Theoretical Physics* (London: Elsevier Butterworth-Heinemann, 1980).
- [146] Fujimoto, M. *The Physics of Structural Phase Transitions* (New York: Springer-Verlag, 1997).
- [147] Toledano, J.-C. & Toledano, P. *The Landau Theory of Phase Transitions* (Singapore, Hong Kong: World Scientific, 1987).
- [148] Kocinski, J. *Theory of Symmetry Changes at Continuous Phase Transitions* (Amsterdam, New York: Elsevier, 1983).
- [149] Kocinski, J. *Commensurate and Incommensurate Phase Transitions* (Amsterdam, New York: Elsevier, 1990).
- [150] Izumov, Y. & Syromyatnikov, V. *Phase Transitions and Crystal Symmetry* (Dordrecht, Boston: Kluwer Academic Publishers, 1990).
- [151] Birman, J. L. Simplified theory of symmetry change in second-order phase transitions: Application to V₃Si. *Phys. Rev. Lett.* **17**, 1216–1219 (1966).
- [152] Goldrich, F. E. & Birman, J. L. Theory of symmetry change in second-order phase transitions in perovskite structure. *Phys. Rev.* **167**, 528–532 (1968).
- [153] Hatch, D. M. & Stokes, H. T. Practical algorithm for identifying subgroups of space groups. *Phys. Rev. B* **31**, 2908–2912 (1985).
- [154] Stokes, H. T. & Hatch, D. M. Group-subgroup structural phase transitions: A comparison with existing tables. *Phys. Rev. B* **30**, 4962–4967 (1984).
- [155] Stokes, H. T. & Hatch, D. M. Equivalence among isotropy subgroups of space groups. *Phys. Rev. B* **31**, 7462–7464 (1985).
- [156] Lifshitz, E. *Zh. Eksp. Teor. Fiziki (J. Phys. USSR)* **11(6)**, 255–269 (61) (1941).

- [157] Dzyaloshinskii, I. *Sov. Phys. JETP* **19**, 960 (1964).
- [158] Haas, C. Phase transitions in ferroelectric and non-ferroelectric crystals. *Phys. Rev.* **140**, A863–A868 (1965).
- [159] Cracknell, A. The application of Landau's theory of continuous phase transitions to magnetic phase transitions. *J. Phys. C: Solid. State Phys.* **4**, 2488–2500 (1971).
- [160] Cracknell, A., Lorenc, J. & Przystawa, J. A. Landau's theory of second-order phase transitions and its application to ferromagnetism. *J. Phys. C: Solid State Phys.* **9**, 1731–1758 (1976).
- [161] Stanley, R. Invariants of finite groups and their applications to combinatorics. *Bull. Amer. Math. Soc.* **1**, 475–511 (1979).
- [162] Sloane, N. Error correcting codes and invariant theory: New applications of a nineteenth-century technique. *Amer. Math. Monthly* **84**, 82–107 (1977).
- [163] Shephard, G. & Todd, J. Finite unitary reflection groups. *Can. J. Math.* **6**, 273–304 (1954).
- [164] Anderson, P. & Blount, E. Symmetry considerations on martensitic transformations: “ferroelectric” metals? *Phys. Rev. Lett.* **14**, 217–219 (1965).
- [165] Yamamoto, A. Crystallography of quasiperiodic crystals. *Acta Cryst.* **A52**, 509–560 (1996).
- [166] Brown, H., Bülow, R., Neubüser, J., Wondratschek, H. & Zassenhaus, H. *Crystallographic Groups of Four-Dimensional Space* (New York: Wiley, 1978).
- [167] Smaalen, S. V. Incommensurate crystal structures. *Cryst. Rev.* **4**, 79–202 (1995).
- [168] Schwarzenberger, R. *N-dimensional Crystallography* (London: Pitman, 1980).
- [169] Rokhsar, D., Mermin, N. & Wright, D. Rudimentary quasicrystallography: The icosahedral and decagonal reciprocal lattices. *Phys. Rev. B* **35**, 5487–5495 (1987).
- [170] Rokhsar, D. Scale equivalence of quasicrystallographic space groups. *Phys. Rev. B* **37**, 8145–8149 (1988).
- [171] Rabson, D., Mermin, N., Rokhsar, D. & Wright, D. The space groups of axial crystals and quasicrystals. *Rev. Mod. Phys.* **63**, 699–733 (1991).
- [172] Mermin, N. The space groups of icosahedral quasicrystals and cubic, orthorhombic, monoclinic and triclinic crystals. *Rev. Mod. Phys.* **64**, 3–13 (1992).
- [173] Senechal, M. *Quasicrystals and Geometry* (Cambridge: Cambridge University Press, 1995).
- [174] Lifshitz, R. The symmetry of quasiperiodic crystals. *Physica* **232A**, 633–647 (1996).
- [175] Lifshitz, R. Theory of color symmetry for periodic and quasiperiodic crystals. *Rev. Mod. Phys.* **69**, 1181–1218 (1997).
- [176] Wolff, P. D. The pseudo-symmetry of modulated crystal structures. *Acta Cryst.* **A30**, 777–785 (1974).
- [177] Wolff, P. M. de Symmetry operations for displacively modulated structures. *Acta Cryst.* **A33**, 493–497 (1977).
- [178] Janner, A. & Janssen, T. Symmetry of periodically distorted crystals. *Phys. Rev. B* **2**, 643–658 (1977).
- [179] Janner, A. & Janssen, T. Superspace groups. *Physica* **99A**, 47–76 (1979).
- [180] Janssen, T. & Janner, A. Incommensurability in crystals. *Adv. Phys.* **36**, 519–624 (1987).

- [181] Iizumi, M., Axe, J., Shirane, G. & Shimaoka, K. Structural phase transformation in K_2SeO_4 . *Phys. Rev. B* **15**, 4392–4411 (1977).
- [182] Janssen, T., Janner, A. & Wolff, P. D. Bravais classes for incommensurate crystal phases. *Acta Cryst. A* **39**, 658–666 (1983).
- [183] Janssen, T., Janner, A. & Wolff, P. D. Determination of the Bravais class for a number of incommensurate crystals. *Acta Cryst. A* **39**, 667–670 (1983).
- [184] Hirshfeld, F. L. Symmetry in the generation of trial structures. *Acta Cryst. A* **24**, 301–311 (1968).
- [185] Wyckoff, R. W. G. *The Analytical Expression of the Results of the Theory of Space-Groups, second edition* (Carnegie Institution of Washington, 1930).
- [186] Heine, V. *Solid State Physics*, Vol. 24, 1–36 (New York: Academic Press, 1970).
- [187] Cohen, M. L. & Heine, V. *Solid State Physics*, Vol. 24, 37–248 (New York: Academic Press, 1970).
- [188] Ziman, J. M. V. *Solid State Physics*, Vol. 26, 1–101 (New York: Academic Press, 1971).
- [189] Kohn, W. & Hohenberg, P. Inhomogeneous electron gas. *Phys. Rev.* **136**, B864–B871 (1964).
- [190] Kohn, W. & Sham, L. J. Self-consistent equations including exchange and correlation effects. *Phys. Rev.* **140**, A1133–A1138 (1965).
- [191] Woods, A. D. B., Cochran, W. & Brockhouse, B. N. Lattice dynamics of alkali halide crystals. *Phys. Rev.* **119**, 980–999 (1960).
- [192] Zak, J. Selection rules for integrals of Bloch functions. *J. Math. Phys.* **3**, 1278–1279 (1962).
- [193] Gufan, Yu. M. *Soviet Phys. Solid State*. **13**, 175 (1971).
- [194] Gufan, Yu. M. & Sakhnenko, V. P. *Soviet Phys. JETP* **36**, 1009 (1973).
- [195] Kim, J. S. Absolute minimum of Landau's thermodynamic potential. *Phys. Rev. B*. **31**, 1433 (1985).
- [196] Hermann, C. Kristallographie in Räumen beliebiger Dimensionszahl. I. Die Symmetrioperationen. *Acta Cryst.* **2**, 139–145 (1949).

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