

Graduate Texts in Physics

Eleftherios N. Economou

The Physics of Solids

Essentials and Beyond

 Springer

GRADUATE TEXTS IN PHYSICS

For further volumes:
<http://www.springer.com/series/8431>

GRADUATE TEXTS IN PHYSICS

Graduate Texts in Physics publishes core learning/teaching material for graduate- and advanced-level undergraduate courses on topics of current and emerging fields within physics, both pure and applied. These textbooks serve students at the MS- or PhD-level and their instructors as comprehensive sources of principles, definitions, derivations, experiments and applications (as relevant) for their mastery and teaching, respectively. International in scope and relevance, the textbooks correspond to course syllabi sufficiently to serve as required reading. Their didactic style, comprehensiveness and coverage of fundamental material also make them suitable as introductions or references for scientists entering, or requiring timely knowledge of, a research field.

Series Editors

Professor William T. Rhodes

Florida Atlantic University
Department of Computer and Electrical Engineering and Computer Science
Imaging Science and Technology Center
777 Glades Road SE, Room 456
Boca Raton, FL 33431, USA
E-mail: wrhodes@fau.edu

Professor H. Eugene Stanley

Boston University
Center for Polymer Studies
Department of Physics
590 Commonwealth Avenue, Room 204B
Boston, MA 02215, USA
E-mail: hes@bu.edu

Eleftherios N. Economou

The Physics of Solids

Essentials and Beyond

With 261 Figures



Springer

Eleftherios N. Economou
University of Crete
Foundation for Research and Technology-Hellas (FORTH)
Department of Physics
P.O.Box 1527
711 10 Heraklion, Crete, Greece
E-mail: economou@admin.forth.gr

ISSN 1868-4513
ISBN 978-3-642-02068-1
DOI 10.1007/978-3-642-02069-8
Springer Heidelberg Dordrecht London New York

e-ISSN 1868-4521
e-ISBN 978-3-642-02069-8

Library of Congress Control Number: 2009929022

© Springer-Verlag Berlin Heidelberg 2010

This work is subject to copyright. All rights are reserved, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilm or in any other way, and storage in data banks. Duplication of this publication or parts thereof is permitted only under the provisions of the German Copyright Law of September 9, 1965, in its current version, and permission for use must always be obtained from Springer. Violations are liable to prosecution under the German Copyright Law.

The use of general descriptive names, registered names, trademarks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

Cover design: eStudio Calamar Steinen

Printed on acid-free paper

Springer is part of Springer Science+Business Media (springer.com)

Preface

In selecting the material and the presentation of this textbook I was aiming at the advanced undergraduate/first year graduate level, or so I was intending. *Chapters 1–8* (with some possible omissions and additions, depending on the students' interests and the instructor's preferences) *can serve as the core of a senior undergraduate course* on Solid State Physics addressed to students in Physics, Chemistry, Materials Science, and Engineering. The book is designed *to serve also as a textbook in a first-year graduate course* on the Physics of Solids. Some familiarity with Electromagnetism, Quantum Mechanics, and Statistical Physics is assumed; anyway, extensive outlines of these subjects are presented in Appendices A, B, and C, respectively.

The emphasis in the book is on understanding the behavior of the various types of solids at a qualitative level and on being able to derive their properties at a quantitative level. To achieve this goal, *concepts and theoretical tools are gradually introduced as needed and the results are continuously tested against the “touchstone” of experimental data.* To be more specific, the book starts with Chap. 1 by reminding the readers of the basic ideas of physics: the atomic structure of matter, the wave–particle duality (which is distilled in the three principles of Quantum Mechanics), and the minimization of the free energy as the criterion of equilibrium. The latter is established through the competition of the squeezing electrostatic forces (characterized by the proton charge, e) and the expansion-driving quantum kinetic energy (characterized by Planck's constant, $\hbar$, the electronic mass, m_e , and, to a lesser degree, the atomic mass, m_a). It is shown in Chap. 2 that *the basic physical constants, $\hbar$, m_e , e , through simple dimensional considerations and “a little thinking” allow us to derive most of the main properties of solids at a semiquantitative level.* Chapter 3, which concludes the first introductory part of the book provides a first acquaintance with solids (their various types, their periodic crystal structures, and the periodicity-based Bloch's theorem).

In the second part of the book, the two simplest approaches to the real world of solids (with diametrically opposite starting points) are presented: The *Jellium Model* (JM), more appropriate for metals, and the *linear combination*

of *atomic orbitals* (LCAO) method, capable of handling semiconductors as well as other classes of solids. The JM is treated in more details than usual, because it offers the opportunity to introduce many important concepts, to calculate explicitly quantities of interest, to compare them with experimental data, and all these in the simplest possible way and with a minimum background. The importance of the LCAO method is emphasized because of its far reaching applicability. This part is concluded in Chap. 8 with an outline of the basic conceptual framework (leading to the independent electron approximation in an effective periodic potential) together with a list of important phenomena going beyond this framework.

In the third part, consisting of Chaps. 9–12, concepts and theoretical tools associated with the periodic order of crystalline solids are presented. These concepts and tools allow us to remedy the qualitative failures of the JM and quantitative inadequacies of the LCAO method.

Equipped with this calculational arsenal, we are in a position to study in the fourth part of the book (Chaps. 13–16) not only the specific classes of solids, such as simple metals, semiconductors, ionic solids, transition metals, and artificial structures, but also particular materials.

In the fifth part of the book (Chaps. 17–19), we are forced to go beyond the familiar ground of the periodic landscape in order to examine phenomena where the breakdown or the absence of periodic order is essential. These phenomena occur in surfaces and interfaces, in glasses, amorphous solids, and other disordered systems, and in finite structures, such as clusters, quantum dots, etc.

Finally, in the sixth part of the book (Chaps. 20–23), we make another excursion to the unknown territory in order to study two important phenomena (Magnetism and Superconductivity) associated with the breakdown of the independent electron approximation and the emergence of the crucial role of correlated electronic motion.

Many *topics of current research interest* (and hopefully of future importance) have found their way in the book: Graphene, Organic Semiconductors, Photonic and Phononic Crystals, Left-Handed Metamaterials, Plasmonics, Spintronics, etc. However, important subjects such as soft matter, nonequilibrium phenomena, and devices were left out (to say nothing about experimental techniques).

I tried to make the book *self-contained* by including 65 pages of appendices (marked by a gray stripe for easy identification). In these appendices, the basic concepts and formulas of Electromagnetism, Quantum Mechanics, Thermodynamics/Statistical Mechanics, and Theory of Elasticity, as well as the LCAO method as applied to molecules are presented. In order to make the book easy to use, I have put together, at the end of the book, the important tables (again marked by a gray stripe); moreover, tables of physical constants and the atomic system of units, as well as frequently used mathematical formulas were placed inside the front and the back hard cover of the book.

I would like to thank Drs. Maria Kafesaki, Stavroula Foteinopoulou, and George Kioseoglou for reading some chapters of the book and for making useful suggestions. I would like also to acknowledge many useful discussions with colleagues concerning the content of the book and its presentation. I am grateful to Mina Papadaki for her invaluable help in bringing to conclusion this text. Finally, I am greatly indebted to the reviewers for reading my manuscript from A to Z, very carefully; they pointed out several typos and made a great number of very valuable modifications for improving the text. I express my deep appreciation and thanks to them.

July 2010

Heraklio

Contents

Part I An Overview

1	Basic Principles Summarized	3
1.1	The Atomic Idea: From Elementary Particles to Solids	4
1.2	Permanent (i.e., Equilibrium) Structures of Matter Correspond to the Minimum of Their (Free) Energy	6
1.3	Condensed Matter Tends to Collapse Under the Influence of Coulomb Potential Energy	9
1.4	Quantum Kinetic Energy Counterbalances Coulomb Potential Energy Leading to Stable Equilibrium Structures	10
1.4.1	Heisenberg's Uncertainty Principle and the Minimum Kinetic Energy	10
1.4.2	Pauli's Exclusion Principle and the Enhancement of the Minimum Kinetic Energy	11
1.4.3	Schrödinger's Spectral Discreteness and the Rigidity of the Ground State	14
1.5	Dimensional Analysis	15
1.6	Key Points	18
1.7	Questions and Problems	19
2	Basic Principles in Action	21
2.1	Size and Energy Scale of Atoms	21
2.2	Why do Atoms Come Together to Form Molecules and Solids?	23
2.3	Ionic Motion: Small Oscillations	27
2.4	Why do the Specific Heats of Solids go to Zero as $T \rightarrow 0\text{ K}$?	29
2.5	When is Classical Mechanics Adequate?	31

2.6	Estimating Magnitudes Through Dimensional Analysis	32
2.6.1	Atomic Radius, R_α	32
2.6.2	Volume per Atom, $\nu_a \equiv \mathbf{V}/\mathbf{N}_a$, in Solids	32
2.6.3	Mass Density, ρ_M	33
2.6.4	Cohesive Energy, U_c	33
2.6.5	Bulk Modulus, B , and Shear Modulus, μ_s	34
2.6.6	Sound Velocities in Solids, c_0 , c_ℓ , c_t	35
2.6.7	Maximum Angular Frequency of Atomic Vibrations in Solids, $\omega_{\max}$	37
2.6.8	Melting Temperature, T_m	37
2.6.9	DC Electrical Resistivity, ρ_e	38
2.7	Key Points	41
2.8	Questions and Problems	42
3	A First Acquaintance with Condensed Matter	47
3.1	Various Kinds of Condensed Matter	47
3.1.1	Monocrystalline and Polycrystalline Atomic Solids . .	48
3.1.2	Atomic or Ionic Compounds and Alloys	49
3.1.3	Molecular Solids	49
3.1.4	Glasses	49
3.1.5	Polymers	50
3.1.6	Colloids	50
3.1.7	Gels	51
3.1.8	Liquid Crystals	51
3.1.9	Self-Assembled Soft Matter	51
3.1.10	Artificial Structures	52
3.1.11	Clusters and Other Finite Systems	52
3.2	Bonding Types and Resulting Properties	53
3.2.1	Simple Metals	54
3.2.2	Transition Metals and Rare Earths	55
3.2.3	Covalent Solids	55
3.2.4	Ionic Solids	56
3.2.5	Van der Waals Bonded Solids	57
3.2.6	Hydrogen Bonded Solids	58
3.3	A Short Introduction to Crystal Structures	59
3.3.1	Some Basic Definitions	59
3.3.2	Unit and Primitive Cells of Some Commonly Occurring 3-D Crystal Structures	64
3.3.3	Systems and Types of 3D Bravais Lattices	67
3.3.4	Crystal Planes and Miller Indices	67
3.4	Bloch Theorem, Reciprocal Lattice, Bragg Planes, and Brillouin Zones	70
3.4.1	Bloch Theorem	70
3.4.2	Reciprocal Lattice	72

3.4.3	Bragg Planes	75
3.4.4	Brillouin Zones	75
3.5	Key Points	77
3.6	Questions and Problems.....	78

Part II Two Simple Models for Solids

4	The Jellium Model and Metals I: Equilibrium Properties ..	83
4.1	Introduction	84
4.2	Electronic Eigenfunctions, Eigenenergies, Number of States ..	86
4.3	Kinetic and Potential Energy, Pressures, and Elastic Moduli	90
4.4	Acoustic Waves are the Ionic Eigenoscillations in the JM	97
4.5	Thermodynamic Quantities	101
4.5.1	General Formulas	101
4.5.2	Specific Heat, C_V	104
4.5.3	Bulk Thermal Expansion Coefficient.....	107
4.6	Key Points	107
4.7	Problems.....	108
5	The Jellium Model and Metals II: Response to External Perturbations	113
5.1	Response to Electric Field	113
5.2	The Dielectric Function	114
5.3	Static Electrical Conductivity	120
5.4	Phonon Contribution to Resistivity	123
5.5	Response in the Presence of a Static Uniform Magnetic Field	127
5.5.1	Magnetic Resonances	128
5.5.2	Hall Effect and Magnetoresistance	131
5.5.3	Magnetic Susceptibility, χ_m	133
5.6	Thermoelectric Response	140
5.7	Key Points	143
5.8	Problems.....	145
6	Solids as Supergiant Molecules: LCAO.....	149
6.1	Diversion: The Coupled Pendulums Model.....	149
6.2	Introductory Remarks Regarding the LCAO Method.....	152
6.3	A Single Band One-Dimensional Elemental “Metal”	153
6.4	One-Dimensional Ionic “Solid”	157
6.5	One-Dimensional Molecular “Solid”	160
6.6	Diversion: Eigenoscillations in One-Dimensional “solid” with two Atoms Per Primitive Cell	163
6.7	One-Dimensional Elemental sp^1 “Semiconductor”	164

6.8	One-Dimensional Compound sp^1 “Semiconductor”	171
6.9	Key Points	174
6.10	Problems	174
7	Semiconductors and Other Tetravalent Solids	177
7.1	Lattice Structures: A Reminder	177
7.2	Band Edges and Gap	178
7.3	Differences Between the 1-D and the 3-D Case and Energy Diagrams	181
7.4	Metals, Semiconductors, and Ionic Insulators	183
7.5	Holes	184
7.6	Effective Masses and DOS	186
7.7	Dielectric Function and Optical Absorption	188
7.8	Effective Hamiltonian	189
7.9	Impurity Levels	191
7.9.1	Impurity Levels: The General Picture	191
7.9.2	Impurity Levels: Doping	192
7.10	Concentration of Electrons and Holes at Temperature T	195
7.10.1	Intrinsic case	197
7.10.2	Extrinsic case	197
7.11	Band Structure and Electronic DOS	198
7.12	Eigenfrequencies, Phononic DOS, and Dielectric Function	200
7.13	Key Points	207
7.14	Problems	208
8	Beyond the Jellium and the LCAO: An Outline	211
8.1	Introductory Remarks	211
8.2	The Four Basic Approximations	212
8.3	Density Functional Theory	215
8.4	Outline of an Advanced Scheme for Calculating the Properties of Solids	219
8.5	Beyond the Four Basic Approximations	221
8.5.1	Periodicity Broken or Absent	223
8.5.2	Electron–Electron Correlations, Quasi-Particles, Magnetic Phases, and Superconductivity	235
8.5.3	Electron–Phonon Interactions, Transport Properties, Superconductivity, and Polarons	237
8.5.4	Phonon–Phonon Interactions, Thermal Expansion, Melting, Structural Phase Transitions, Solitons, Breathers	238
8.5.5	Disorder and Many Body Effects in Coexistence	239
8.5.6	Quantum Informatics and Solid State Systems	240
8.6	Key Points	240
8.7	Problems	241

Part III More About Periodicity & its Consequences

9	Crystal Structure and Ionic Vibrations	245
9.1	Experimental Determination of Crystal Structures	245
9.2	Determination of the Frequency vs. Wavevector	251
9.3	Theoretical Calculation of the Phonon Dispersion Relation	256
9.4	The Debye–Waller Factor and the Inelastic Cross-Section	263
9.5	Key Points	268
9.6	Problems	269
10	Electrons in Periodic Media. The Role of Magnetic Field	273
10.1	Introduction	273
10.2	Dispersion Relations, Surfaces of Constant Energy, and DOS: A Reminder	274
10.3	Effective Hamiltonian and Semiclassical Approximation	276
10.4	Semiclassical Trajectories in the Presence of a Magnetic Field	280
10.5	Two Simple but Elucidating TB Models	281
10.6	Cyclotron Resonance and the de Haas–van Alphen Effect	287
10.7	Hall Effect and Magnetoresistance	290
10.8	Key Points	298
10.9	Problems	299
11	Methods for Calculating the Band Structure	301
11.1	Introductory Remarks	301
11.2	Ionic and Total Pseudopotentials	303
11.3	Schrödinger Equation, Plane Wave Expansion, and Bloch’s Theorem	309
11.4	Plane Waves and Perturbation Theory	310
11.5	Muffin–Tin Potential	313
11.6	Schrödinger Equation and the Augmented Plane Wave (APW) Method	313
11.7	Schrödinger Equation and the Korringa–Kohn–Rostoker (KKR) Method	315
11.8	The $k \cdot p$ Method of Band Structure Calculations	317
11.9	Key Points	321
11.10	Problems	322
12	Pseudopotentials in Action	325
12.1	The One-Dimensional Case	325
12.2	The Two-Dimensional Square Lattice	327
12.2.1	<i>Spaghetti</i> Diagrams	327
12.2.2	Fermi Lines	330
12.3	Harrison’s Construction	336

12.4	Second-Order Correction to the Total JM Energy	337
12.5	Ionic Interactions in Real Space	338
12.6	Phononic Dispersions in Metals	340
12.7	Scattering by Phonons, Mean Free Path, and the Dimensionless Constant λ in Metals	342
12.8	Key Points	345
12.9	Problems	346

Part IV Materials

13	Simple Metals and Semiconductors Revisited	351
13.1	Band Structure and Fermi Surfaces of Simple Metals	351
13.1.1	Alkali Metals	351
13.1.2	Alkaline Earths: Be, Mg, Ca, Sr, Ba, and Ra	354
13.1.3	Trivalent Metals	354
13.1.4	Tetravalent Metals	358
13.2	Band Structure of Semiconductors	360
13.3	The Jones Zone and the Disappearance of the Fermi Surface	363
13.4	Mechanical Properties of Semiconductors	365
13.5	Magnetic Susceptibility of Semiconductors	368
13.6	Optical and Transport Properties of Semiconductors	371
13.6.1	Excitons	371
13.6.2	Conductivity and Mobility in Semiconductors	374
13.7	Silicon Dioxide (SiO_2)	378
13.8	Graphite and Graphene	380
13.9	Organic semiconductors	386
13.10	Key Points	388
13.11	Questions and Problems	389
14	Closed-Shell Solids	393
14.1	Van Der Waals Solids	393
14.2	Ionic Compounds I: Types and Crystal Structures	397
14.3	Ionic Compounds II: Mechanical Properties	399
14.4	Ionic Compounds III: Optical Properties	401
14.5	Key Points	406
14.6	Problems	407
15	Transition Metals and Compounds	409
15.1	Experimental Data for the Transition Metals	409
15.2	Calculations I: APW or KKR	412
15.3	Calculations II: LCAO	417
15.4	Calculations III: The Simple Friedel Model	421

15.5	Compounds of Transition Elements, I: Perovskites	423
15.6	Compounds of Transition Elements, II: High T_c Superconducting Materials	426
15.7	Compounds of Transition Metals, III: Oxides, etc.	430
15.8	Key Points	434
15.9	Problems	435
16	Artificial Periodic Structures	437
16.1	Semiconductor Superlattices	437
16.2	Photonic Crystals: An Overview	439
16.3	Photonic Crystals: Theoretical Considerations	443
16.4	Phononic Crystals	450
16.5	Left-Handed Metamaterials (LHMs)	456
16.6	Designing, Fabricating, and Measuring LHMs	461
16.7	Key Points	466
16.8	Problems	468
Part V Deviations from Periodicity		
17	Surfaces and Interfaces	471
17.1	Surface Preparation	471
17.2	Relaxation and Reconstruction	472
17.3	Surface States	474
17.4	Work Function	479
17.5	Measuring the Work Function	481
17.6	The p–n Homojunction in Equilibrium	483
17.7	The p–n Homojunction Under an External Voltage V	487
17.8	Some Applications of Interfaces	491
17.9	Key Points	494
17.10	Problems	497
18	Disordered and Other Nonperiodic Solids	499
18.1	Introductory Remarks	499
18.2	Alloys and the Hume-Rothery Rule	500
18.3	Glasses and other Amorphous Systems	502
18.4	Distribution and Correlation Functions	504
18.5	Quasi-Crystals	506
18.6	Electron Transport and Quantum Interference	510
18.7	Band Structure, Static Disorder, and Localization	513
18.7.1	3D Case	513
18.7.2	2D Case	517
18.7.3	1D and quasi 1D Systems	518

18.8	Calculation Techniques.....	522
18.8.1	Coherent Potential Approximation	522
18.8.2	Weak Localization due to Quantum Interference	526
18.8.3	Scaling Approach	529
18.8.4	Quasi-One-Dimensional Systems and Scaling	532
18.8.5	Potential Well Analogy	533
18.9	Quantum Hall Effect	534
18.10	Key Points	538
18.11	Problems.....	540
19	Finite Systems	543
19.1	Introduction	543
19.2	Metallic Clusters	544
19.3	Fullerenes	545
19.4	C ₆₀ -Based Solids	549
19.5	Carbon Nanotubes	551
19.6	Other Clusters	556
19.7	Quantum Dots	557
19.7.1	An Overview	557
19.7.2	Optical Transitions.....	558
19.7.3	QDs and Coulomb Blockade.....	561
19.8	Key Points	564
19.9	Problems.....	565

Part VI Correlated Systems

20	Magnetic Materials, I: Phenomenology	569
20.1	Which Property Characterizes These Materials?.....	569
20.2	Experimental Data for Ferromagnets.....	573
20.2.1	Saturation Magnetization vs Temperature for Simple Ferromagnets	573
20.2.2	Magnetic Susceptibility of Simple Ferromagnet for $T > T_c$	573
20.2.3	Saturation Magnetization vs Temperature for Ferrimagnets	574
20.2.4	Magnetic Susceptibility of Ferrimagnets vs Temperature ($T > T_c$)	575
20.3	Experimental Data for Antiferromagnets	576
20.3.1	Determination of the Antiferromagnetic Ordered Structure	576
20.3.2	Magnetic Susceptibility vs Temperature.....	577

20.4	Materials	577
20.4.1	Simple Ferromagnetic Materials	577
20.4.2	Ferrimagnetic Materials	579
20.4.3	Antiferromagnetic Materials	580
20.5	Thermodynamic Relations	580
20.5.1	Thermodynamic Potentials	580
20.5.2	Mean Field Approximation (Landau's Approach) ...	583
20.5.3	Why are Magnetic Domains Formed?	584
20.5.4	How Thick is the Bloch Wall?	586
20.5.5	Examples of Magnetic Domains	586
20.5.6	Thermodynamics of Antiferromagnets	587
20.6	Spintronics	588
20.7	Key Points	592
20.8	Problems	593
21	Magnetic Materials II: Microscopic View	595
21.1	Introduction	595
21.2	Jellium model and el-el Coulomb Repulsion	599
21.2.1	Is There Ferromagnetic Order in the JM?	599
21.2.2	Magnetic Susceptibility Within the JM in the Presence of Electron-Electron Interactions	601
21.2.3	Is There Antiferromagnetic Order in the JM?	603
21.3	The Hubbard Model	607
21.4	The Heisenberg Model	613
21.4.1	The Hamiltonian	613
21.4.2	Mean Field Approximation	615
21.4.3	The Ferromagnetic Case, ($J_{ij} > 0$) and its spin waves	617
21.4.4	The AF Case	619
21.5	Key Points	622
21.6	Problems	624
22	Superconductivity, I: Phenomenology	625
22.1	Materials	625
22.2	Properties of Superconductors	627
22.2.1	Zero DC Resistivity	627
22.2.2	Expulsion of the Magnetic Field B from the Interior of a Superconductor	627
22.2.3	Critical Value of the Magnetic Field Beyond Which Superconductivity Disappears	629
22.2.4	Specific Heat and Other Thermodynamic Quantities	632
22.2.5	Response to Microwave or Far Infrared EM Radiation	634
22.2.6	Ultrasound Attenuation	635

22.2.7	Tunneling Current in Metal/Insulator/ Superconductor Junctions	635
22.2.8	Temperature Dependence of the Superconducting Gap	635
22.2.9	Isotope Effect	637
22.2.10	Relaxation Times for Nuclear Spin	638
22.2.11	Thermoelectric Coefficients	638
22.3	Thermodynamic Relations	639
22.4	London Equation	641
22.5	Pippard's Generalization	644
22.6	Ginzburg–Landau Theory	645
22.7	Quantization of the Magnetic Flux	651
22.8	Key Points	652
22.9	Problems	654
23	Superconductivity, II: Microscopic Theory	655
23.1	Electron–Electron Indirect Attraction	655
23.2	Cooper Pairs	657
23.3	Comments	659
23.4	Corrected Binding Energy and the Critical Temperature	661
23.5	Further Corrections to the Formula for T_c	663
23.6	The Bardeen–Cooper–Schrieffer (BCS) Theory	664
23.7	Thermodynamic Quantities	669
23.8	Response to Electromagnetic Fields	672
23.9	Towards Material-Specific Calculations of Superconducting Quantities	674
23.10	Josephson Effects and SQUID	677
23.11	Key Points	680
23.12	Problems	682
Part VII Appendices		
A	Elements of Electrodynamics of Continuous Media	685
A.1	Field Vectors, Potentials, and Maxwell's Equations	685
A.2	Relations Among the Fields	688
B	Elements of Quantum Mechanics	697
B.1	General Formalism	697
B.2	Bra and Ket Notation	700
B.3	Spherically Symmetric Potentials	702
B.4	Perturbation Results	708
B.5	Interaction of Matter with an External Electromagnetic Field	711

C	Elements of Thermodynamics and Statistical Mechanics	713
C.1	Thermodynamic Relations	713
C.2	Basic Relations of Statistical Mechanics	716
C.3	Non-Interacting Particles	718
C.3.1	Non-Interacting Electrons	718
C.3.2	Phonons	721
D	Dielectric Function, $\varepsilon(\mathbf{k}, \omega)$: Formulas and Uses	723
D.1	Uses	724
D.2	Expressions for $\varepsilon(\mathbf{k}, \omega)$ within the JM	728
D.3	Phenomenological Expressions for the Dielectric Function . . .	730
E	Waves in Continuous Elastic Media	733
E.1	Strains	733
E.2	Equations of Motion	733
E.3	Connecting Stress and Strain	734
E.4	The Elastic Wave Equation	735
F	The Method LCAO Applied to Molecules	737
F.1	Formulation of the LCAO Method	737
F.2	Some Important Examples	740
F.2.1	Covalent Diatomic Molecule	740
F.2.2	Ionic Diatomic Molecule	742
F.3	Hybridization of Atomic Orbitals	743
F.3.1	sp^1 Hybrid Atomic Orbitals	744
F.3.2	sp^2 Hybrid Atomic Orbitals	748
F.3.3	sp^3 Hybrid Atomic Orbitals	749
G	Boltzmann's Equation	755
H	Tables	759
	Solutions of Selected Problems and Answers	779
	General Reading	826
	References	837
	Index	849

Part I

An Overview

Basic Principles Summarized

If, in some cataclysm, all of scientific knowledge were to be destroyed, and only one sentence passed on to the next generation of creatures, what a statement would contain the most information in the fewest words? I believe it is the atomic hypothesis that all things are made of atoms – little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another. In that one sentence, there is an enormous amount of information about the world, if just a little imagination and thinking are applied.

R.P. Feynman, *The Feynman Lectures on Physics*

Summary. The equilibrium state of matter in general (and condensed matter in particular) corresponds to the minimum value of its energy E (when $P_0 = T_0 = 0$), or of its Gibbs free energy, $G \equiv E + P_0V - TS$, (when $P_0 = \text{const.}$, $T_0 = \text{const.}$), where P_0 is the external pressure, T is the absolute temperature, V is the volume, and S is the entropy. This statement implies, among other things, that (when $P_0 = 0$) the internal squeezing pressure due to the attractive forces among the elementary particles making up the matter is counterbalanced by the internal expanding pressure due to the perpetual motion of these particles. This, crucial for equilibrium perpetual motion, stems mainly or exclusively from the wave nature of matter and is summarized in the three basic principles of Quantum Mechanics (QM). For condensed matter, the forces are mainly electric and are characterized by the charge e , while the perpetual motion depends mainly on Planck's constant, $\hbar$, and the electronic mass, m_e . Thus, properties of condensed matter depend on e , $\hbar$, m_e and possibly on other physical constants. This observation together with dimensional considerations leads to several semiquantitative results.

1.1 The Atomic Idea: From Elementary Particles to Solids

Matter is made up from microscopic elementary particles interacting with each other to form composite particles; the latter in turn combine with each other and/or with other elementary particles to create the next level in the hierarchy of the structures of matter, etc.

Thus: Two u quarks and one d quark make up the proton, while two d quarks and one u quark make up the neutron; protons and neutrons combine to create the various atomic nuclei; a nucleus attracts and traps electrons around it to form a neutral atom (when the number of trapped electrons equals the number Z of protons in the nucleus).¹ Atoms (and/or ions) come together to form molecules; atoms and/or ions² and/or molecules in huge numbers are more or less close-packed to form ordinary solids and liquids and other condensed macroscopic structures such as polymers. And the hierarchy continues to larger scales all the way to astronomical objects (planets, stars, galaxies, cluster of galaxies, etc.).

In this book we shall deal with the Physics of Solids such as metals, semi-conductors, alloys etc.; our aim is to *understand* their various properties. The key word in Solid State Physics (SSP) is *understanding*: It means that we do not restrict our search to find out what the magnitudes of the diverse quantities characterizing this or that type of solid are; we insist on finding out *why* these magnitudes are what they are. An answer to this “*why*” ought to stem from a few basic properties of the atoms making up the solid in order to be considered satisfactory. For example, one task of *SSP* is to *derive the observed value of the electrical resistivity of a copper wire at 300 K* ($\rho_e = 1.72 \mu\Omega \text{ cm}$) *starting from the information that the neutral atom of copper has 29 electrons* ($Z = 29$) *and a mass of 63.546 atomic units*.³

To go from the basic quantities characterizing the microscopic constituents of matter (essentially the atomic number Z of the participating atoms) to the various properties of a macroscopic system, such as a solid, it is a truly challenging task. It involves the employment of three essential ingredients (as shown in Fig. 1.1.):

1. *The forces* (or more generally the interactions), which are responsible for binding the constituents together. From the scale of atoms all the way up

¹ If the number of electrons is smaller than Z , a positively charged ion is formed called *cation*, while, if it is larger than Z , a negatively charged ion is formed called *anion*; Isolated ions are metastable structures, because they tend to combine with oppositely charged particles to form neutral structures.

² and possibly electrons (which are considered as point particles).

³ The atomic unit of mass, m_u , is equal to $1.660539 \times 10^{-27} \text{ kg}$, i.e., 0.992776 times the proton mass, m_p , or 1822.89 times the electron mass, m_e . Note that the value of 63,546, as any other atomic mass, is derivable by employing some principles of Nuclear Physics and by using the value of the atomic number Z (which for copper is 29).

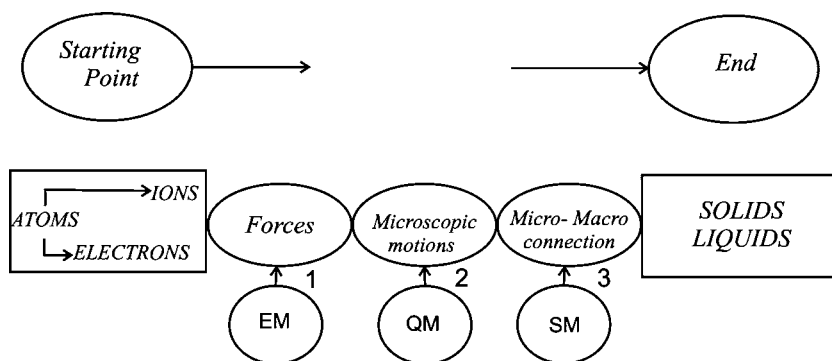


Fig. 1.1. To bridge the huge gap from atoms to solids (or liquids) three basic “foundations” are needed: Electromagnetism (EM), Quantum Mechanics (QM), and Statistical Mechanics (SM)

to that of an asteroid, the only force that plays a nonnegligible role is the *electromagnetic (EM)* one.⁴

2. *The microscopic motions* of the constituents under the action of the forces. The laws that govern these motions are those of *Quantum Mechanics (QM)* stemming from the fact that both interactions and particles have a dual wave–particle nature. We stress the fact that the World in all scales obeys quantum, not classical laws, although under some limited circumstances, it is possible that the conclusions of QM and Classical Mechanics practically coincide.
3. *The connection* between microscopic motions and macroscopic properties. This connection is provided by *Statistical Mechanics* and *Thermodynamics*.

In Appendices A, B, and C we give an outline of electromagnetism, QM, and thermodynamics/statistical mechanics respectively. In the next Sects. 1.2–1.4 we summarize the most important relations and principles of these three fundamental branches of Physics.

We conclude this section with two remarks:

Taking into account: (a) the ambitious goals of SSP; (b) the huge number of types of solids including man-made structures; (c) the various and diverse properties of solids (thermal, mechanical, electrical, magnetic, etc.); and (d) the large number of parameters affecting these properties of solids (e.g., temperature, pressure, external fields, methods of preparation, etc.), it is clear that the subject matter of SSP is enormous and it is capable of practically unlimited expansion as scientific research is exploring new uncharted regimes (e.g., nanotechnology).

⁴ Living matter could be considered as an indirect exception in the sense that its survival seems to require a planetary system with its central star; for the latter, gravitational and nuclear forces (as well as electromagnetic) are essential.

Table 1.1. Connections between subareas of condensed-matter physics and applications of wider interest

Sub-area	Information Processing	Speech and data communications	Energy	Medical	Transportation	Space Technology	National Security
Electronic properties	●	◐	●	○	●	○	●
Phonons/ Electron-Phonon interaction	◐	○	◐	◐	○	○	○
Phase transitions	◐	○	◐	○	◐	○	●
Magnetism	●	●	●	◐	●	◐	◐
Semiconductor	●	●	●	◐	●	●	●
Defects/ diffusion	●	●	●	●	●	◐	●
Surfaces/interfaces	●	●	●	◐	●	◐	●
Low-temperature physics	◐	○	●	◐	○	○	○
Liquids	◐	○	◐	○	◐	◐	○
Polymers	●	◐	◐	●	●	◐	◐
Nonlinear dynamics, instabilities, chaos	◐	○	○	○	○	○	●

A solid circle indicates a critical connection between the subarea of condensed-matter physics and the area of application; a half-filled circle indicates an important or emerging connection; an open circle denotes the possibility of a connection; a blank implies connection is not known.

The achievement of a deeper understanding of why solids behave the way they do not only satisfied our intellectual desire to comprehend the World around us, but also allowed us to control the behavior of solids and to enrich them with new desirable features, leading thus to the development of new technology. As a matter of fact, solids have been historically proved to be of paramount importance for technological and economic development (starting from the Neolithic Age and the Age of metals (copper, iron) to the modern era of transistors, integrated circuits, chips, magnetic memories, computers, magnetic resonance imaging (MRI), solid state lasers, etc.).

Table 1.1 (taken from a 1986 publication of the National Academy Press⁵) shows the impact of *Condensed Matter Physics (CMP)* on various aspects of a modern society. CMP includes the study of Solids, Liquids, and states of matter intermediate between Solids and Liquids such as Polymers, Liquid Crystals, Glasses, Gels, etc. Special quantum states such as superfluids, Bose–Einstein condensates, etc. are also part of the content of CMP.

1.2 Permanent (i.e., Equilibrium) Structures of Matter Correspond to the Minimum of Their (Free) Energy

It is well known from Mechanics that *the stable equilibrium of a system corresponds to the absolute minimum of its total energy and vice versa*. What makes this principle very important for determining the properties and the

⁵ “Physics through the 1990s: Condensed-Matter Physics,” National Academy Press, 2101 Constitution Ave, NW Washington, DC 20418.

structure of matter is that physical systems do possess a finite minimum of their total energy; this minimum is realized because of the presence of both the potential energy (which, as we shall see, is negative and tends to squeeze the system) and the quantum kinetic energy (which is always positive and tends to blow the system apart). In other words, the total energy E of a system is the sum of two⁶ terms opposing each other: the total potential energy E_P and the total kinetic energy E_K :

$$E = E_K + E_P. \quad (1.1)$$

Both E_P and E_K depend on many parameters: For example, the volume V of the system, the electronic concentration $n_e(\mathbf{r})$, the placement $\mathbf{R}_\alpha$ of the atoms or ions of a solid in space, the orientation of the spins of the atoms or the ions, etc.

If one succeeds in minimizing the total energy E with respect to all of these free parameters, one has obtained a full determination of the *ground state* of the system (assuming that no external pressure is exercised on the system). As an example, let us minimize E with respect to the volume (assuming zero absolute temperature):

$$\frac{\partial E}{\partial V} = \frac{\partial E_K}{\partial V} + \frac{\partial E_P}{\partial V} = 0. \quad (1.2)$$

However, $-(\partial E/\partial V)_{T=0}$ is the total pressure,⁷ $-(\partial E_K/\partial V)_{T=0}$ is the positive pressure P_K due to the finite kinetic energy, and $-(\partial E_P/\partial V)_{T=0}$ is the negative pressure P_P due to the attractive potential energy. Thus, we conclude that the minimization of the total energy with respect to the volume implies that the total pressure must be equal to zero, or equivalently, that $P_K = |P_P|$; hence, it follows from (1.2) that the squeezing pressure of the potential energy is balanced exactly at equilibrium by the repulsive pressure of the kinetic energy. If there is a non-zero *external* squeezing pressure P_0 , equilibrium demands that the difference $P_K - |P_P|$ must be equal to P_0 :

$$P_0 = P_K - |P_P|, \quad (1.3)$$

This is equivalent to the minimization (with respect to the volume) of the quantity $E + P_0 V$, which is called *enthalpy*.

Finally, if the system is placed in an environment of pressure P_0 and absolute temperature T_0 , the stable equilibrium corresponds to the minimization

⁶ A third term in the total energy is the so called rest energy, $\sum m_{io}c^2$, where m_{io} are the rest masses of the nuclei and the electrons making up the solid. However the formation, transformations and other changes in solids do not involve measurable changes in m_{io} ; thus, this third term is a constant which can be eliminated by a redefinition of the zero of the energy.

⁷ Remember the first law of Thermodynamics, $dE = -PdV + TdS$ and set $T = 0$.

of the quantity $E + P_0V - T_0S$, where S is the *entropy* of the system.⁸ Since at equilibrium $P = P_0$ and $T = T_0$, the quantity $E + P_0V - T_0S$ reduces to the so-called *Gibbs free energy*, $G \equiv E + PV - TS$. Hence,

Under conditions of constant pressure and temperature (and no exchange of matter), the stable equilibrium of a system corresponds to the minimization of its Gibbs free energy $G \equiv E + PV - TS$. (1.4)

Notice that when $P = T = 0$, the Gibbs free energy G reduces to the energy E , and thus, we recapture the initial statement of this section. The important message to be remembered is that we possess a recipe to predict (or to justify a posteriori) the equilibrium structures of matter and their properties. Here is the recipe:

For the system under study, obtain the Gibbs free energy G (under conditions of constant P and T), or the energy E (under conditions $P = T = 0$), as a function of various free parameters (such as the volume, the positions of the atoms or ions, the electronic concentration $n_e(\mathbf{r})$, etc.); minimize G or E with respect to all these free parameters; the resulting state is one of stable equilibrium to be observed in nature.

A word of caution is in order at this point: A system may stay for a very long time (even infinite for all practical purposes) in a state of metastable equilibrium corresponding to a local minimum of G (under conditions $T = \text{const}$, $P = \text{const}$). This may happen because the energy barrier separating this local minimum from the absolute minimum (corresponding to stable equilibrium) can be large enough to be practically impenetrable by quantum mechanical tunneling even in the presence of some external perturbations. It is even possible for a system to stay in an unstable state (corresponding to no minimum of E or G) for a very long time (practically infinite), if there is no mechanism for unloading its excess energy (e.g., a planet going around the Sun in the absence of gravitational waves), or, if the unloading of energy (or free energy) involves extremely slow motions of a huge number of microscopic particles (e.g., deformations of ordinary glasses under the influence of gravity take centuries); in the latter case, we are dealing with the so-called *kinetically arrested* unstable configurations.

⁸ This very important principle is an immediate consequence of the first ($dE = dQ - PdV$) and the second ($dQ \leq TdS$) law of thermodynamics. Indeed, by combining the two laws, we obtain $dE \leq TdS - PdV$, or $dE + PdV - TdS \leq 0$, or (taking into account that T and P are constant) $dG \leq 0$, where $G \equiv E + PV - TS$. The last inequality, under the said conditions, means that the Gibbs free energy G decreases with time (or, in extreme cases, remains constant), until its minimum value is reached, upon which no further spontaneous change can occur, and consequently, stable equilibrium is established.

1.3 Condensed Matter Tends to Collapse Under the Influence of Coulomb Potential Energy

The main contribution to the potential energy of ions and electrons making up molecules, solids, liquids, etc. is the Coulomb interaction among the electrical charges q_i of the constituent particles:

$$E_P = 1/2 \sum_{ij} \frac{q_i q_j}{r_{ij}}, \quad \text{G-CGS units.}^9 \quad (1.5)$$

The various terms contributing to the sum in (1.5) can be either positive (when $q_i q_j > 0$), meaning repulsion, or negative (when $q_i q_j < 0$), meaning attraction. For an electrically neutral system (where $\sum_i q_i = 0$), under the self-adjusting placement of the charges, E_P , as given by (1.5), becomes more and more negative meaning not only that attraction wins over repulsion, but also that the electrostatic forces tend to squeeze the system leading, if unopposed, to its eventual collapse.¹⁰

⁹ G in G-CGS stands for Gauss (see [E17], and App. A). In the SI system, (1.5) is written as $E_P = 1/2 \sum_{ij} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}$.

¹⁰ It is worth to point out that the role of electromagnetism is *dual*: First, it provides the Coulomb forces that keep atoms or ions and electrons bound together to form larger structures such as molecules, solids, liquids, etc. Second, electromagnetic fields generated by external sources penetrate into the system under study, and drive it out of equilibrium or to a modified equilibrium state. This second role of electromagnetic forces is also extremely important both biologically and technologically (we see because, on the one hand, visible objects are secondary emitters of EM waves, and on the other hand, the receiving chain from the eye to the brain interacts strongly with EM fields; our telecommunications are based on the interaction of EM waves with matter, the latter being usually properly designed and fabricated solid state devices).

Several quantities characterize the response of materials to EM fields. Probably, the most important among them is the well-known *permittivity* (or *electrical permeability*, or *dielectric function*, if dimensionless), which connects the *electric induction* $\mathbf{D}$ to the *electric field* $\mathbf{E}$ (see Appendices A and D). The permittivity ϵ is simply connected to the conductivity σ through the relation $\epsilon(\mathbf{k}, \omega) = \epsilon_0 + (i\sigma(\mathbf{k}, \omega)/\omega)$ in SI [or $1 + (4\pi i\sigma(\mathbf{k}, \omega)/\omega)$ in G-CGS]. Knowing the permittivity of a material, we can determine the propagation, reflection, transmission, etc. of EM waves through this material (assuming that the magnetic permeability is equal to one); we can find how external charged particles interact with this material; we can find how the constituent particles interact among themselves and thus determine the average value of the potential energy of the material; finally we can determine the elementary collective excitations of the material such as longitudinal and transverse acoustic waves. In other words, the permittivity $\epsilon(\mathbf{k}, \omega)$ appears again and again in the course of studying condensed matter and constitutes a powerful tool for analyzing the behavior of solids.

1.4 Quantum Kinetic Energy Counterbalances Coulomb Potential Energy Leading to Stable Equilibrium Structures

Quantum Mechanics embodies the basic experimental fact that matter and interactions possess both particle and wave features. As a result, an angular frequency ω is associated with the energy ε of a particle¹¹ and a wavevector $\mathbf{k}$ is associated with the momentum $\mathbf{p}$ of a particle¹¹ (or of a quasi-particle such as a phonon or a magnon as we shall see later on in Chapters 6 and 21):

$$\varepsilon = \hbar\omega, \quad (1.6)$$

$$\mathbf{p} = \hbar\mathbf{k}, \quad (1.7)$$

where $\hbar$, Planck's constant (divided by 2π), is the “trade mark” of QM and probably the most important universal physical constant.

1.4.1 Heisenberg's Uncertainty Principle and the Minimum Kinetic Energy

From the wave-particle duality follows¹² Heisenberg's uncertainty principle, stating that

$$\Delta p_x \Delta x \geq \frac{\hbar}{2}, \quad (1.8)$$

where Δp_x is the standard deviation¹³ of the x -component of the particle's momentum vector and Δx is the standard deviation of the projection of the particle's position along the x -axis. The most important consequence of (1.8) is that it sets a lower non-zero limit to the average value ε_K of the kinetic energy of a particle confined in a volume V . Indeed, using the definition of standard deviation, we have

$$\langle \varepsilon_K \rangle = \frac{1}{2m} (\langle p_x^2 \rangle + \langle p_y^2 \rangle + \langle p_z^2 \rangle) \geq \frac{1}{2m} (\Delta p_x^2 + \Delta p_y^2 + \Delta p_z^2) \geq 4.87 \frac{\hbar^2}{mV^{2/3}}, \quad (1.9)$$

where V is the volume (assumed spherical) within which the particle is confined and m is the mass of a particle (for a proof of (1.9) see Problem 1.5s).¹⁴

¹¹ and vice versa, a quantum of energy ε is associated with a wave of frequency ω and a quantum of momentum $\mathbf{p}$ is associated with a wave of wavevector $\mathbf{k}$.

¹² The spatial extent Δx of an one-dimensional wave packet involving plane waves of wavevectors covering a range Δk satisfies the relation $\Delta x \Delta k \gtrsim \frac{1}{2}$. Taking into account (1.7) we end up with (1.8).

¹³ The square of the standard deviation, ΔQ^2 , of a random quantity Q is defined as follows $\Delta Q^2 \equiv \langle Q^2 \rangle - \langle Q \rangle^2$, where the symbol $\langle \rangle$ denotes average value.

¹⁴ Notice that (1.9) is based on the nonrelativistic expression, $\mathbf{p}^2/2m$, for the kinetic energy. If the latter is equal to cp , as in the extreme relativistic case, or, as in the

Notice that in the classical limit ($\hbar = 0$) the lowest kinetic energy is zero, as it should be; notice also that the mass of the particle is in the denominator, which means that the smaller the mass, the larger the minimum kinetic energy; for this reason the latter is dominated by the electronic kinetic energy; finally, since the available volume to the $2/3$ power is in the denominator, more confinement increases the minimum kinetic energy.

The importance of a nonzero lower limit of the form of (1.9) for the kinetic energy can hardly be overestimated. A nonzero minimum kinetic energy implies a tendency for the constituent particles to fly apart; this tendency counterbalances the squeezing effect of the electrostatic Coulomb forces and the system ends up *in a unique equilibrium state of lowest total energy*. This unique equilibrium state is also *stable*, i.e., if the Coulomb forces momentarily squeeze the system further, the volume V would decrease, the kinetic energy, according to (1.9), would increase *more* than the potential energy, and it would drive the system back to equilibrium; similarly, if the kinetic energy inflates momentarily the volume away from its equilibrium value, the Coulomb forces would overcome the repulsive tendencies of the kinetic energy and they would drive the system back to equilibrium.

In conclusion, the permanent equilibrium structures of matter (for negligible external pressure P_0 and temperature T_0) is the outcome of two opposing factors: the potential energy, which tends to squeeze and eventually collapse the system, and the kinetic energy – of quantum origin stemming from Heisenberg’s uncertainty principle – which tends to blow the system apart to its constituent particles.

1.4.2 Pauli’s Exclusion Principle and the Enhancement of the Minimum Kinetic Energy

A second quantum principle of equal importance as the first one is *Pauli’s exclusion principle*; this principle stems also from the wave nature of particles, which makes identical particles *sharing the same space* indistinguishable;¹⁵ for half-integer spin particles ($s = 1/2, 3/2, \dots$), (called fermions), Pauli’s principle implies that:

classical wave case, then $\langle \varepsilon_\kappa \rangle \gtrsim 3\hbar c/V^{1/3}$. Note that V (assumed spherical) is proportional to $\Delta x^3 = \Delta y^3 = \Delta z^3$. Hence, Δx is proportional to $V^{1/3}$ and Δx^2 is proportional to $V^{2/3}$.

¹⁵ The connection between spin and the behavior of identical particles under interchanging any two of them is also playing an important role. The indistinguishability implies that the absolute square, $|\Psi(1, 2, 3, \dots)|^2$, of the wave function $\Psi(1, 2, 3, \dots)$ remains invariant under the interchange of any two particles (e.g. 1 and 2; 1 stands for $\mathbf{r}_1, s_1$, etc.). Hence, the wave function itself either remains invariant under interchanging of any two particles, (e.g. $\Psi(1, 2, 3, \dots) = \Psi(2, 1, 3, \dots)$) for particles of integer spin, called bosons) or is multiplied by -1 (e.g. $\Psi(1, 2, 3, \dots) = -\Psi(2, 1, 3, \dots)$ for particles of half-integer spin, called fermions).

The probability of finding two or more identical fermions in the same orbital-spin state is zero. (1.10)

For spin one half particles, e.g., electrons, statement (1.10) means that at most two electrons (one with spin up and the other with spin down) can occupy the same *orbital* state. The role of Pauli's exclusion principle in explaining the structure of the Periodic Table of the Elements (Table H.5), and consequently, the basic principles of Chemistry is well-known. Perhaps not so well appreciated is its role in amplifying the kinetic energy of identical fermions sharing the same volume V . Indeed, as it is clear from Fig. 1.2, Pauli's exclusion principle forces fermions to occupy higher levels, while, if this principle were absent, the lowest total energy of N noninteracting identical particles would be obtained by placing all of them at the ground level ε_G .

Thus, the *minimum average energy per particle*, $\langle \varepsilon \rangle \equiv E_{\min}/N$ (where N is the total number of identical fermions), instead of being equal to the ground state energy ε_G , is raised to be somewhere between ε_G (chosen usually as zero), and the highest occupied level called the *Fermi energy*,^{16,17} E_F .

An easy, *approximate*, but physically transparent way to obtain the minimum total kinetic energy per particle of N identical spin 1/2 fermions is the following: The N particles divide the available common (homogeneous) space of volume V into $N/2$ equal subvolumes; in order to satisfy Pauli's principle, only two fermions are placed in each subvolume (one with spin up and the other with spin down). However, now the available volume for each fermion is $V/(N/2) = 2V/N$. Substituting $2V/N$ instead of V in (1.9), we obtain¹⁸

$$\langle \varepsilon_K \rangle = 3.07 \frac{\hbar^2 N^{2/3}}{m V^{2/3}}, \quad (3.07 \rightarrow 2.87), \quad (1.11)$$

while an accurate calculation by summing up the kinetic energies of all N fermions and dividing by N gives a similar expression with the only

¹⁶ More accurately the Fermi level lies in the middle between the highest occupied and the lowest empty state (under conditions of minimum total energy). See footnote in next page.

¹⁷ As we shall see, for a three-dimensional, spin 1/2, nonrelativistic, free fermion system $\langle \varepsilon_K \rangle = 0.6 E_F$ and $E_F = \hbar^2 (3\pi^2 N/V)^{2/3} / 2m$. (If ε_G is chosen as the zero of energy).

¹⁸ From the definition of $\langle \varepsilon_K \rangle \equiv E_{K,\min}/N$ and (1.11), it follows that $E_{K,\min} \sim N^{5/3}$. A more general definition of E_F , applicable to interacting systems as well, is the following: $E_F(N) \equiv U(N+1) - U(N) \xrightarrow{N \rightarrow \infty} \partial U / \partial N$ (where U is the total energy (written usually either as U or E ; see also (C.8) and (C.49)). This more general definition reduces to the one given in Fig. 1.2, if the particles do not interact with the following clarification: $E_F(N)$ coincides with the lowest unoccupied level, if N is even, and with the highest occupied level, if N is odd. Thus, E_F , on average, is exactly at the middle of these two levels. Hence, in the present case, where $U = E_K$, $E_F = \partial E_{K,\min} / \partial N = \frac{5}{3} \frac{1}{N} E_{K,\min} = \frac{5}{3} \langle \varepsilon_K \rangle$ or $\langle \varepsilon_K \rangle = 0.6 E_F$.

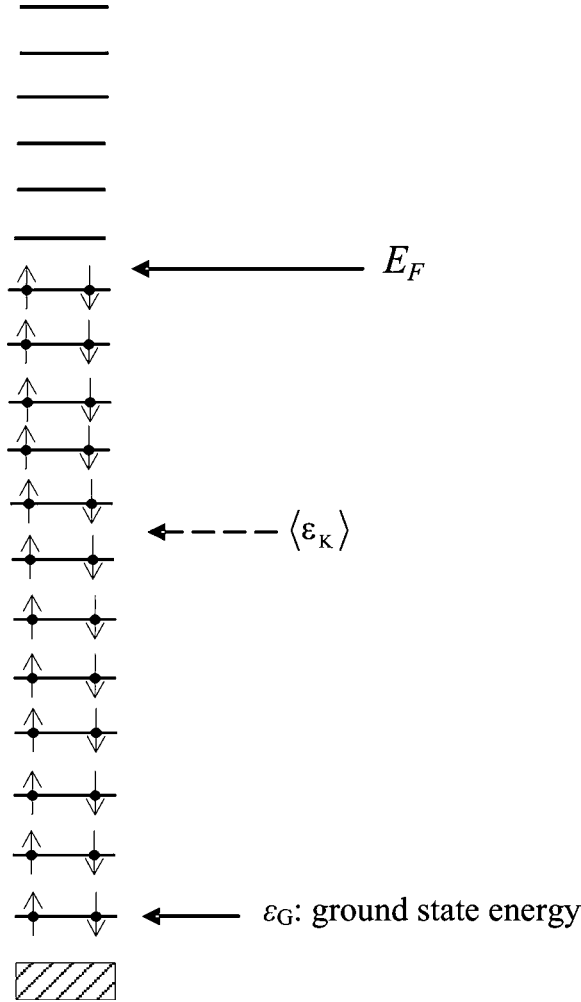


Fig. 1.2. The energy levels associated with each spatial single-electron state are given in order of increasing energy starting from the ground state. The lowest total kinetic energy of N (e.g., $N = 20$) electrons, consistent with Pauli's principle, is obtained by occupying the lowest ten spatial states by two electrons each (one with spin up and one with spin down). The highest occupied state is called the *Fermi level*¹⁶ and is denoted by E_F

difference in the numerical prefactor, which is smaller¹⁹ than 3.07 and equal to $0.3 (3\pi^2)^{2/3} = 2.87$ (see footnote 18).

¹⁹ It is expected to be smaller, since any approximate solution raises the total energy.

Thus, the presence of N identical fermions in the *same volume* amplifies the Heisenberg based average kinetic energy per particle by a factor proportional to $N^{2/3}$ as a result of Pauli's exclusion principle. This kinetic energy of quantum origin is essential in establishing and stabilizing the structure of solids. So, do not ever forget it!

1.4.3 Schrödinger's Spectral Discreteness and the Rigidity of the Ground State

The third principle, which could be called *Schrödinger's principle*, states that the energy spectrum of a particle confined in a finite volume V is discrete; the energy separation $\delta\varepsilon$ between two consecutive low-lying energy levels is given by a similar expression as in (1.9):

$$\delta\varepsilon = \eta \frac{\hbar^2}{mV^{2/3}}, \quad (1.12)$$

where η is a numerical factor typically of the order of unity; its value depends on the form of the confining potential. This discreteness stems again from the wave nature of the particles. (It is well known that EM waves confined to a finite volume, e.g., in a cavity, acquire a discrete frequency spectrum; for a more familiar case, think of a guitar string, which produces only the fundamental note and its harmonics and nothing in between; this discreteness in frequency is transferred to the energy spectrum because of (1.6). The explicit form of (1.12) can be obtained by the following arguments: The quantity $\delta\varepsilon$ ought to depend on $\hbar$ (as a quantum effect), on m (since m is a characteristic of the particle), and on V (as a measure of the confinement); the only combination of these three quantities with dimensions of energy is the one shown in (1.12)).

Equation (1.12) implies in particular that the first excited state is separated from the ground state by a nonzero energy difference $\delta\varepsilon_0 \sim \hbar^2/mV^{2/3}$. Now, if an external perturbation (e.g., a quantum, $\varepsilon = \hbar\omega$, of an EM wave of frequency ω) is applied to our particle (or, more generally, to our system), the latter may attempt to absorb this quantum of energy; however, if $\hbar\omega < \delta\varepsilon_0$, this absorption cannot take place, since $\hbar\omega$ is not enough to kick up the system to the next level; thus, the system will remain in its ground state. In other words, the discreteness of the energy spectrum bestows *stability* on the physical systems (against external temporary perturbations unable to transfer energy higher than $\delta\varepsilon_0$), while, nevertheless, it allows *changes* (if the available energy exceeds $\delta\varepsilon_0$). Because of (1.12), the smaller the volume, the larger the excitation energy $\delta\varepsilon_0$; hence, the tinier the system the more stable it is. This is why atomic nuclei are absolutely unchanged under ordinary perturbations.²⁰ This extended stability to external perturbations explains why atoms

²⁰ For example, the first excited energy level of the nucleus of C^{12} is according to (1.12) equal to 1, 41 η MeV (the experimental value is 4, 43 MeV) to be compared

and small molecules exhibit the same features and possess the same properties in very diverse environments leading thus to their admirably predictable and repeatable physicochemical behavior.

Notice also that (1.12) in combination with Pauli principle implies that each discrete level can accept a finite number of spin $1/2$ particles, i.e., twice the degeneracy²¹ of the level. This observation explains the shell atomic structure of the electrons trapped around the nucleus. (See Figs. 2.1 and 2.2 in the next chapter).

1.5 Dimensional Analysis

The dimensional analysis may allow us, under certain circumstances, to find out how a quantity of interest depends on other known quantities and/or on some parameters assumed known; in other words it may allow us to produce (instead of memorize) physics formulae. To apply this analysis, a physical insight is required as to identify all possible known quantities or parameters on which the quantity of interest may depend.

To clarify this matter, let us examine the specific example of the phase velocity v of sea waves: v must depend on the acceleration of gravity g , since the gravitational forces are the ones that tend to restore a flat equilibrium surface of the sea water and thus drive the oscillatory motion of the water near the surface; the wavelength λ may play a role, since it is the most important parameter characterizing a wave; the physical properties of the sea water such as its density ρ_m is another candidate quantity for entering the formula for v . Let us assume at this point that we have exhausted²² the list of quantities influencing v . The three quantities g , λ , ρ_m can define a system of units; this means that a combination of the form $g^\mu \lambda^\nu \rho_m^\xi$ can produce the dimensions of length, time, and mass and hence, the dimensions of any physical quantity²³ with a proper choice of the exponents μ , ν , ξ . To produce dimensions of velocity, we have to choose $\mu = 1/2$, $\nu = 1/2$ and $\xi = 0$ (any other choice for ξ will retain a power of mass besides powers of length and time, the latter coming from λ and g). Hence,

with the thermal energy $k_B T = 26 \text{ meV}$ for $T = 300 \text{ K}$, i.e., $k_B T / \delta \varepsilon_0 = 5.8 \times 10^{-9}$ for C^{12} at $T = 300 \text{ K}$.

²¹ The degeneracy of a discrete level is the maximum number of different spatial eigenstates belonging to this level.

²² Actually, the depth of the sea d may play a role, if $d \lesssim \lambda$. The surface tension coefficient, a_s , may also enter since the surface tension tends to minimize the surface, and consequently, tends to restore a flat surface; however, this restoring force is insignificant in comparison with the gravitational force unless the wavelength is of the order of centimeters or less.

²³ The unit of absolute temperature can be produced from the unit of energy by dividing by k_B , the Boltzmann's constant. Length is produced by choosing $\nu = 1$, $\mu = \xi = 0$; time is produced by choosing $\mu = -1/2$, $\nu = 1/2$, and $\xi = 0$; finally mass is produced by choosing $\mu = 0$, $\nu = 3$, and $\xi = 1$.

$$v = \eta \sqrt{g\lambda}, \quad (1.13)$$

where the numerical constant η cannot be determined from dimensional analysis (it is actually equal²⁴ to $1/\sqrt{2\pi}$). Formula (1.13) is correct as long as the depth d of the sea is much larger than the wavelength λ ; otherwise v would depend also on the dimensionless ratio $x \equiv 2\pi d/\lambda = kd$

$$v = \sqrt{\frac{g\lambda}{2\pi}} f(x), \quad (1.14)$$

where the function $f(x)$, $x = 2\pi d/\lambda$, cannot be determined from dimensional analysis; actually $f(x) = \tanh x$. Can you employ dimensional analysis to answer the following questions: *What is the velocity of propagation of a tsunami (for which $d \ll \lambda$)? What is the value of v if $d = 1$ km and $\lambda \simeq 60$ km?*

Another example worth presenting is the EM energy per unit time and unit surface, J , emitted by a black body of temperature T (in K). The quantities that we expect to enter in the formula for J are: (1) Obviously, the absolute temperature, T ; remember, however, that *the quantity of physical meaning is not T itself but the combination $k_B T$ (always) where k_B is Boltzmann's constant*, see [ST35, §9]; (2) the velocity of light c (since we are dealing with EM radiation); (3) the Planck constant $\hbar$ (since black body radiation is a quantum effect; actually this is the phenomenon that led to the introduction of $\hbar$ for the first time). In the absence of any other obvious additional quantity let us be optimistic and assume that $k_B T$ (with dimensions of energy), c , and $\hbar$ (with dimensions of energy time) are the only ones determining J . The latter has dimensions of energy over time and over length square. Now $\hbar/k_B T$ has dimensions of time, and $c\hbar/k_B T$ has dimensions of length. Hence, the only combination of $k_B T$, c , $\hbar$ that has the same dimensions as J is $k_B T / (\hbar/k_B T) \cdot (c\hbar/k_B T)^2$. Thus,

$$J = \eta \frac{(k_B T)^4}{c^2 \hbar^3}, \quad (1.15)$$

where η is a numerical factor (actually it turns out that $\eta = \pi^2/60$).

How can dimensional analysis²⁵ be applied to the determination of the properties of solids? Since the kinetic energy of the electrons (which involves

²⁴ To make the numerical constant closer, or even equal, to one it is better to use $\lambda/2\pi$ instead of λ , since the phase of the wave involves the combination x ($2\pi/\lambda$) and not x/λ .

²⁵ In the general case, the dimensional analysis works as follows:

1. We identify all possible quantities $A_1, \dots, A_n$ on which the quantity of interest, X , may depend. (This is a crucial and far from trivial step.)
2. If $n \leq 3$, there is usually a unique combination of the form $A_1^{\mu_1} \dots A_n^{\mu_n}$ which has the same dimensions as X . Then the desired formula for X has been found: $X = \eta A_1^{\mu_1} \dots A_n^{\mu_n}$ where η is an undetermined numerical constant

Planck's constant $\hbar$ and the electronic mass, m_e) and the Coulomb forces (which involve the proton and electron charge $\pm e$) are the main actors in determining the state of solids, we conclude that solid-state properties would depend in general on $\hbar$, e , and m_e . These three quantities define a system of units (with the help of k_B and ε_0 , μ_0 (in SI), see Table H.2) that is called atomic²⁶ system of units; in particular the unit of length in this system is the well-known **Bohr radius**, $a_B = \hbar^2/e^2m_e$ ($= 4\pi\varepsilon_0\hbar^2/e^2m_e$ in SI), $a_B = 0.529 \text{ \AA}$, and the unit of time, $t_0 = m_e a_B^2/\hbar = \hbar^3/e^4m_e$ ($= (4\pi\varepsilon_0)^2 \hbar^3/e^4m_e$ in SI), $t_0 = 2.419 \times 10^{-17} \text{ s}$. Usually, it is more convenient to use the triad $\hbar$, m_e , a_B , instead of the triad $\hbar$, m_e , e .

Besides the fundamental physical constants $\hbar$, m_e , a_B (and k_B if temperature is needed) the properties of solids are expected to depend on the type of atoms involved, i.e., on their atomic numbers Z_i ; other properties of atoms such as their mass $m_{\alpha i}$ may also be involved.²⁷ External conditions such as the temperature T and to a lesser degree the pressure P may influence the properties of solids²⁸ as well. Other hidden quantities may also enter. Thus, any quantity X pertaining to the solid state can be expressed in terms of known quantities and parameters as follows:

$$\frac{X}{X_0} \equiv \bar{X} = f_x \left(Z_i, \frac{m_{\alpha i}}{m_e}(Z_i), \frac{T}{T_0}, \frac{P}{P_0}, \frac{c}{v_0}, \dots \right), \quad (1.16)$$

-
3. If $n > 3$, we choose three quantities A_1, A_2, A_3 , which define a system of units (in the sense that three different combinations of the form $A_1^{\mu_1} A_2^{\mu_2} A_3^{\mu_3}$ can be found which have the dimension of length, time, and mass respectively)
 4. By a proper choice of ν_1, ν_2, ν_3 , we form the combination $A_1^{\nu_1} A_2^{\nu_2} A_3^{\nu_3} \equiv X_0$, where X_0 has the same dimensions as the quantity of interest X
 5. We create also combinations $A_1^{\xi_{1n}} A_2^{\xi_{2n}} A_3^{\xi_{3n}} \equiv A_{n0}$ which have the same dimensions as A_n , ($n = 4, 5, \dots$) and we define the dimensionless quantities A_n/A_{n0} ($n = 4, 5, \dots$)
 6. Having determined the quantities $X_0, A_{40}, A_{50}, \dots$ in terms of the chosen quantities A_1, A_2, A_3 , we are ready to express X in terms of $A_1, \dots, A_n$ as follows

$$X = X_0 f \left(\frac{A_4}{A_{40}}, \frac{A_5}{A_{50}}, \dots \right),$$

where the unknown function f cannot be determined from dimensional analysis; additional information(s) or even a complete physical theory is needed to find out what f is.

-
- ²⁶ The unit of mass in this system is m_e ; however, notice that the mass $m_u \equiv \frac{1}{12}m_C$, where m_C is the mass of carbon-12, is also defined as the atomic unit of mass; $m_u = 1822.89m_e$.
- ²⁷ We remind the readers that the properties of an atom can be derived in terms of Z by employing methods of nuclear and atomic physics.
- ²⁸ The velocity of light, c , may also appear especially for heavy atoms where relativistic effects are not negligible; some nuclear properties may also play a role.

where $\bar{X}$ is the value²⁹ of X in atomic units, X_0 is the combination $X_0 = \hbar^{v_1} m_e^{v_2} a_B^{v_3}$, which has the same dimensions as X (see Table H.2) and f_x is a function of the *dimensionless* quantities Z_i , $m_{\alpha i}/m_e, \dots$; T_0 is the atomic unit of temperature, $T_0 = \hbar^2/m_e a_B^2 k_B = 315,775 \text{ K}$, P_0 is the atomic unit of pressure, $P_0 = \hbar^2/m_e a_B^5 = 2.9421 \times 10^{13} \text{ N/m}^2 = 2.9421 \times 10^8 \text{ bar}$, and $v_0 = \hbar/m_e a_B = c/137 = 2187.69 \text{ km/s}$ is the atomic unit of velocity. The success or not of (1.16) in providing quick and reliable estimates for the magnitude of physical quantities depends on whether or not f_x is a smooth function of Z_i and of other hidden dimensionless variables (which are implicit functions of Z_i). In the next chapter we shall present applications of (1.16) in estimating several quantities of physical interest. As we shall see, there are impressively accurate estimates (given the generality and simplicity of (1.16)) as well as some “first attempt” failures which are, however, very instructive.

To summarize: Equation (1.16) is extremely important because it allows us to obtain “an enormous amount of information” regarding the qualitative and quantitative behavior of condensed matter “if just a little imagination and thinking is applied.”

1.6 Key Points

Three ideas are “sine qua non” for understanding the properties of solids:

- The *atomic idea*, according to which solids are made of atoms (or ions and electrons), which are brought together mainly by the action of electrostatic forces; the latter if unopposed, would squeeze the solid to its collapse.
- What counterbalances the squeezing electrostatic pressure is the pressure of the *kinetic energy*, which is of quantum nature; the latter embodies three basic principles:
 - *Heisenberg’s* uncertainly principle, which leads to the existence of a minimum kinetic energy inversely proportional to the mass of the particle and to the $2/3$ power of the volume within which the particle is confined (nonrelativistic behavior is assumed).
 - *Pauli’s* exclusion principle, which enhances the average kinetic energy per particle of a system (consisting of N identical fermions sharing the same volume V) by a factor proportional to $N^{2/3}$.
 - *Schrödinger’s* discreteness principle, which makes the ground state rigid to some extent by inhibiting excitation of the system by external perturbations, if the energy of the latter is lower than the energy of the first excited state above the ground state.
- Stable equilibrium states of matter (such as solids) correspond to the minimum value of the total energy, which consists of the potential part and the kinetic part (if $P = T = 0$); or the total Gibbs free energy,

²⁹ Throughout this book a bar over any physical quantity X denotes its value at the atomic system of units: $\bar{X} \equiv X/X_0$.

$G \equiv E + PV - TS$, (if $P = \text{const}$, $T = \text{const}$). The minimization is with respect to various adjustable quantities such as the volume, the position of atoms in space, the concentration of electrons, etc. The potential energy is characterized mainly by the electron or proton charge, $\mp e$, and the kinetic energy by Planck's constant, $\hbar$, and the mass of the electron m_e . Thus, all properties of solids would depend at least on e , $\hbar$, m_e , or equivalently on a_B , $\hbar$, m_e . This observation coupled with dimensional considerations and “a little thinking” produces a wealth of information regarding macroscopic properties of solids (see (1.16)).

1.7 Questions and Problems

- 1.1 Why is the quantum kinetic energy characterized mainly by the electronic mass m_e and not by the ionic mass, m_a ?
- 1.2 Why was the thermal kinetic energy of electrons and ions in a solid ignored in comparison with the quantum kinetic energy?
Hint: Consider the case of aluminum (for which $V/N_e = 5.5 \text{ \AA}^3$) at $T \simeq 300 \text{ K}$ (see Tables H.2 and H.4).
- 1.3 Can you show that the equilibrium established between the quantum kinetic energy and the electrostatic energy is stable?
Hint: From (1.5) it follows that E_P/N is proportional to $e^2 N^{1/3}/V^{1/3}$.
- 1.4 Consider two identical particles confined within the same volume V . Since the two particles do not follow some orbit, they are indistinguishable; their indistinguishability implies that all observable properties, such as the absolute value of the square of their total wavefunction, $|\Psi(1, 2)|^2$, remain invariant under the interchange of the particles, $1 \rightarrow 2$ and $2 \rightarrow 1$: $|\Psi(1, 2)|^2 = |\Psi(2, 1)|^2$. Using the last relation, show that $\Psi(1, 2) = \pm \Psi(2, 1)$.
For half-integer spin particles the minus sign holds, while for integer spin particle the plus sign applies. How Pauli's principle, as stated in (1.10), follows from this?
- 1.5s Prove (1.9) by employing Heisenberg's uncertainty principle and the relation $\varepsilon_k = p^2/2m$.³⁰
- 1.6 Show that in the extreme relativistic limit, $mc^2 \ll cp$, Heisenberg's principle leads to the relation $\varepsilon_k \gtrsim 3\hbar c/V^{1/3}$, where V is the spherical volume within which the particle is confined.
- 1.7 Combining the result of Problem 1.5s with Pauli's exclusion principle prove (1.11). How will (1.11) be modified if $\langle \varepsilon_k \rangle$ is much larger than the rest energy mc^2 ?

³⁰ The letter s after the number of the problem means that the corresponding problem is solved; the solution can be found in the part “solution of selected problems” p. 779

Answer:

$$\langle \varepsilon_K \rangle = E_{K,\min}/N = \eta \hbar c (N/V)^{1/3}, \quad E_F = \frac{4}{3} \langle \varepsilon_K \rangle, \quad \eta = 2.32.$$

- 1.8 For the hydrogenic s states calculate the energy difference $\delta\varepsilon$ between two consecutive levels and check whether (1.12) is satisfied. What is the value of η ?
- Hint:* Identify the $V^{-2/3}$ appearing in (1.12) with $(4\pi/3)^{-2/3} \langle r^{-2} \rangle$.
- 1.9s By employing dimensional analysis, find the wavelength λ_m at which the spectral distribution $dJ_\lambda/d\lambda$ of black body's radiation exhibits a maximum.
- 1.10s By employing dimensional analysis, find the scattering cross-section for a photon by an isolated electron.
- 1.11s By dimensional analysis, find the natural linewidth and the corresponding life-time of an excited atomic level which decays by dipole type emission.
- 1.12s A black hole of mass M , as a result of its strong gravitational field, emits black body radiation through a quantum fluctuation mechanism proposed by Hawking. By dimensional analysis find the effective temperature of this radiation.
- 1.13s High-frequency electric currents in a good conductor of conductivity σ are confined in a region of width δ near the surface. How does δ , the so-called *skin depth*, depend on the relevant parameters?

Further Reading

- Landau & Lifshitz, *Stat. Phys.* [ST35], Chap. 20, pp. 59–63.
- Eisberg & Resnick, *Quantum Physics of Atoms, Molecules, Solids, Nuclei and Particles* [Q23], pp. 6–21.

Basic Principles in Action

Summary. Atoms come close together, (at a distance of the order of Angstroms) to form molecules and solids, because by doing so, they lower their total energy; faithful to Heisenberg's principle, they undergo small oscillations around their fixed equilibrium positions. The basic physical constants $\hbar$, m_e , and e (instead of e we can use the Bohr radius $a_B = 4\pi\epsilon_0\hbar^2/m_e e^2 = 0.529 \text{ \AA}$) with the possible inclusion of the atomic mass, m_a , and the temperature, T , through dimensional analysis, allow us to estimate the values of several quantities pertaining to the solid state of matter, such as density, cohesive energy, bulk modulus, sound velocity, melting temperature, etc.

2.1 Size and Energy Scale of Atoms

Dimensional analysis suggests that the size of atoms must be of the order of Bohr radius, $a_B = 4\pi\epsilon_0\hbar^2/m_e e^2$, since this is the only length one can make out of $\hbar$, m_e , and e^2 . (The factor $4\pi\epsilon_0$ is present in SI, but not in G-CGS). The unavoidable numerical factor cannot be determined from dimensional analysis; something more is needed, which, of course, is the general principle of the minimization of the energy.

Let us consider the simplest atom, the hydrogen atom, consisting of a proton (which, to a very good approximation, can be considered as immobile) and an electron. The energy of the system consists of the kinetic energy of the electron and the electron-proton Coulomb potential energy:

$$\varepsilon = \frac{\mathbf{p}^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0 r}. \quad (2.1)$$

We shall express the average energy in terms of Δr , where by definition $\Delta r^2 \equiv \sum \Delta x_i^2$ and Δx_i^2 ($i = 1, 2, 3$) is the variance of the Cartesian coordinate, x_i ($i = 1, 2, 3$), of r . Since $\langle x_i \rangle = 0$, $\Delta x_i^2 = \langle x_i^2 \rangle = \langle r^2 \rangle / 3^1$ and $\Delta r^2 = \langle r^2 \rangle$. The average of $\mathbf{p}^2$ equals to $3\langle p_i^2 \rangle = 3\Delta p_i^2 = 3\eta_2 \hbar^2 / 4\Delta x_i^2 =$

¹ This last equality assumes spherical symmetry.

$(9/4)\eta_2\hbar^2/\Delta r^2$, where $\eta_2 \geq 1$, because of the Heisenberg inequality. Hence, $\langle p^2/2m_e \rangle = (9/8)\eta_2\hbar^2/m_e\Delta r^2$.

Similarly, $\langle e^2/4\pi\epsilon_0 r \rangle = \eta_1 e^2/4\pi\epsilon_0\Delta r$, where η_1 is another numerical constant.²

$$\langle \varepsilon \rangle = \frac{9\eta_2}{8} \frac{\hbar^2}{m_e\Delta r^2} - \eta_1 \frac{e^2}{4\pi\epsilon_0\Delta r}. \quad (2.2)$$

Minimizing $\langle \varepsilon \rangle$ with respect to Δr we have

$$\frac{\partial \langle \varepsilon \rangle}{\partial \Delta r} = 0 \Rightarrow \frac{9\eta_2}{4} \frac{\hbar^2}{m_e\Delta r^3} = \eta_1 \frac{e^2}{4\pi\epsilon_0\Delta r^2} \Rightarrow \Delta r = \frac{9\eta_2}{4\eta_1} \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = \frac{9\eta_2}{4\eta_1} a_B. \quad (2.3)$$

Hence, a_B gives the order of magnitude of the radius of the hydrogen atom. Actually, the average of $1/r$ for the ground state of the hydrogen atom equals $1/a_B$ and the numerical factors η_1 , η_2 turn out to be equal to $\sqrt{3}$ and $4/3$ respectively. (See Problem 2.5s). Consequently,

$$\Delta r = \sqrt{3}a_B, \quad (2.4)$$

$$\langle p^2/2m \rangle = \hbar^2/2m_e a_B^2, \quad (2.5)$$

$$\langle -e^2/4\pi\epsilon_0 r \rangle = -e^2/4\pi\epsilon_0 a_B = -\hbar^2/m_e a_B^2, \quad (2.6)$$

and

$$\langle \varepsilon \rangle = -e^2/4\pi\epsilon_0 2a_B = -\hbar^2/2m_e a_B^2 = -\frac{1}{2}(e^2/4\pi\epsilon_0)(m_e/\hbar^2) = -13.6 \text{ eV}. \quad (2.7)$$

Equations (2.5)–(2.7) determine the energy scale of the outer electrons in atoms. Notice that the average kinetic energy equals minus the total energy or minus one half of the potential energy. This is consistent with the general virial theorem for potentials that are of the form A/r .

It is worthwhile to point out that the radius³ R_α of all atoms (see Table H.8) is of the order of a_B :

$$R_a = \bar{R}_a a_B, \quad 1 \lesssim \bar{R}_a \lesssim 5. \quad (2.8)$$

The smallest values of $\bar{R}_a$ appear at the upper right part of the periodic table, while the largest appear in the lower left part. Local minimum values of $\bar{R}_a$ are associated with atoms of completed shell (noble gases) or subshell, while local maximum values of $\bar{R}_a$ with atoms having one more electron beyond a completed shell (alkali metals) or subshell (see Fig. 2.1).

² The explicit calculation of η_1 and η_2 requires the knowledge of the wave function $\psi(\mathbf{r})$ (see (B.3), (B.5), (B.6), and (B.10) and Problem 2.5s).

³ The atomic radius is not a uniquely defined quantity and it cannot be measured accurately experimentally. The theoretical values given in Table H.8 are the ones where the most external occupied orbital has its maximum density. Consequently, there is nonzero electronic density beyond R_α , although it is gradually tailing off to zero.

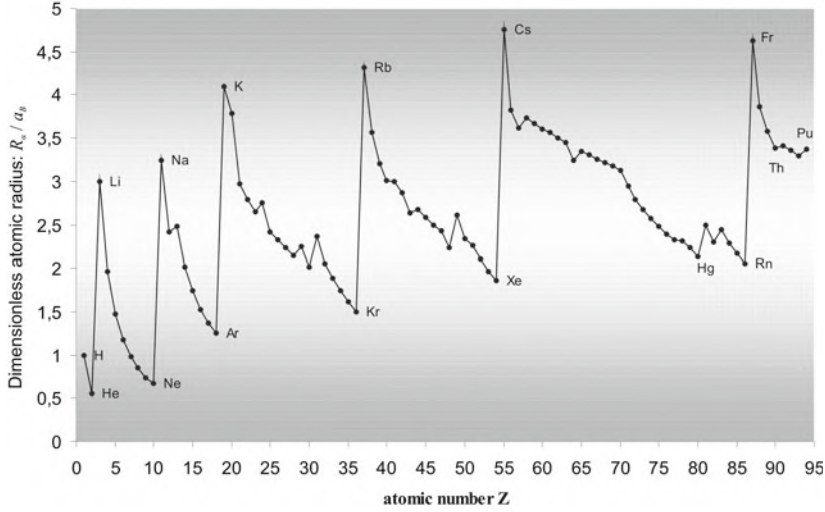


Fig. 2.1. Dimensionless radius of atoms, R_a , vs. their atomic number, Z . Local minima are associated with noble gases and local maxima with alkalis [2.1]

Similarly, the *first ionization potential*,⁴ I_α , of the atoms is of the order of $\hbar^2/2m_e a_B^2$ (see Table H.12)

$$I_\alpha = \eta'_\alpha \frac{\hbar^2}{2m_e a_B^2} = 13.6\eta'_\alpha \text{ eV}, \quad 0.28 \lesssim \eta'_\alpha \lesssim 1.8. \quad (2.9)$$

The largest values of η'_α correspond to the smallest values of R_α and vice versa as expected from (1.12). Compare Figs. 2.1 and 2.2.

Thus, the simple application of the uncertainty and minimization principles in combination with (1.5) reproduced the size and the energy scale of atoms, i.e., quantities of fundamental importance by themselves and necessary for understanding the properties of molecules and solids. Furthermore, the shell and subshell arrangement of electrons in atoms is a consequence of the discrete character of the energy spectrum and of Pauli's principle (see Table B.2, p. 706). The shell and subshell structure accounts for the gross features in Figs. 2.1 and 2.2.

2.2 Why do Atoms Come Together to Form Molecules and Solids?

Let us consider two neutral atoms at a distance d' ; let their typical excitation energy be $\delta\varepsilon$. When the distance d' is much larger than $R_{a1} + R_{a2}$ (but much smaller than $\lambda = 2\pi\hbar c/\delta\varepsilon \approx 1000 \text{ \AA}$), the two atoms attract each other

⁴ The first ionization potential is the *minimum* energy required for extracting an electron from a neutral atom in its ground state.

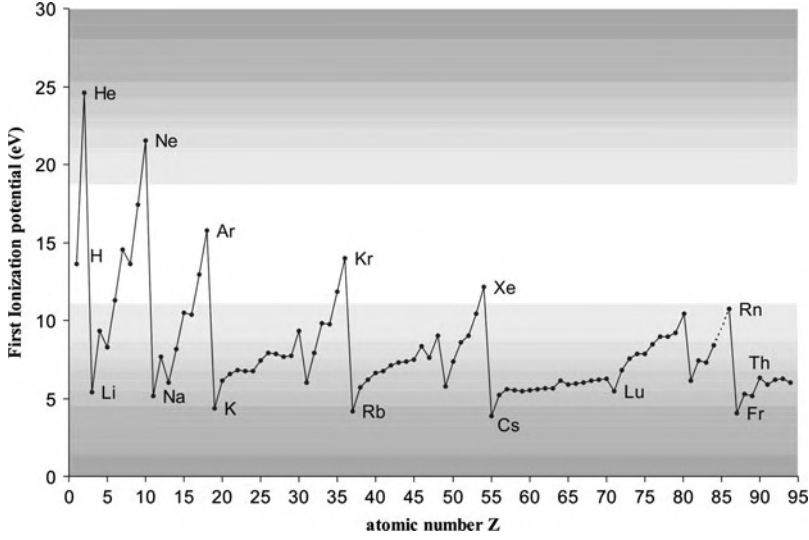


Fig. 2.2. First ionization potential vs. the atomic number Z (after [D2]). The local maxima are associated with completed shells, as in noble gases, and subshells. The local minima are associated mainly with alkalis and the boron column of the periodic table

through a potential of the form

$$\mathcal{V}(d') = -\frac{A}{d'^6}, \quad A > 0, \quad \lambda \gg d' \gg R_{a1} + R_{a2}. \quad (2.10)$$

This attraction is called *van der Waals* interaction⁵ and it is due to a rearrangement of the electron(s) *within each atom* as to take advantage of the presence of the other atom. As the atoms approach each other, this electronic rearrangement becomes more extensive and finally involves a partial transfer

⁵ The electrostatic interaction energy H_{12} of two neutral objects at a large distance d' apart is mainly through their dipole moments $\mathbf{p}_1$, $\mathbf{p}_2$ and it has the form, $H_{12} = p_1 p_2 f / 4\pi\epsilon_0 d'^3$, where $\mathbf{p}_1 = \sum q_i \mathbf{r}_{1i}$, $\mathbf{p}_2 = \sum q_i \mathbf{r}_{2i}$ and f depends on the angles between $\mathbf{p}_1$, $\mathbf{p}_2$, and $\mathbf{d}'$. However, for isolated atoms the average values of their dipole moments are zero, $\langle \mathbf{p}_1 \rangle = \langle \mathbf{p}_2 \rangle = 0$. Thus, the average interaction is coming from second-order in perturbation theory (see (B.54)):

$$\mathcal{V}(d') = \eta_1 \langle p_1^2 p_2^2 f^2 \rangle / (E_0 - E_1) (4\pi\epsilon_0)^2 d'^6.$$

where η_1 is of the order of one, E_0 is the sum of ground state energies of both atoms, E_1 is the sum of the excited states of both atoms: $E_0 - E_1 \simeq -(I_{\alpha 1} + I_{\alpha 2})$. The quantity, $\langle p_1^2 p_2^2 f^2 \rangle = \eta_2^4 \zeta_1 \zeta_2 e^4 R_{\alpha 1}^2 R_{\alpha 2}^2$, where η_2 is of the order of one, ζ_a ($a = 1, 2$) is the number of electrons in the outer occupied sub-shell, and R_a ($a = 1, 2$) is the atomic radius. Hence, $A \simeq \eta e^4 R_{\alpha 1}^2 R_{\alpha 2}^2 \zeta_1 \zeta_2 / (4\pi\epsilon_0)^2 (I_1 + I_2)$, where $\eta = \eta_1 \eta_2^4$. For hydrogen atoms, $\eta_2 \simeq \sqrt{3}$, $\eta_1 \simeq 0.72$, and $R_\alpha = a_B$, $I_\alpha = e^2 / 4\pi\epsilon_0 2a_B$

of electrons from one atom to the other.⁶ When the distance d' is forced to become considerably less than $R_{a1} + R_{a2}$, the electrons cannot follow the nuclei and cannot be squeezed in the space around and between them of volume proportional to d'^3 , because such a squeezing would cost a lot of kinetic energy (see (1.11)). As a result, with d' becoming smaller and smaller, there is less and less electronic charge between the two nuclei; hence, their Coulomb repulsion is not screened as effectively as before and the potential energy rises as $q'^2/4\pi\epsilon_0 d'$ where q'^2 is an increasing function of $1/d'$ tending to $Z_1 Z_2 e^2$ as d' becomes much smaller than the radius of the orbital of the innermost electrons, while all the other terms in the total energy remain finite.

Taking into account that in the limit $d' \gg R_{a1} + R_{a2}$, the total energy is negative and decreasing with decreasing d' (see (2.10)), while in the opposite limit, $d' \ll R_{a1} + R_{a2}$, it is positive and increasing with decreasing d' , we conclude that it must exhibit at least a negative minimum as a function of d' . In realistic cases, there is only one minimum; thus, the plot of the total energy of two neutral atoms versus the distance d' between their nuclei is as in Fig. 2.3. It is clear from Fig. 2.3 that the lowest energy will be achieved when $d' = d$ and, consequently, the stable equilibrium state of the two atoms (at $T = 0$ K) will be obtained when they form a molecule of bond length d .

We expect d to be of the order of the sum of the two atomic radii, $d \simeq R_{a1} + R_{a2}$. The argument goes as follows: As long as there is no appreciable overlap of the electronic densities of the two atoms, their interaction would be more or less of the form of (2.10), i.e., attractive. For the repulsion to start, there, must be appreciable overlap of the two electronic clouds. This happens when $d \simeq R_{a1} + R_{a2}$ (see the definition of the atomic radius in the

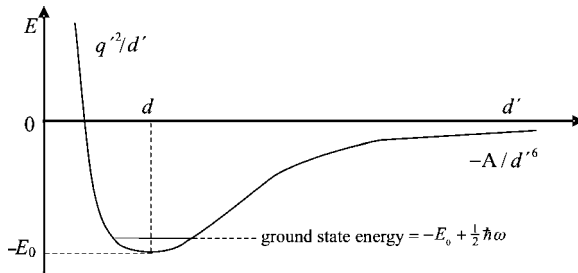


Fig. 2.3. Schematic plot of the variation of the total energy of two (neutral) atoms (assuming that the velocities of the nuclei are zero), versus the distance d' between the two nuclei. The ground state energy of the two neutral atoms when $d' = \infty$ is chosen as the zero of energy. Around the minimum the curve can be approximated by the following empirical formula: $E \simeq E_0 \varphi(x)$ where $x = (d' - d)/\ell$, $\varphi(x) = -\exp(-x)(1 + x + 0.05x^3)$ and ℓ is a length characterizing each molecule. The zero point motion of the nuclei increases the minimum energy by $\frac{1}{2} \hbar \omega$

⁶ Atoms of the noble gases are exceptions, because of their fully occupied outer shell.

footnote 3, p. 22). In Table H.8 it is shown that for most elemental solids consisting of atoms with partially filled orbitals, the relation $d \simeq 2R_a$ is valid. However, for the noble elements He, Ne, Ar, Kr, Xe because of their fully filled orbitals, d is six to two times larger than $2R_a$. This is so, because the atoms of the noble gases cannot tolerate any appreciable overlap, since it would lead to occupation of high lying excited orbitals; as a result the curve in Fig. 2.3 will turn upwards just when the overlap begins, i.e., at larger d , and the minimum will be much shallower. In contrast, atoms having empty orbitals of the same energy as the higher occupied ones can tolerate a substantial overlap without significant energy increase. Hence, their smaller $d(d \simeq 2R_a)$ and deeper minimum.

Solids can be viewed as super-gigantic molecules. Thus, the same arguments that produce the energy plot in Fig. 2.3 are applicable to solids as well. The role of d' can be played by the distance between nearest neighbors, d'_{nn} , or by the $\nu'^{1/3}$, where $\nu' \sim d'_{nn}{}^3$ is the *volume per atom* $\nu' \equiv V'/N_\alpha$. For metals, we can easily find how their total energy depends on ν' . Taking into account that the number of free electrons N_e equals ζN_a , where ζ is the valence and N_a the number of atoms, we have for the minimum free-electron kinetic energy per atom according to (1.11):

$$\frac{E_{K,\min}}{N_\alpha} = 2.87\zeta \frac{\hbar^2}{m_e} \left(\frac{\zeta N_\alpha}{V'} \right)^{2/3} = 2.87\zeta^{5/3} \frac{\hbar^2}{m_e} \frac{1}{\nu'^{2/3}}. \quad (2.11)$$

The potential energy, according to (1.5) is proportional to $1/d'_{nn} \sim \nu'^{-1/3}$. Hence, the total energy per atom, $\varepsilon_t \equiv E_t/N_\alpha$, for a metal around the equilibrium value of ν' (ignoring the kinetic energy of the ions) is of the form

$$\varepsilon_t \equiv \frac{E_t}{N_\alpha} = \frac{A'}{\nu'^{2/3}} - \frac{C}{\nu'^{1/3}}, \quad \nu' \approx \nu, \quad (2.12)$$

where A' , C are constants to be discussed later. In Fig. 2.4 we plot ε_t vs. the volume per atom ν' . The equilibrium value ν of ν' (under conditions $P = 0$ and $T = 0$ K) is determined by minimizing ε_t with respect to ν' :

$$-\frac{2}{3\nu} \frac{A'}{\nu'^{2/3}} + \frac{1}{3\nu} \frac{C}{\nu'^{1/3}} = 0 \Rightarrow \nu^{1/3} = \frac{2A'}{C}. \quad (2.13)$$

Taking into account that the bulk modulus⁷ B at $T = 0$ K is given by $V'(\partial^2 E_t / \partial V'^2)_{V'=V} = \nu'(\partial^2 \varepsilon_t / \partial \nu'^2)_{\nu'=\nu}$, we have

$$B = \frac{5}{3} \frac{2}{3\nu} \frac{A'}{\nu'^{2/3}} - \frac{4}{3} \frac{1}{3\nu} \frac{C}{\nu'^{1/4}} = \frac{2}{9} \frac{A'}{\nu^{5/3}} = \frac{2}{9\nu} \frac{E_{K,\min}}{N_\alpha} = \frac{2\langle \varepsilon_\kappa \rangle}{9\nu}. \quad (2.14)$$

⁷ The bulk modulus B is the inverse of the compressibility. B is defined as the ratio of a pressure change, ΔP , (necessary to produce a small change $|\Delta V|$ in the volume) to the relative change $|\Delta V|/V$, i.e., $B \equiv -V(\partial P / \partial V)$. For $T = 0$ K, $P = -\partial U / \partial V$ and $B = V\partial^2 U / \partial V^2$ (See also (C.10) and (C.11)). [In thermodynamics instead of E_t we use quite often the symbol U for the average total energy].

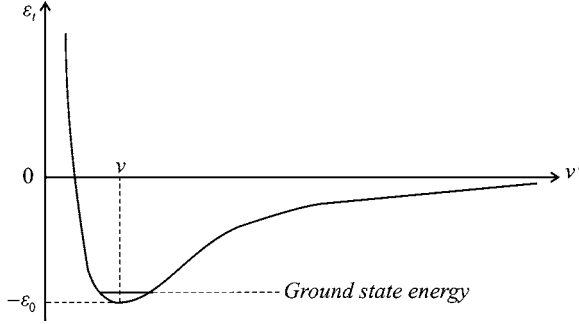


Fig. 2.4. Schematic plot of the total energy per atom, ε_t , of a solid (excluding the kinetic energy of the ions) versus the volume per atom $\nu' \equiv V'/N_a$. The equilibrium value of ν' is ν , which corresponds to the minimum of ε_t . By adding the zero point energy of the ions we find the ground state energy. The curve around the minimum can be described either by (2.12), if it is a metal, or, more accurately, by $\varepsilon_t = \varepsilon_0 \varphi(x)$, where $x = (\nu'^{1/3} - \nu^{1/3})/\ell$, ℓ is a length characterizing each solid, and $\varphi(x)$ is of identical form as the one given in Fig. 2.3

To obtain (2.14), we have used (2.12) and (2.13). We point out that $E_{K,\min}/N_\alpha$ in (2.14) is the equilibrium kinetic energy of the free electrons per atom at $T = 0$ K. Thus, $B = 0.64 \hbar^2 \zeta^{5/3} / m_e \nu^{5/3}$.

The conclusion of these considerations is that atoms form molecules and solids, because by doing so they actually lower their total energy.

2.3 Ionic Motion: Small Oscillations

So far we have omitted the kinetic energy of the ions both in molecules and in solids. We shall examine first the ionic motion in the case of a diatomic molecule and in particular the *relative* ionic motion along the axis⁸ of the molecule. The kinetic energy of such a motion is of the form $p^2/2\mu$, where p is the component of the relative ionic momentum along the axis of the diatomic molecule and μ is the reduced mass of the two ions, $\mu = m_1 m_2 / (m_1 + m_2)$ (see Problems 2.6s and 2.7). The potential energy is the one shown in Fig. 2.3;

⁸ The other motions of the two ions are the following: Three translational motions of the whole molecule as a rigid object along the three mutually perpendicular x, y, z axes. Such motions produce a continuous spectrum starting from zero, because the available volume V to the molecule is macroscopic, i.e. practically infinite (see (1.12)). There are also two rotational motions of the diatomic molecule as a whole around two axes passing through the center of mass of the molecule and perpendicular to each other as well as to the axis of the molecule. These rotational motions (of classical energy given by $L^2/2I$, where L is the total angular momentum, I is the moment of inertia, $I = \mu d^2$, and μ is the reduced mass of the two nuclei ($\mu = m_1 m_2 / (m_1 + m_2)$)) produce a spectrum of the form $\hbar^2 F(F+1)/2I$ where $F = 0, 1, 2 \dots$

for small values of $x \equiv d' - d$, it can be expanded up to second order in x , and it will have the form $\mathcal{V}(x) = -E_0 + \frac{1}{2}\kappa x^2$, where $\kappa = (\partial^2 E / \partial d'^2)_{d'=d}$. Thus, the total energy for the relative ionic motion along the axis of the diatomic molecule has been reduced to that of an one-dimensional harmonic oscillation: $E = -E_0 + (p^2/2\mu) + (\kappa x^2/2)$. According to Heisenberg's principle, the minimum value of the average, $\langle p^2 \rangle$, of the square of the momentum, $p = \mu \dot{x}$, is given by⁹ $\hbar^2/4 \Delta x^2$, where $\Delta x^2 = \langle x^2 \rangle$, since $\langle x \rangle = 0$. Hence, the total average energy, $\langle E \rangle$, of the ionic vibration is

$$\langle E \rangle = \frac{1}{8} \frac{\hbar^2}{\mu \Delta x^2} + \frac{1}{2} \kappa \Delta x^2 - E_0. \quad (2.15)$$

By minimizing $\langle E \rangle$ with respect to Δx we find

$$\frac{\partial \langle E \rangle}{\partial \Delta x} = 0 \Rightarrow \kappa \Delta x = \frac{1}{4} \frac{\hbar^2}{\mu \Delta x^3}, \quad \Delta x^2 = \frac{1}{2} \frac{\hbar}{\sqrt{\kappa} \mu} = \frac{1}{2} \frac{\hbar}{\mu \omega}, \quad \omega = \sqrt{\frac{\kappa}{\mu}}, \quad (2.16)$$

$$E_G \equiv -E_0 + \frac{1}{2} \hbar \omega. \quad (2.17)$$

Thus, the ground state energy is higher than the minimum, $-E_0$, of the potential energy by an amount $\frac{1}{2} \hbar \omega$. Similarly the first excited state is above the ground state by an amount (according to (1.12)) equal to $\eta \hbar^2 / \mu \Delta x^2 = 2 \eta \hbar \omega$. It turns out that in the present case the numerical factor $\eta = \frac{1}{2}$ for all consecutive level separations. The fluctuation, Δx , of the bond length is equal to $\sqrt{\hbar/2\mu\omega}$. For a particle moving in a 1-D attractive potential of the form, $\pm|x|^\beta$, one can argue that the eigenenergy of the n th excited state is of the form $E(n) \sim n^a$, where $a = \left(\frac{1}{2} + \frac{1}{\beta}\right)^{-1}$. Thus for $\beta = 2$, $a = 1$ (see Problem 2.8s)

To summarize: If one manages to calculate the curve shown in Fig. 2.3, one can obtain the bond length, d ; the dissociations energy, $E_0 - \frac{1}{2} \hbar \omega$, i.e., the minimum energy required to split the molecule into two independent neutral atoms; the vibration frequency, $\omega = \sqrt{\kappa/\mu}$; the quantum fluctuation $\sqrt{\hbar/2\mu\omega}$ of the bond length d ; and the moment of inertia of the molecule, $I = \mu d^2$. Furthermore, the rotational spectrum, $\hbar^2 F(F+1)/2I$ ($F = 0, 1, 2, \dots$) and the vibrational spectrum $\hbar \omega (n + \frac{1}{2})$ ($n = 0, 1, 2, \dots$) of the molecule have also been determined.

This approach for the ionic vibration of the diatomic molecule can be generalized to polyatomic molecules and solids, since in these more complicated systems, ions still undergo small *coupled* oscillations around their equilibrium positions. The small amplitude of these oscillations allows us to successfully approximate the restoring force on each atom as a *linear* combination of their displacements from their equilibrium positions (this is the so-called *harmonic approximation*). Under those circumstances, there are special solutions, called *normal modes* (of oscillations) or *eigenoscillations*, or *eigenvibrations*,

⁹ For the ground state of the harmonic oscillation, the Heisenberg relation (1.8) is reduced to an equality, $2\Delta p_x \Delta x = \hbar$.

or *eigenmodes*, where all atoms or ions oscillate with the same frequency ω_ν , but, generally, with different amplitudes and phases; the index ν characterizes the various normal modes.¹⁰ Their total number equals the number of degrees of freedom minus 6 ($\nu = 1, \dots, 3N_a - 6$, where N_a is the total number of atoms or ions).¹¹ By introducing the so-called collective displacement, x_ν , associated with the normal mode¹² ν , the corresponding kinetic and potential energies of each normal mode are of the form $\frac{1}{2}m_\nu \dot{x}_\nu^2$ and $\frac{1}{2}\kappa_\nu x_\nu^2$ respectively, where m_ν are effective masses and κ_ν effective spring constants. Thus, the problem of small harmonic coupled oscillations has been reduced to that of $3N_a - 6$ independent one-dimensional harmonic oscillators; each one of them is in one to one correspondence with each one of the $3N_a - 6$ normal modes.

The conclusion of this subsection is that, through a simple application of the principles exposed in Sects. 1.2 and 1.4.1, we managed to obtain the basic features of the ionic (or atomic) motions in molecules and solids by reducing the problem to that of independent one-dimensional harmonic oscillators. Each one of these oscillators is characterized by its eigenfrequency, ω_ν , and its mass m_ν . For a nonperiodic solid, it is practically impossible to know the numerical value of each individual eigenfrequency ω_ν or any other characteristic of each eigenmode ν . Thus, we restrict ourselves to gross features, such as how many eigenvibrations have eigenfrequencies ω_ν 's in each frequency interval $[\omega, \omega + \delta\omega]$.

2.4 Why do the Specific Heats of Solids go to Zero as $T \rightarrow 0$ K?

It is well known that, according to classical physics, the average energy of an one-dimensional harmonic oscillator in equilibrium with an environment of temperature T is equal to $k_B T$, where k_B is Boltzmann's constant.

¹⁰ If a solid is approximated by a uniform and isotropic medium, *the normal modes are nothing else than acoustic waves*, characterized by their wavevector $\mathbf{q}$, and the polarization index $s = 1, 2, 3$, where $s = 1$ corresponds to longitudinal wave and $s = 2, 3$ correspond to the two independent transverse waves. In this case the index ν coincides with the pair $\mathbf{q}, s$. (See appendix E, sect. E.4)

¹¹ The three in front of N_a is there because of the 3-dimensional character of motion; the minus 6 comes because 3 degrees of freedom are associated with displacements of the solid as a rigid body and another 3 with its rotations as a rigid body.

¹² The quantity x_ν is in general a specific (for each ν) linear combination of the atomic displacements $\mathbf{u}_n$ ($n = 1, \dots, N_a$) of the atoms from their equilibrium positions. A simple but very illuminating one-dimensional model, namely that of a chain of N coupled pendulums, is shown in Fig. 6.1 (p. 150). This model will be studied in Ch. 6 and the relations between the collective displacements x_ν associated with each normal mode and the displacement u_n of each mass located at site n will be explicitly displayed. It will also be demonstrated there that *the normal modes are waves propagating along the chain*.

Furthermore, again according to classical physics, the average kinetic energy of a free particle moving in a three-dimensional space and in equilibrium with a thermal bath of temperature T is equal to $\frac{3}{2}k_B T$. Thus, if a solid is considered to consist of N_α ions¹³ and $N_e = \zeta N_\alpha$ electrons, we would expect (if classical physics were valid, and if ions did not have internal degrees of freedom) the total average energy at temperature T to be equal to $3N_\alpha k_B T + \frac{3}{2}N_e k_B T$. Hence, the expected (according to classical physics) specific heat must be equal to $3N_\alpha k_B + \frac{3}{2}N_e k_B = (3 + \frac{3}{2}\zeta) N_\alpha k_B$. Actually it is expected to be higher than that because of the ionic internal degrees of freedom. For a mole the number N_α equals to Avogadro's number, $N_a \approx 6 \times 10^{23}$, and $N_a k_B = R = 8.3 \text{ Jmol}^{-1} \text{ K}^{-1}$; R is the gas constant. Thus, the specific heat, C , of one mol of any solid substance is expected to be larger than $24.94 (1 + \frac{1}{2}\zeta) \text{ JK}^{-1}$. As can be seen in Table H.14 the overwhelming majority of elemental solids at $T = 25^\circ \text{C}$ have specific heats in the range between 23 and $30 \text{ Jmol}^{-1} \text{ K}^{-1}$ indicating that the electrons have a much smaller than the expected contribution. For Be, B, and diamond the numbers are 16.44, 11.09, $8.52 \text{ Jmol}^{-1} \text{ K}^{-1}$ respectively in clear disagreement with the classical theoretical results. This disagreement becomes very dramatic at very low temperatures (e.g., the specific heat of copper at $T \approx 3 \text{ K}$ is about $0.0012 \text{ Jmol}^{-1} \text{ K}^{-1}$ instead of at least $37 \text{ Jmol}^{-1} \text{ K}^{-1}$ predicted by classical physics). Let us try to explain these serious discrepancies by resorting to the basic principles of Quantum Mechanics:

1. *Why do free electrons in metals contribute much less than $\frac{3}{2}N_e k_B$?*

The answer comes naturally from Pauli's principle and the fact that $k_B T \ll E_F$ ($E_F \simeq 4.78 \hbar^2 N_e^{2/3} / m_e V^{2/3} \simeq 10 \text{ eV}$ (see (1.11) and the footnote 18, p. 12, Ch. 1), while $k_B T \simeq (T \text{ (in K)} / 11600) \text{ eV} \ll E_F$). Under those circumstances, the only electrons that can accept an energy of the order of $\frac{3}{2}k_B T$ are those occupying levels below but very close to E_F , i.e., roughly speaking, in the range between $E_F - \frac{3}{2}k_B T$ and E_F . The rest of the free electrons, if they were to absorb energy $\frac{3}{2}k_B T$, would end up at an already fully occupied level and consequently they would violate Pauli's principle. The conclusion is that *only the N'_e electrons occupying levels ε_i in the range $E_F - \frac{3}{2}k_B T \lesssim \varepsilon_i \lesssim E_F$ will be capable of being thermally excited, while the rest, $N_e - N'_e$, are completely inert*. Hence, the electronic specific heat will be equal to $\frac{3}{2}N'_e k_B$. To estimate the value of the number N'_e , we need to multiply the number of levels per unit energy at E_F , $\rho(E_F) \equiv \rho_F$, by the active energy range, $\frac{3}{2}k_B T$, and by 2, because each level accepts two electrons (one with spin up and one with spin down).

¹³ It is reminded that the coupled harmonic vibrations of N_a ions are equivalent to $3N_a - 6 \approx 3N_a$ one-dimensional uncoupled harmonic oscillators of frequencies ω_ν ($\nu = 1, 2, \dots, 3N_a - 6$).

Hence, $N'_e \approx 3\rho_F k_B T$ and

$$C_{Ve} \approx \frac{9}{2} \rho_F k_B^2 T.$$

A detailed calculation to be performed in a later chapter gives a similar formula but with a numerical factor $2\pi^2/3 \simeq 6.58$ instead of 4.5.

2. *Why is the ionic contribution to the specific heat at low temperatures much lower than $3N_a k_B$?*

The answer stems naturally from the discreteness of the vibrational excitation spectrum, i.e., the third basic principle of QM presented in Sect. 1.4.3. All we have to do is to compare $k_B T$ with the various ionic excitation energies, $\hbar\omega_\nu$ ($\nu = 1, \dots, 3N_a$). *Those eigenoscillations for which $\hbar\omega_\nu \gg k_B T$ cannot be excited thermally and are “frozen” in their ground state. Only those for which $\hbar\omega_\nu \lesssim k_B T$ contribute to the specific heat; let N'' be their number;¹⁴ then the ionic specific heat would be equal to $3N'' k_B$.* Obviously, because of the inequality, $\hbar\omega_\nu \lesssim k_B T$, $N'' \rightarrow 0$ as $T \rightarrow 0$ K and $N'' \rightarrow 3N_a$ as $k_B T$ exceeds the maximum value of $\hbar\omega_\nu$.

2.5 When is Classical Mechanics Adequate?

It is by now clear that only QM provides the framework for understanding both qualitatively and quantitatively the behavior of solids (and all material structures for that matter). Nevertheless, there are limiting cases where the easier-to-handle Classical Mechanics gives adequate results. For example, we have shown that the ionic specific heat is in agreement with the classical result if $k_B T$ is considerably larger than the maximum $\hbar\omega_\nu$; similarly, the free-electron contribution to the specific heat would coincide with the classical result, if the inequality $k_B T \gg E_F$ were possible.

These two examples are representative of the general case: There are two types of novel energy scales which are introduced by QM: The first is related to the energy separation, $\delta\varepsilon_0$, between the ground and the first excited level (the quantities $\hbar\omega_\nu$ constitute an example of the first type); the second, is Pauli-based, and has been denoted by $\langle\varepsilon_k\rangle$ or E_F in Sect. 1.4.2. *For the classical thermodynamic results to be valid, $k_B T$ must be much larger than both types of quantum energy scales:*

$$k_B T \gg \delta\varepsilon_0, E_F.$$

¹⁴ To estimate the value of N'' we need to know the number of *eigenmodes* per unit frequency, $\phi_{ph}(\omega)$, ($\phi_{ph}(\omega)d\omega$ gives the number of eigenmodes with ω_ν in the interval $(\omega, \omega + d\omega)$). Then $N'' = \int_0^{\eta k_B T} \phi_{ph}(\omega)d\omega$, where η is a numerical factor of the order of one. At low frequencies, as we shall see later, $\phi_{ph}(\omega)$ is proportional to ω^2 . Hence, at low temperatures, N'' and consequently the ionic specific heat C_i are proportional to T^3 .

2.6 Estimating Magnitudes Through Dimensional Analysis (see (1.16))

2.6.1 Atomic Radius, R_α

Let us start by eliminating parameters that seem irrelevant to the size of atoms: First, it is rather obvious that the nuclear mass¹⁵ does not play any significant role in determining the atomic radius,¹⁵ because it is so much larger than m_e . Similarly the temperature and the pressure do not influence the atomic radius unless their values are extremely high (comparable to the values of their units in the atomic system: $P_0 = 294 \times 10^6$ bar and $T_0 = 3.16 \times 10^5$ K). Hence, according to the general equation (1.16), we have

$$\bar{R}_a \equiv \frac{R_a}{a_B} = f_1(Z), \quad (2.18)$$

which coincides with (2.8). The function, $f_1(Z)$, as shown in Fig. 2.1, has ups and downs (due to the shell and subshell structure of atoms), but it is more or less confined between 1 and 5 with an average value over the periodic table around 2.6.

2.6.2 Volume per Atom, $\nu_a \equiv V/N_a$, in Solids

Atoms in solids are more or less close-packed; as a result, we can conclude that the volume per atom, ν_a , is about 50% more than the atomic volume, $(4\pi/3)R_a^3$; this extra 50% is roughly the empty space between atoms considered as spheres touching each other.¹⁶ Hence,

$$\bar{\nu}_a \equiv \frac{\nu_a}{a_B^3} \simeq 1.5 \frac{4\pi}{3} \bar{R}_a^3, \quad (2.19)$$

which means (using our previous estimate for $\bar{R}_a$) that the volume per atom in various solids is in the range roughly between 1 and $110 \text{ \AA}^3$ with a typical value of about $15 \text{ \AA}^3$. Actually, the volume per atom for elemental solids is in the range between 4.4 and $120 \text{ \AA}^3$ ($1 \text{ \AA} = 10^{-10} \text{ m}$). Usually, instead of ν_a we are using the radius r_a of a fictitious sphere of volume, ν_a :

$$\frac{4\pi}{3} r_a^3 \equiv \nu_a. \quad (2.20)$$

Combining (2.19) and (2.20) we find a rough relation¹⁷ between r_a (or $\bar{r}_a \equiv r_a/a_B$) and R_a (or $\bar{R}_a$): $\bar{r}_a = 1.14 \bar{R}_a$, which means that the average value

¹⁵ What actually enters in the size of the simplest atom is the reduced mass, $\mu = m_e m_p / (m_e + m_p) \simeq m_e$, where m_p is the proton mass.

¹⁶ Close-packed spheres of equal size fill up no more than 74% of space. (See tables 3.1 and 3.2)

¹⁷ For solids of the noble gas elements $\bar{r}_a$ is much larger than $\bar{R}_a$ (see section 2.2).

(over the elements of the periodic table) of $\bar{r}_\alpha$ is about 3. Related with the volume per atom is the concentration of atoms in solids, n_a , i.e., the number of atoms per unit volume:

$$n_a \equiv \frac{N_a}{V} = \frac{1}{\nu_a} = \frac{3}{4\pi} \frac{1}{\bar{r}_a^3} = \frac{0.239}{\bar{r}_a^3} \frac{1}{a_B^3} \simeq \frac{161}{\bar{r}_a^3} \times 10^{22} \text{ cm}^{-3}. \quad (2.21)$$

Thus, a typical value of n_a is of the order of $6 \times 10^{22} \text{ cm}^{-3}$ corresponding to the value of $\bar{r}_a = 3$.

2.6.3 Mass Density, ρ_M

The mass density is by definition the ratio of mass to volume:

$$\rho_M \equiv \frac{M}{V} = \frac{m_\alpha N_\alpha}{V} = A_w m_u n_\alpha, \quad (2.22)$$

where the atomic mass, m_α , is by the definition of the atomic weight, A_w , the product of the unit of mass, m_u and A_w ; the latter almost coincides with the mass number A (if there is only one stable isotope¹⁸). Taking into account (2.21) and that the product $N_A m_u = 1 \text{ g}$, where $N_A = 6.022 \times 10^{23}$ is Avogadro's number, we have

$$\rho_M = A_w \frac{n_\alpha}{N_A} \times 1 \text{ g} = \frac{2.675 A_w}{\bar{r}_\alpha^3} \text{ g/cm}^3. \quad (2.23)$$

Taking as typical values $A_w \approx 50$ and $\bar{r}_\alpha \approx 3$, we obtain $\rho_M \approx 5 \text{ g/cm}^3$ as the typical value for the density of solids (The average density of Earth is 5.52 g/cm^3). Actually, the density of elemental solids is in the range between 0.53 g/cm^3 (for Li) and 22.5 g/cm^3 (for Ir) with the exception of H and He. Equation (2.23) is very important, because it allows us to obtain the value of $\bar{r}_\alpha$, and then the values of n_α , ν_α for each elemental solid (see Table H.7) from the values of the density and the atomic weight given in Table H.5.

2.6.4 Cohesive Energy, U_c

The cohesive energy, U_c , of a solid is defined as the minimum energy required to separate it into its constituent (neutral) atoms (or molecules, if we are dealing with a molecular solid) under conditions of temperature $T \rightarrow 0 \text{ K}$ and pressure $P = 1 \text{ atm}$.

Hence, the cohesive energy per atom, $u_c \equiv U_c/N_\alpha$, is the difference between the horizontal, $\varepsilon_t = 0$, axis and the ground state energy in Fig. 2.4. Its value for elemental solids ranges from about 1 to 8.9 eV/atom (for tungsten). Again,

¹⁸ Otherwise atomic weight is a weighted average over all stable isotopes having the same Z .

the solids of the noble gas elements are exceptions, due to their fully occupied outer shell ($u_c \approx 0.02 \text{ eV/atom}$ for Ne, while for Xe it is 0.16 eV/atom).

Now, using the general formula (1.16) and taking into account that (a) the atomic mass, m_α , plays a very minor role for the same reasons as in Sect. 2.6.1; (b) the temperature, by the definition of u_c , is zero, and (c) the pressure of 1 atm is negligible in comparison to P_K or $|P_P|$ we have

$$u_c = \frac{\hbar^2}{m_e a_B^2} f_2(Z), \quad (2.24)$$

where the function $f_2(Z)$ has ups and downs (as the function $f_1(Z)$ in (2.9)). Roughly speaking, one would expect as a result of (1.9), that $f_2(Z) \sim 1/\bar{r}_a^2$. Thus,

$$u_c \approx \text{const.} \times \frac{\hbar^2}{m_e a_B^2} \frac{1}{\bar{r}_a^2} = \text{const.} \times \frac{\hbar^2}{m_e r_a^2}, \quad \text{const.} \approx 1, \quad (2.25)$$

which could be considered as coming from the unit of energy $\hbar^2/m_e a_B^2$ by the substitution of a_B by the actual radius per atom,

$$a_B \rightarrow r_a = \bar{r}_a a_B. \quad (2.26)$$

We obtain reasonable estimates for u_c , if we choose the “constant” in (2.25) equal to one. The readers may test how reasonable these estimates are by comparing them with experimental values for various solids. Examples are shown in the table below

Solids	<i>Na</i>	<i>Cs</i>	<i>Mg</i>	<i>Ba</i>	<i>Al</i>	<i>Au</i>
$\bar{r}_\alpha$ (exp.) ¹⁹	3.93	5.62	3.34	4.67	2.99	3.01
u_c (eV) (exp.)	1.11	0.804	1.51	1.90	3.39	3.81
u_c (eV) (2.25)	1.76	0.86	2.44	1.25	3.04	3.0

2.6.5 Bulk Modulus, B , and Shear Modulus, μ_s

The bulk modulus, already introduced in Sect. 2.2, is a measure of how difficult it is to compress uniformly a solid. It is defined as the hydrostatic pressure, δP , you need to apply in order to produce a relative change, $-\delta V/V$, in volume, over this relative change:

$$B \equiv -V \left(\frac{\partial P}{\partial V} \right). \quad (2.27)$$

The derivative is usually taken either under constant temperature (and B is written then as B_T) or under constant entropy (and then B is denoted by B_s).

¹⁹ Using (2.23) and experimental values for A_w and ρ_M .

One can prove that $B_s = (C_P/C_V) B_T$ (see (C.24)). Notice that B has the dimensions of pressure. To estimate the values of B for various solids, we are going to employ again (1.16) and the substitution (2.26). For similar reasons as before we expect that the role of atomic mass, and ordinary temperature and pressure not to be significant. Then

$$B \simeq \text{const.} \times \frac{\hbar^2}{m_e a_B^5} \frac{1}{\bar{r}_a^5} = \text{const.} \times \frac{\hbar^2}{m_e r_a^5}. \quad (2.28)$$

The “constant” turns out to be $0.059\zeta^{5/3}$, if we combine (2.14) and (2.11). A simpler, and usually better, choice is to take it as 0.6, and then, we find

$$B \simeq \frac{177}{\bar{r}_\alpha^5} \text{ Mbar} = \frac{1.77 \times 10^{13}}{\bar{r}_\alpha^5} \text{ N/m}^2. \quad (2.29)$$

The readers could test the effectiveness of (2.29) in estimating the values of B for various solids by choosing his own examples as in the table below.

Solids	<i>Na</i>	<i>Cs</i>	<i>Mg</i>	<i>Ba</i>	<i>Al</i>	<i>Fe</i>
$\bar{r}_\alpha(\text{exp.})$	3.93	5.62	3.34	4.67	2.99	2.7
$B(\text{exp.})$ (Mbar)	0.068	0.020	0.354	0.103	0.722	1.683
$B((2.29))$ (Mbar)	0.189	0.0316	0.426	0.080	0.74	1.23

Besides the bulk modulus, the elastic properties of isotropic solids are characterized by the *shear modulus*, μ_s , which measures the degree of resistance to stresses that tend to change the shape but not the volume of solids (see (E.4) and (E.12)). The shear modulus for most solids is comparable to but smaller than B . For hard solids μ_s could be almost equal to or even larger than B (but not larger than 1.5 times B). For softer solids μ_s could be one order of magnitude or even smaller than B (e.g., for lead $\mu_s/B = 0.122$). Typical values of the ratio μ_s/B for most metals are in the range 0.3–0.6. It is worthwhile to point out that μ_s for liquids is zero (since liquids do not present any resistance to changes in their shape).

2.6.6 Sound Velocities in Solids, c_0 , c_ℓ , c_t

According to formula (1.16), the sound velocity in solids is given by an expression of the form:

$$c_0 = \frac{\hbar}{m_e a_B} f_3 \left(Z, \frac{m_a}{m_e}, \frac{T}{T_0}, \frac{P}{P_0} \right), \quad (2.30)$$

where $\hbar/m_e a_B (= c/137 = 2188 \text{ km/s})$ is the unit of velocity in the atomic system of units. Employing the same arguments as before, we expect the

dependence on T/T_0 and P/P_0 to be insignificant for the usual range of values of T and P . On the contrary, the dependence on m_α is expected to be important, since the sound waves propagate in a solid through *migrating small oscillations of individual atoms* (see Sect 2.3 and Fig. 6.1 in p. 150). At this point we recall that the velocity of a wave is equal to the frequency times the wavelength and that the angular frequency of an harmonic oscillation is given by $\sqrt{\kappa/m_\alpha}$, i.e., it is proportional to the inverse square root of the atomic mass. Hence, taking into account the reasoning above, we expect $f_3(m_a/m_e)$ to be proportional to $\sqrt{m_e/m_a}$; then, implementing also the replacement $\alpha_B \rightarrow \bar{r}_\alpha \alpha_B = r_\alpha$, (2.30) becomes

$$c_0 = \text{const.} \times \frac{\hbar}{m_e a_B \bar{r}_a} \sqrt{\frac{m_e}{m_a}}. \quad (2.31)$$

Choosing the “constant” to be equal to 1.6, taking into account that $m_\alpha = A_w m_u$, and introducing the numerical values of the universal constants, we obtain the following estimate

$$c_0 \approx \frac{82}{\bar{r}_a \sqrt{A_w}} \text{ km/s}, \quad (2.32)$$

which for $\bar{r}_\alpha = 3$ and $A_w = 50$ gives $c_0 \simeq 3.9 \text{ km/s}$, a typical value for solids. Actually, in isotropic solids there are two sound velocities: the first, c_ℓ , corresponds to the so-called *longitudinal waves* (where the direction of motion of each atom is along the direction of propagation) and the second, c_t , corresponds to the two independent *transverse or shear waves* (where the direction of motion of each atom is perpendicular to the direction of propagation). As shown in Appendix E, c_ℓ and c_t are given by the following formulae

$$c_\ell = c_0 \sqrt{1 + \frac{4}{3}x}, \quad (2.33)$$

$$c_t = c_0 \sqrt{x}, \quad (2.34)$$

where

$$c_0 = \sqrt{B/\rho_M}, \quad (2.35)$$

$$x \equiv \mu_s/B. \quad (2.36)$$

Notice that, by replacing in (2.35), ρ_M and B from (2.23) and (2.29) respectively, we obtain again (2.31) with the “const.” close to 1. It is worthwhile to point out that (2.31) was obtained from dimensional analysis and elementary understanding of the mechanism of sound propagation in solids, without any reference to formula (2.35). To check how well (2.32) is doing numerically, we can compare its estimates with the experimental value of c_0 (obtained by measuring c_ℓ , c_t and using (2.33) and (2.34)), for the representative solids shown in the following table.

Solids	<i>Pb</i>	<i>Be</i>	<i>Mg</i>	<i>Fe</i>	<i>Al</i>
c_ℓ (km/s)(exp.)	2.16	13.11	5.77	5.95	6.79
c_t (km/s)(exp.)	0.7	9.08	3.05	3.24	3.23
x (exp.)	0.122	1.33	0.445	0.49	0.325
c_0 (km/s)(exp.)	2.00	7.88	4.57	4.63	5.67
c_0 (km/s) Eq. (2.32)	1.57	11.62	4.98	4.11	5.28

2.6.7 Maximum Angular Frequency of Atomic Vibrations in Solids, $\omega_{\max}$

We have already mentioned in Sect. 2.3 that the coupled small oscillations of atoms (or ions) in solids can be reduced to $3N_\alpha - 6 \simeq 3N_\alpha$ independent one-dimensional harmonic oscillations of eigenfrequencies ω_ν ($\nu = 1, \dots, 3N_\alpha$); the latter have values ranging from zero to a maximum frequency $\omega_{\max}$. Employing the same arguments as in Sect. 2.6.6 (i.e., the $1/\sqrt{m_\alpha}$ dependence, and the negligible role of T and P) and implementing the by now standard substitution $a_B \rightarrow \bar{r}_\alpha a_B$ we obtain the following estimate for $\omega_{\max}$

$$\omega_{\max} = \text{const.} \times \frac{\hbar}{m_e a_B^2} \frac{1}{\bar{r}_\alpha^2} \sqrt{\frac{m_e}{m_\alpha}}, \quad (2.37)$$

$$\omega_{\max} \approx \frac{300}{\bar{r}^2 \sqrt{A_w}} 10^{13} \text{ rad/s}. \quad (2.38)$$

In (2.38) we assumed that the “const.” is about π . For $\bar{r}_\alpha = 3$ and $A_w = 50$, we obtain $\omega_{\max} \simeq 4.7 \times 10^{13} \text{ rad/s}$ or $\hbar\omega_{\max} \simeq 31 \text{ meV}$, which is typical of solids.

2.6.8 Melting Temperature, T_m

At the melting temperature by definition the *solid state* and the *liquid state* coexist in equilibrium. This, according to the general principle of minimum Gibbs free energy at equilibrium, means that the solid state free energy, G_s , and the liquid state free energy, G_ℓ , are equal at $T = T_m$, because if they were not equal, $G_s \neq G_\ell$, the system would be in the lower G state between the two and consequently there would be no coexistence. The equality $G_s = G_\ell$ implies that

$$U_s + PV_s - T_m S_s = U_\ell + PV_\ell - T_m S_\ell. \quad (2.39)$$

Since the difference $V_\ell - V_s$ is in general very small we can omit the terms PV_s and PV_ℓ and we find

$$T_m = \frac{U_\ell - U_s}{S_\ell - S_s}. \quad (2.40)$$

For dimensional reasons $S_\ell - S_s$ is of the order of $N_\alpha k_B$. The difference $U_\ell - U_s$ is a small fraction (let us say 3%) of the cohesive energy U_c ; this follows from

the fact that in the liquid state the system is close to the minimum of Fig. 2.4 (since the volume V_ℓ is almost the same as V_s) but above it, since in the liquid state the atoms pass through many configurations of slightly higher energies. Hence

$$T_m = \text{const.} \times \frac{\hbar^2}{m_e a_B^2 k_B} \frac{1}{\bar{r}_a^2}, \quad (2.41)$$

$$\approx \frac{10^4}{\bar{r}_a^2} \text{K}, \quad (2.42)$$

where the numerical factor of 10^4 was obtained by choosing the “const.” to be about 3%. Equation (2.41) gives, for $\bar{r}_a \simeq 3$, $T_m \simeq 1100 \text{K}$, which is a typical value. Actually, T_m can be as high as 3680K (for W).

2.6.9 DC Electrical Resistivity, ρ_e

It is easy to prove that the unit of electrical resistivity for three-dimensional materials in the atomic system is given by²⁰ $\hbar a_B / e^2 = 21.74 \mu\Omega \text{cm}$. Hence, according to the general formula (1.16), we have

$$\rho_e = \text{const.} \times \frac{\hbar a_B}{e^2} f\left(Z, \frac{m_a}{m_e}, \frac{T}{T_0}, \frac{P}{P_0}, \dots\right). \quad (2.43)$$

If we make the assumptions that T and P do not play an important role, that the atomic mass is not so important,²¹ and that a_B must be replaced everywhere by $\bar{r}_a a_B$, we have

$$\rho_e = \text{const.} \times \frac{\hbar a_B}{e^2} \bar{r}_a \simeq 20 \bar{r}_a \mu\Omega \text{cm}. \quad (2.44)$$

Thus, the dimensional analysis combined with the physical picture described in the footnote 21, estimates the electrical resistivity of solids to be of the order of $50 \mu\Omega \text{cm}$. This value is not far from the experimental values of ρ_e for certain metals at $T = 295 \text{K}$ as shown in the following table.

²⁰ The unit of voltage is energy over charge: $[E]/e$. The unit of current is charge over time: $e/[t]$. Hence, the unit of electrical resistance, R , which is voltage over current, is $[E][t]/e^2$. But $[E][t] = \hbar$, in the atomic system. Since $R = \rho_e \ell / S$, it follows that $[\rho_e] = [R][\text{length}] = \hbar a_B / e^2$. In 2-D systems R and ρ_e have the same units. Notice that the resistance $R = 2\pi\hbar/e^2 = \hbar/e^2 = 25812.8 \text{ohm}$ appears in the phenomenon known as Quantum Hall effect (see Sect. 18.9). Its inverse $e^2/\hbar$ is called the **von Klitzing** conductance.

²¹ These assumptions seem justified if we adopt the picture that the electrical resistivity is due to the collisions of the current-carrying electrons (behaving as classical particles) with the more or less immobile ions.

Metal	<i>Ti</i>	<i>Pb</i>	<i>Nb</i>	<i>Bi</i>	<i>Pr</i>	<i>U</i>	<i>Cs</i>	<i>Mn</i>
ρ_e ($\mu\Omega$ cm) at $T = 295$ K	43.1	21	14.5	116	67	25.7	20	139

However, other metals (such as the noble ones) have resistivities at room temperature more than one order of magnitude lower than our rough estimate:

Metal	<i>Na</i>	<i>Ca</i>	<i>Cu</i>	<i>Ag</i>	<i>Au</i>	<i>Al</i>
ρ_e ($\mu\Omega$ cm) at $T = 295$ K	4.75	3.6	1.7	1.61	2.2	2.74

Furthermore, these low-resistivity metals, at liquid He temperatures, exhibit resistivities of the order of $10^{-3} \mu\Omega$ cm, i.e., four orders of magnitude lower than the value of $50 \mu\Omega$ cm. To make things even worse, very pure single-crystal specimens of, e.g., Cu at liquid He temperatures, have resistivities as low as $10^{-5} \mu\Omega$ cm. To the other extreme, there are solid substances (e.g., sulfur in its yellow form) exhibiting resistivities as high as $2 \times 10^{23} \mu\Omega$ cm at $T = 293$ K! Thus, it is obvious that the simple formula (2.44) fails completely to account for the electrical resistivities, which actually span 30 orders of magnitude for various solids.

It is very instructive to ask ourselves what went wrong in deriving (2.44), which failed so dismally. As we mentioned before, our assumptions, such as weak temperature dependence, etc, rely on the picture of current-carrying electrons as classical particles colliding with ions; this classical picture implies a mean free path between collisions of the order of a few lattice constants. As we shall see later, such a mean free path combined with a classical expression for free electron concentration leads to an expression for ρ_e similar to (2.44). Hence, classical mechanics is the culprit for the failure of (2.44). We should have used quantum instead of classical mechanics for the motion of electrons. More specifically, we should have taken into account that electrons propagate in the solid as waves, and consequently, *they may exhibit constructive or destructive interference*. If the scattered electronic waves interfere constructively in a *systematic way*, the effects of scattering could be compensated for and the electrons could propagate as if they were free of any force; in other words their mean free path would be infinite. However, such a systematic constructive interference requires placement of the scattering centers (i.e., the ions) in an ordered way to make sure that waves arrive in phase. The perfect crystalline structure, due to its periodic positions of the ions, satisfies this requirement and provides thus the mechanism for essentially free-like propagation, infinity mean free path, and zero electrical resistivity. According to this argument, the observed nonzero small metallic resistivity is due to elastic scattering by structural imperfections, by foreign atoms, and by other

deviations from the perfect periodic structure, as well as to inelastic scattering by the inevitable (at $T \neq 0$ K) ionic oscillations. Keep in mind that a periodic placement of the scatterers (i.e., the ions) could lead not only to perfectly systematic constructive interference but to perfectly *systematic destructive interference* as well. So it is possible in a periodic medium to have regions of energies (called *bands*) where the interference is systematically constructive and *the propagation is free-like*, and regions of energy called *gaps* where it is systematically destructive and the electronic waves cannot even exist.²²

This wave-based, alternating band/gap structure of the energy spectrum in periodic materials explains the huge differences in electrical resistivities among various solids. If every band is either fully occupied by electrons or completely empty (which means that the Fermi level is in the middle of the gap separating the highest fully occupied band, called *valence band* from the lowest completely empty band, called *conduction band*), the resistivity (at $T = 0$ K) is infinite and the material is insulating. This is so because the electrons in a *fully occupied band, even if they are infinitely mobile and free-like*, cannot respond to the electric field and produce a current, because any such response requires electrons to be excited from occupied to empty states. But in a *fully occupied band* there are no empty states.²³ In reality, the resistivity in insulators is huge but finite, because of the thermal excitation of a few electrons to the conduction band (at $T > 0$ K), or, because of the ionic migration in the presence of impurities and imperfections.

On the other hand, in materials in which a band is not fully occupied at $T = 0$ K (this means that the Fermi level lies within this band), the electrons can easily be excited by an electric field to nearby empty levels and produce thus large electric currents (such materials behave as good conductors). As it was mentioned before, what makes the current in good conductors finite and the resistivity non-zero (but small) is the fact that in real materials the periodic order is never perfect. For pure good conductor such as noble metals and at room temperatures, the main deviations from periodicity are due to the ionic oscillations; these produce an extra nonperiodic potential that is proportional to the amplitude of the oscillations. The scattering is proportional to the square of this extra nonperiodic potential, i.e., proportional to the amplitude-square, which in turn is proportional to the energy of oscillation; the latter (at room and higher temperatures) is given approximately by the classical expression of $3k_B T$ per atom. We conclude that *for good conductors and for not-so-low temperatures, the resistivity is proportional to the absolute temperature*. Hence, instead of (2.44), we have the following expression for the

²² It should be pointed out that gaps may appear even in non-periodic systems, if a large fraction of space is classically inaccessible; on the other hand, destructive interference in two and three dimensional periodic media is not always capable of opening gaps.

²³ There are empty states in the conduction band. However, the excitations of electrons there, requires usually a huge electric field; this is the phenomenon of electric breakdown of insulators.

resistivity of good conductors at room temperatures and higher:

$$\rho_e = \text{const.} \times \frac{\hbar a_B}{e^2} \frac{3T}{T_0} \rightarrow \text{const.} \times \frac{3\hbar a_B \bar{r}_a}{e^2} \frac{m_e a_B^2 \bar{r}_a^2}{\hbar^2} k_B T, \quad a_B \rightarrow r_a = \bar{r}_a a_B, \quad (2.45)$$

$$\rho_e = \text{const.} \times 2.07 \times 10^{-4} \bar{r}_\alpha^3 T \mu\Omega \text{ cm, metals } (T \text{ in K and not very low}). \quad (2.46)$$

Actually, the “const.” varies in a broad range from metal to metal. For very good conductors (such as noble metals and alkalis), a rough representative value of the “const” is about 1.5, which makes the resistivity formula in (2.46), $\rho_e \approx 3.1 \times 10^{-4} \bar{r}_\alpha^3 T \mu\Omega \text{ cm}$, where T is in Kelvin. For transition and rare earth metals, the “const.” is about an order of magnitude larger, i.e., about 15. Thus, (2.46) yields the following values of ρ_e (in $\mu\Omega \text{ cm}$) at $T = 295 \text{ K}$ and for the experimental value of $\bar{r}_\alpha$.

	<i>Ti</i>	<i>Nb</i>	<i>Pr</i>	<i>U</i>	<i>Cs</i>	<i>Mn</i>	<i>Na</i>	<i>Ca</i>	<i>Cu</i>	<i>Ag</i>	<i>Au</i>	<i>Al</i>
$\bar{r}_\alpha$	3.05	3.07	3.82	3.22	5.62	2.7	3.93	4.12	2.67	3.02	3.01	2.99
ρ_e (2.45)	26	26.5	51	30	16	18	5.6	6.4	1.74	2.52	2.5	2.4
ρ_e (exp.)	43.1	14.5	67	25.7	20	139	4.75	3.6	1.7	1.61	2.2	2.74

For extremely pure semiconductors and insulators, the resistivity is inversely proportional to the number of carriers, i.e., the number of electrons excited in the conduction band from the valence band plus the missing electrons (*holes*) in the valence band. This number, as we shall see later, depends exponentially on the dimensionless ratio $E_g/2k_B T$, where E_g is the *energy gap*, i.e., the energy separation between the bottom of the conduction band and the top of the valence band. Thus, for very pure semiconductors and insulators the resistivity is proportional to $\exp[E_g/2k_B T]$

$$\rho_e \sim \exp \left[\frac{E_g}{2k_B T} \right], \text{ pure semiconductors, insulators.} \quad (2.47)$$

It must be stressed that the resistivity in semiconductors may be reduced by several orders of magnitudes if appropriate substitutional impurities are incorporated in the lattice (see Chap. 7).

2.7 Key Points

- *Heisenberg's* principle, the electrostatic potential, and the minimization of energy determined the size and the energy scale of the simplest atom, that of hydrogen. *Pauli's* and *Schrödinger's* principles lead to the shell and subshell structure of atoms and their saw-like vs. Z radius and ionization energy as given in Figs. 2.1 and 2.2 respectively.

- Atoms form molecules and solids, because by doing so they lower their energy as shown in Figs. 2.3 and 2.4 respectively. The equilibrium bond length, d , is of the order of the sum of the corresponding atomic (or ionic) radii: $d \simeq R_1 + R_2$.
- Ions (or atoms) in solids (and in molecules) undergo small coupled oscillations ($\Delta d/d$ typically of the order of 5%) around their equilibrium positions; these oscillations are approximately equivalent to $3N_a$ independent 1-D harmonic oscillations of frequencies ω_ν ranging from zero to a maximum value $\omega_{\max}$.
- Classical mechanics fails to account for the properties of both the ground state of solids and of their thermal excitations. The latter are controlled by two kinds of energies: one kind, E_F , is Pauli-based, while the other, such as ε_0 or E_g , is Schrödinger-based; only when $k_B T$ is larger than both of them, classical thermodynamic results are adequate.
- The basic formula (1.16) with “*a little imagination and thinking*” produces reasonable expressions and semiquantitative estimates for various quantities characterizing the solid state. Some of these quantities are: density, cohesive energy, compressibility (or bulk modulus), sound velocities, maximum eigenfrequency, $\omega_{\max}$, and melting temperature. The case of DC electrical resistivity is very instructive, because it implies the wave character of electronic propagation in solids, the band and gap structure of their spectrum, the classification of solids into conductors and insulators and the dominant role of disorder (thermal, structural, or compositional) in transport properties.

2.8 Questions and Problems

- 2.1 Why do alkali atoms have local maxima in R_a vs. Z (Fig. 2.1) and local minima in I vs. Z (Fig. 2.2)?
- 2.2 Why do noble gases give local minima in R_a vs. Z and local maxima in I vs. Z ?
- 2.3s Consider two hydrogen atoms at a distance, d' , between their protons. Plot as accurately as you can the total ground state energy of this system as d' varies from 5 to 0.5 a.u. Ignore the kinetic energy of the protons. Choose as the zero of energy the ground state energy at $d' = \infty$. (See M. Karplus and R.N. Porter, *Atoms and Molecules*, W.A. Benjamin (1970), p. 287.)
- 2.4 Plot as accurately as you can the total energy per atom of Al vs. the volume per ion. Use data from Tables H.7, H.10, and H.11, and the formula in the caption of Fig. 2.4. Compare with the corresponding computational results from the book of Marder [SS82], p. 281.
- 2.5s Assume that the electronic ground state in the hydrogen atom is of the form $\psi \sim \exp(-r/a)$. Calculate the average of $1/r$, of $p^2/2m_e$, and of r^2 . Obtain the value of the product $\Delta p_i \Delta x_i$ ($i = 1, 2, 3$).

2.6s Show that the Hamiltonian of two particles of mass m_1 and m_2 respectively,

$$\hat{H} = \frac{\mathbf{p}_1^2}{2m_1} + \frac{\mathbf{p}_2^2}{2m_2} + \mathcal{V}(\mathbf{r}_1 - \mathbf{r}_2),$$

can be written equivalently as follows:

$$\hat{H} = \frac{\mathbf{P}^2}{2M} + \frac{\mathbf{p}^2}{2\mu} + \mathcal{V}(\mathbf{r}),$$

where

$$\begin{aligned}\mathbf{r} &= \mathbf{r}_1 - \mathbf{r}_2, \\ \mathbf{R} &= \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{m_1 + m_2}, \\ M &= m_1 + m_2, \\ \mu &= m_1m_2/(m_1 + m_2), \\ \mathbf{P} &= M\dot{\mathbf{R}} = \mathbf{p}_1 + \mathbf{p}_2, \\ \mathbf{p} &= \mu\dot{\mathbf{r}} = (m_2/M)\mathbf{p}_1 - (m_1/M)\mathbf{p}_2.\end{aligned}$$

Hence, the Hamiltonian splits into two noninteracting parts: $\hat{H} = \hat{H}_{\text{CM}} + \hat{H}_r$, where $\hat{H}_{\text{CM}} = \mathbf{P}^2/2M$ describes the free motion of the center of mass, and $\hat{H}_r = (\mathbf{p}^2/2\mu) + \mathcal{V}(\mathbf{r})$ describes the relative motion of the two particles, which is equivalent to the motion of a single particle of mass μ in the potential $\mathcal{V}(\mathbf{r})$.

2.7 For a particle of mass μ moving in a spherically symmetric potential $\mathcal{V}(|\mathbf{r}|)$, show that the Hamiltonian $\hat{H} = (\mathbf{p}^2/2\mu) + \mathcal{V}(r)$ can be written as follows

$$\hat{H} = \frac{\hat{p}_r^2}{2\mu} + \mathcal{V}(r) + \frac{\hat{\ell}^2}{2\mu r^2}, \quad (2.48)$$

where $\hat{p}_r$ is the radial and $\mathbf{p}_\perp$ the perpendicular to $\mathbf{r}$ component of the momentum²⁴ and $\hat{\ell} = \mathbf{r} \times \hat{\mathbf{p}} = \mathbf{r} \times \hat{\mathbf{p}}_\perp$ is the angular momentum. Quantum mechanically

$$\hat{p}_r^2 = -\frac{\hbar^2}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right), \text{ and } \hat{\ell}^2 \text{ is given by (B.41)}. \quad (2.49)$$

Show, then, that the equation $\hat{H}\psi = E\psi$ can be written as follows, by introducing $\chi = r\psi = u(r)Y(\theta, \phi)$:

$$\frac{r^3}{u} \left(\hat{p}_r^2 \frac{u}{r} \right) + \frac{\hat{\ell}^2 Y}{Y} = (E - \mathcal{V})2\mu r^2. \quad (2.50)$$

²⁴ $\hat{p}_r = -i\hbar \frac{1}{r} \frac{\partial}{\partial r} r$ and $\hat{p}_r \neq -i\hbar \frac{\partial}{\partial r}$. The first operator is hermitean in the domain, $0 \leq r \leq \infty$, while the second is not.

Argue that the quantity $\hat{\ell}^2 Y/Y$ ought to be a constant independent of r, ϕ, θ and of $\mathcal{V}(|\mathbf{r}|)$. To find its value, we shall choose $\mathcal{V} = E$ in which case Schrödinger's equation becomes the Laplace equation, the regular solutions to which at $r = 0$ are of the form $u/r = r^F Y_{Fm}(\theta, \phi)$ ($F = 0, 1, 2, \dots$) (see Table H.18). Substituting in (2.50) this solution, $r^F Y$, setting $E = \mathcal{V}$, and taking into account (2.49), we find

$$-\hbar^2 F(F+1) + \frac{\hat{\ell}^2 Y}{Y} = 0, \quad (2.51)$$

(we use the symbol F instead of the more familiar ℓ to stress the possibility that $\hbar^2 F(F+1)$ may refer to ionic rotation instead of electronic). Substituting in (2.50) this value of $\hat{\ell}^2 Y/Y$ (which is valid for any $\mathcal{V}(|\mathbf{r}|)$) we find

$$-\frac{\hbar^2}{2\mu} \frac{d^2 u}{dr^2} + \left[\mathcal{V}(r) + \frac{\hbar^2 F(F+1)}{2\mu r^2} \right] u = Eu, \quad F = 0, 1, 2, \dots \quad (2.52)$$

If r is the distance between the two atoms of a diatomic molecule, we can approximate the term $\hbar^2 F(F+1)/2\mu r^2$ by $\hbar^2 F(F+1)/2\mu d^2$, and the term $\mathcal{V}(r)$ by $\mathcal{V}(d) + \frac{1}{2}\kappa(r-d)^2$, where d is the equilibrium distance. Hence, with these approximations, show that

$$E = \mathcal{V}(d) + \frac{\hbar^2 F(F+1)}{2\mu d^2} + \left(n + \frac{1}{2} \right) \hbar\omega, \quad n = 0, 1, 2, \dots, \omega = \sqrt{\kappa/\mu}. \quad (2.53)$$

Better approximations can be obtained by expanding the effective potential $\mathcal{V}_e(r) = \mathcal{V}(r) + \hbar^2 F(F+1)/2\mu r^2$ in powers of $r-d_e$ up to second order, where d_e is determined by the condition $[d\mathcal{V}_e(r)/dr]_{r=d_e} = 0$.

- 2.8s The n th excited level associated with an 1-D attractive potential of the form $\pm|x|^\beta$ (the upper sign for $\beta > 0$ and the lower for $\beta < 0$), is expected to depend on $n \gg 1$ as follows: $E(n) \sim n^a$, where $a = \left(\frac{1}{2} + \frac{1}{\beta}\right)^{-1}$. Could you argue in favor of this guess? What do you conclude for the spectrum of a 1-D harmonic oscillator?
- 2.9 Using the experimental data of ε vs. d' for the hydrogen molecule from the book of Karplus and Porter (reproduced in the solution of Problem 2.3s) calculate:
- the frequency ω of oscillation
 - the fluctuation of the bond length
 - the moment of inertia
 - the first excited rotational level
 - the first excited vibrational level
- 2.10 Show that at low temperatures the quantum fluctuation, Δd , of the equilibrium bond length, d , is of the order of $(m_e/m_a)^{1/4}d$.

- 2.11s Consider a two-dimensional motion of a particle of mass m in the presence of a circular potential well: $\mathcal{V}(r) = -|\varepsilon|$ for $r < a$ and $\mathcal{V}(r) = 0$ for $r > a$. Show that this 2-D potential well always sustains at least a bound state no matter how shallow it is. Show also that the binding energy is given by

$$\varepsilon_b = \frac{2}{e^{2\gamma}} E_0 \exp \left[-2 \frac{E_0}{|\varepsilon|} \right],$$

in the limit $|\varepsilon| \ll E_0$, where $E_0 \equiv \hbar^2/ma^2$ and $\gamma = 0.577 \dots$ is Euler's constant. The exponent can also be written as follows:

$$-\frac{2E_0}{|\varepsilon|} = -\frac{1}{\rho|\varepsilon|},$$

where ρ is the free particle DOS in 2-D per unit area times the area of the well, $\pi a^2 : \rho = (m/2\pi\hbar^2)\pi a^2$.

- 2.12 The same problem as the previous one but for a 1-D and 3-D potential well. Calculate explicitly and plot ε_b vs. $|\varepsilon|$. *Hint*: See Landau & Lifshitz, QM [Q25], §22, problem 2, and problem 1 in §33.
- 2.13 Estimate the velocity of sound in water (*Hint*: Since water molecules are held together by the weak hydrogen bond, take the “const.” in (2.31) as 0.5 instead of 1.6).

Further Reading

- Landau & Lifshitz, *Mechanics*, [Me10], p. 23 (for virial theorem).
- Landau & Lifshitz, *QM* [Q25], pp. 117–120 (For hydrogen atom).
- Landau & Lifshitz, *QM* [Q25], pp. 67–69 (For harmonic oscillator).
- Landau & Lifshitz, *Mechanics* [Me10], pp. 65–68, and 70–74 (For coupled harmonic oscillators).

A First Acquaintance with Condensed Matter

Summary. Various kinds of condensed matter are mentioned, and bonding types are briefly presented. The most common crystal structures are described. Wave eigenfunctions in periodic media, such as a crystalline solid, are characterized by a phase, $\phi = \mathbf{k} \cdot \mathbf{r}$, and an amplitude of the same periodicity as the underlying medium, according to Bloch's theorem; $\hbar\mathbf{k}$ is called crystal momentum and its physical content remains unaffected by the addition of $\hbar\mathbf{G}$, where $\mathbf{G}$ is any vector of the so-called reciprocal lattice. In the latter, Bragg planes and Brillouin zones are defined.

3.1 Various Kinds of Condensed Matter

As it was mentioned in Sect. 1.1, condensed matter includes solids, liquids, and a broad and diverse group of materials/states of matter intermediate between solids and liquids such as polymers, colloids, gels, foams, micelles, membranes, proteins, liquid crystals, quantum condensates, etc.

It is commonly stated that the main feature of a solid, which distinguishes it from a liquid, is its resistance to shear stresses, i.e., to forces that tend to change its shape but not its volume. In more technical terms, this means that the shear modulus, μ_s , defined as the ratio of shear stress to twice the shear strain (see Sect. 2.6.5 and Appendix E), is not zero; for simple isotropic solids and not-very-large stresses, μ_s is independent of the stresses and the strains; we say then that the solid obeys Hooke's law, or equivalently, that it exhibits elastic response. In contrast, ordinary liquids have $\mu_s = 0$, i.e., they do not put up any resistance to shear stress; instead, they give in and start flowing; in other words, their response to shear stresses is not displacements to new equilibrium positions (i.e., strains), but velocities (i.e., time derivatives of strains). The ratio of shear stress to twice the time derivative of shear strain is called *viscosity* and it is usually symbolized by η ; for simple liquids and not-very-large strains, η is a constant, i.e., independent of stress (or rate of strain). Then, the liquid is called *Newtonian*. Notice that from a dimensional

point of view, we can write

$$\eta = \mu_s \tau. \quad (3.1)$$

If we can identify a characteristic time τ for the liquid, we can estimate the size of the viscosity, η , from the typical magnitude of μ_s in the solid phase (see Problem 3.1s); furthermore, if τ is really a physical time scale, then, the distinction between solids and liquids is a matter of time scale, at least in principle. This means that for stresses acting on a time scale $t \ll \tau$, the response of the substance will be that of a solid, while for $t \gg \tau$ a typical liquid behavior will be exhibited.

If $T'_{\nu\mu}$ is the shear stress tensor and $2\dot{u}'_{\nu\mu} \equiv (\partial v_\nu/\partial x_\mu) + (\partial v_\mu/\partial x_\nu) - (2/3)\delta_{\nu\mu} \sum_\ell \partial v_\ell/\partial x_\ell$ is the time derivative of twice the shear strain tensor, we have by definition of η that

$$T'_{\nu\mu} \equiv 2\eta \dot{u}'_{\nu\mu}. \quad (3.2)$$

The corresponding relation for the isotropic compression tensor, $T''_{\nu\mu} \equiv \delta_{\nu\mu} \text{Tr}(T_{\nu\mu})/3$, is

$$T''_{\nu\mu} = \delta_{\nu\mu} \zeta \nabla \cdot \dot{\mathbf{u}}, \quad (3.3)$$

where the total stress $T_{\nu\mu} \equiv T'_{\nu\mu} + T''_{\nu\mu}$ with $\text{Tr}(T'_{\nu\mu}) = 0$. These relations are the analog of (E.14) with η instead of μ_s , ζ instead of B , and $\dot{u}_{\nu\mu}$ in the place of $u_{\nu\mu}$ (see [Me13], §15).

In this section we give a brief and incomplete list of various kinds of condensed matter structures starting with ordinary solids (for which τ is infinite, as in crystalline solids, or practically infinite), otherwise called *hard matter*, and proceeding to substances for which τ is finite; these substances, generically called *soft matter*, exhibit both viscous flow (for long times t) and elastic response (for short times t), a behavior referred to as viscoelastic.

3.1.1 Monocrystalline and Polycrystalline Atomic Solids

This category includes elemental metals (such as copper), elemental semiconductors (such as silicon), elemental insulators (such as diamond), etc. A perfect periodic crystalline arrangement of the atoms is an idealization: there is always some kind of defects. Crystalline solids in the absence of two-dimensional defects along internal surfaces are called *monocrystals*. The preparation of monocrystals of any solid requires special sophisticated techniques and extra care. Most crystalline materials are *polycrystalline*, i.e., they consist of crystallites of various orientations and mesoscopic or macroscopic sizes coexisting in the solid; the interfaces of the crystallites constitute two-dimensional defects. Linear defects, the so-called *dislocations*, are always present and play a crucial role in determining the ductile vs. brittle behavior exhibited by different solids, in influencing the crystal growth, etc. *Point defects*, such as *vacancies*, *interstitials*, *foreign atoms*, are also always present

and are very important in determining the electrical and other properties of solids especially of semiconductors.

3.1.2 Atomic or Ionic Compounds and Alloys

These are usually polycrystalline solids such as ionic insulators (e.g., NaCl), composite semiconductors (e.g., GaAs), oxides (e.g., SiO₂, TiO, FeO, V₂O₃), perovskites (e.g., SrTiO₃, Na_xWO₃, KFeF₃), high temperature superconductors (e.g., YBa₂Cu₃O_{7-x}, HgBa₂Ca₂Cu₃O₈), alloys (e.g., Cu_xAu_{1-x}, Si_xGe_{1-x}, SiC), etc. In certain alloys, e.g., Al₈₆Mn₁₄ fast cooled from the melt, the atoms arrange themselves in an ordered highly symmetric but *not periodic* manner, which usually consists of a nonperiodic assembly of clusters of 13 atoms forming regular icosahedra.

3.1.3 Molecular Solids

These solids are made up of molecules that retain their identity to a large degree in spite of the formation of the solid. This is so because the binding of the atoms within each molecule is much stronger than the binding among neighboring molecules. Typical examples are solids made up of nitrogen (N₂) or oxygen (O₂), or hydrogen (H₂) or CO₂ (dry ice), or C₆₀ (fulleride); these molecules are held together by weak van der Waals forces to form solids.

Water molecules in ice employ the relatively stronger hydrogen bond (see Sect. 3.2 below) to keep themselves together in more or less fixed positions.

3.1.4 Glasses

Several materials, when they are solidified as their melt is cooled under usual conditions, do not form polycrystalline structures; instead, the atoms arrange themselves in a disordered manner. Order is present usually *only locally* (i.e., at the scale of a few angstroms), while for larger distances their relative positions are random. In other words, there is *no positional long-range order* as in crystalline materials; only *short-range order* may exist and even this is not perfect. Solids that exhibit this type of positional disorder are called *glasses*. Common examples of glasses are the ordinary window glasses (consisting of 70% SiO₂, 20% Na₂O, and 10% CaO), the chalcogenide glasses of the elements S, Se, and Te, such as As₂S₃, As₂Se₃, etc. Among the elements, S, P, and Se solidify to the glassy state. Very fast cooling from the melt drives many materials (e.g., transition metals) to a glassy state instead of their normal crystalline state, because the atoms have no time to place themselves in a lattice; instead, they are frozen more or less in the positions they had in the liquid phase. Molecular solids (e.g., polymers) consisting of medium- and/or large-size organic molecules form usually glasses. The transition from the liquid phase to the glassy state is mainly characterized by a huge change in the viscosity over a very narrow temperature range centered at the so-called *glass*

transition temperature, T_g . Thus, glasses can also be characterized as “frozen liquids”. However, neither this characterization nor the one classifying them simply as “amorphous solids” would be sufficient. These two seemingly self-contradictory definitions are brought into agreement by noting that one is dealing with an intrinsically “non-ergodic” system. This term simply means that the system does not pass through all possible states with equal probability according to the rules of thermodynamic equilibrium (see (C.35) and text below (C.37)). In practice this term implies that on the sufficiently short time scales of usual experiments the system can be considered as a solid, but on an extremely long time scale, e.g. that of decades or centuries, it may behave as a liquid.

3.1.5 Polymers

These are very important molecular materials both scientifically and technologically. They exhibit most of the characteristic properties of the so-called soft matter: Their structural length scales are intermediate between atomic and macroscopic; their time scales, τ , may cover many orders of magnitude and depend strongly on the temperature; their interaction energies are comparable to $k_B T$ so that Brownian motion is important and the entropic term, $-TS$, in competition with the energy (more correctly the enthalpy) determines the various equilibrium phases including self-assembled structures.

Polymeric materials are usually made of long linear molecular chains consisting of elementary molecular units called monomers; a polymer chain can be made by repeating the same monomer or by repeating several different monomers. Besides the linear polymers, other forms such as branched polymers or star polymers do exist. The so-called copolymers consisting of two (or more) different linear polymers joined together by a strong homopolar bond find many applications, including the possibility of forming self-assembled periodic structures.

In polymeric melts or glasses (containing typically large amorphous parts) the long flexible molecules are intertwined together “touching” each other at many points in a random orientation, a situation called *entanglement*. The latter plays a large role in creating a loose network. Under stress, slow flow can take place, during which polymers slide along their complicated intertwined paths dictated by the entanglement; this slow sliding is known as *reptation*. There is a possibility of making chemical links at the points of “touching” between different polymers. This cross linking, known as rubber vulcanization, inhibits the reptation and produces rubber-like response.

3.1.6 Colloids

Several systems consist of small (diameter of $10\,\mu\text{m}$ or less) solid or liquid particles dispersed in a liquid medium. These systems are known as *colloidal dispersions*. The particles may arrange themselves in an ordered periodic

structure, as their concentration increases beyond a certain critical value. The liquid medium may evaporate and the system may solidify in a periodic arrangement of the particles. In fact, the gemstone *opal* is a natural colloidal crystal consisting of silicon dioxide (SiO_2) spherical particles the diameter of which is less than $1\text{ }\mu\text{m}$. Opal-like solids may be formed with polymeric particles instead of SiO_2 spheres. Colloidal structures, as every other equilibrium structure of matter, are determined by the interplay of the enthalpic and the entropic terms in the Gibbs free energy. The enthalpic term is, due mainly to various weak interactions among the particles of van der Waals origin, of screened Coulombic nature (for charged particles in ionic solutions), and/or mediated, e.g., by polymers grafted on the surface of the particles or small polymer coils dispersed in the solution. For the ideal case of only hard sphere interaction, the structure is determined solely by the entropic term, which in an apparent paradox drives the system through a first-order phase transition to a periodic state for volume fractions between 0.494 and 0.545.

3.1.7 Gels

We met an example of gel in the case where polymers crosslink and undergo a rubber vulcanization. More generally, a gel is a system where its nano- or meso-scopic building units are bonded together to form a macroscopic connected network. Some examples, besides the vulcanized rubbers, are the thermosetting *resins* and the so-called *Sol-gel glasses*. The former consist of small polymers with reactive groups on both ends and reactive molecule that can bond with up to four polymers; the Sol-gel glasses are organic derivatives of certain oxides that in the presence of water undergo hydrolysis and form substances similar to inorganic glasses.

3.1.8 Liquid Crystals

Liquid crystals are made of rigid polymers, or molecular aggregates with rigid rod-like shapes, or organic compounds with highly anisotropic molecular shapes. As a result of this almost rod-like structure of their constituents, liquid crystals may exhibit *orientational* long-range order, while they lack long-range positional order: a situation called *nematic* liquid crystallinity. In *smetic* liquid crystals, besides the orientational, there is also a one-dimensional long-range positional order, in the sense that the molecules arrange themselves in sheets; within each sheet, the molecules are aligned but their position is random.

3.1.9 Self-Assembled Soft Matter

We mentioned before an example of self-assembled soft matter: Copolymers, consisting of two mutually repelling polymers joined together covalently, form various ordered structures; these structures depend mainly on the size of each polymer component in the copolymer and on the temperature.

The most common self-assembled structures are based on the so-called amphiphilic molecules, which have one part of the molecule with an affinity for water (hydrophilic) and the other part repelled by water (hydrophobic). As a result of these interactions, various phase or microphase separations take place; the latter result in aggregates of microscopic size and spherical or cylindrical shapes called *micelles* as well as in *bilayers*, which can also fold to form the so-called *vesicles*.

Biological elemental units such as *membranes*, *proteins*, *polysaccharides*, and *nucleic acids*, although enormously more complex and operating out of thermodynamic equilibrium, share some structural elements and principles with their distant non-living self-assembled soft matter.

3.1.10 Artificial Structures

Scientific curiosity and technological demands have led to the creation of artificial condensed matter structures such as novel chemical compounds, a wealth of mesoscopic and nanoscopic structures, such as superlattices *nipi*, (i.e., periodic layers consisting of n-doped semiconductor, intrinsic semiconductor, p-doped semiconductor, intrinsic semiconductor), quantum wells, quantum dots, nanocomposites, etc., transistors, integrated circuits, photonic crystals (i.e., periodic structures to manipulate the flow of electromagnetic waves), phononic crystals (periodic structures to control the flow of acoustic waves), and left-handed materials (exhibiting over a frequency range simultaneously negative permittivity, $\epsilon(\omega)$, and negative permeability, $\mu(\omega)$).

Finally, we must mention the achievement of supercold atoms (their temperature can reach the 10^{-9} K range); these atoms, if bosons, may undergo a phase transition, known as the BCS transition, into a metastable coherent quantum state, the Bose–Einstein condensate (BEC).

3.1.11 Clusters and Other Finite Systems

When we study solids and other condensed matter structures, we usually assume implicitly that their size is large enough not to affect their bulk properties.¹ As the size becomes very small (of the order of a few tens of nanometers or less), we cannot distinguish anymore between bulk and surface properties, nor can we ignore the role of the size on the observed behavior. Under those circumstances, we use the rather vague term “finite systems” to emphasize the role of the size on the properties of the systems. There are many types of finite systems ranging in size from millions to a few tens of atoms and including, among others, man-made structures such as quantum dots, metallic clusters, etc. (see Ch. 19) and important biological molecules such as DNA, RNA, and proteins.

¹ Of course near the surface different features appear. But what is going on near the surface leaves the interior of the structure unaffected.

We mention here the so-called *quantum dots*, which are semiconductor nanoparticles of linear dimension, d , typically less than 30 nm. By controlling the size of these particles, we change the magnitude of the gap and the position of other levels taking advantage of the $\hbar^2/m_e d^2$ dependence of the electronic kinetic energy (see Sect. 1.4). *Metallic clusters* of tens of atoms have been produced by the supersonic expansion of metallic vapors; these clusters exhibit magic number behavior. Particular attention has been paid to *carbon clusters* such as the so-called *fullerenes*, the smaller of which consist of 60 carbon atoms arranged in a sphere-like cage, the face of which consists of 12 pentagons and 20 hexagons (like a soccer ball). Of significant technological promise are the so-called *carbon nanotubes*, which can be thought of as the result of the rolling up on themselves of *graphene* sheets of finite width. Other *organic* as well as *organometallic clusters* have been produced and studied.

3.2 Bonding Types and Resulting Properties

We can distinguish six types of elementary chemical bonds in solids:

- Simple metallic bond
- Transition (d or f) metallic bond
- Covalent bond
- Ionic bond
- Van der Waals bond
- Hydrogen bond

Only simple solids employ a single type of bond for their formation. For example, the atoms in alkaline metals or Mg or Al or Pb or Bi, etc. are held together by a *simple metallic bond* involving mainly s, or s and p electronic states (see Appendix F and in particular Fig. F.1). Transition metals such as Fe, Ni, etc., rare earths, such as Gd, Sm, etc., and actinides such as U, Pu, etc. involve in their bonding not only electrons in s states but also *electrons in d states*, and to a lesser degree, electrons *in f states* as well (for lanthanides and actinides). Insulators and semiconductors such as diamond, silicon, germanium are 100% *covalently bonded*; on the other hand, compounds such as LiF or NaCl, etc. are almost 100% *ionically bonded*; more common than pure covalent or almost pure ionic is a bond of *mixed character* of $x\%$ covalent and $y\%$ ionic ($x + y = 100$) as in many compound semiconductors such as GaAs, InP, AlN, etc. Noble atoms such as Ne, Ar, Kr, and Xe solidify (at low temperatures) by employing *van der Waals bonds*.

Compounds and other more complicated materials employ usually several types of bonds: For example, the water molecule H_2O is formed by a mixed covalent/ionic bond between the oxygen and each hydrogen, while the water molecules in ice are held together by hydrogen bonds; molecular solids such as N_2 , O_2 , etc. employ covalent bond for their molecule formation and van der Waals bonds among the different molecules for condensation into a solid. In graphite atomic sheets of carbon atoms, the so-called *graphenes* are

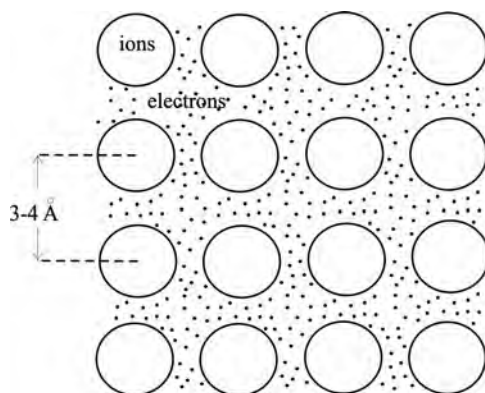


Fig. 3.1. Schematic presentation of valence electrons and ions in simple metals

formed by making use of covalent and metallic (more correctly semimetallic, see Sect. 13.8) bonds, while the sheets are held loosely together by van der Waals bonds.

In the following section, we describe the main features of each type of bonding by examining simple solids, which are formed by using only one type of bonds.

3.2.1 Simple Metals

The formation of these solids is associated with the liberation of the external shell (s or p or s and p) electrons from the atomic confinement; these liberated electrons spread themselves out to the whole volume of the solid in a more or less uniform concentration. The ions left behind are arranged in close-packed periodic crystalline structures such as *fcc* or dense-packed such as *bcc* (see Sect. 3.3 below). The nearest neighbor ionic distance (typically around 3–4 Å) is determined by the competition between Coulomb interactions on the one hand and free electron quantum kinetic energy on the other (Fig. 3.1).

Typical values for some important quantities in simple metals are as follows:

Cohesive energy, U_c : Large, from 3.39 eV/atom for *Al* to 0.934 eV/atom for *Na*.

Bulk modulus, B : Large to medium, from 0.722 Mbar² for *Al* to 0.068 Mbar for *Na*.

Shear modulus, μ_s : Large to medium, from 0.23 Mbar for *Al* to 0.05 Mbar for *Na*.

Electrical resistivity, ρ_e , (at 300 K): Small, 3 $\mu\text{ohm} \cdot \text{cm}$ for *Al*, 5 $\mu\text{ohm} \cdot \text{cm}$ for *Na*.

Magnetic response: Paramagnetic ($\chi_m > 0$, or $\mu_r > 1$).

Mechanical properties: Ductile but not hard.

² Mbar = $10^{11} \text{ N/m}^2 = 10^{12} \text{ dyn/cm}^2$

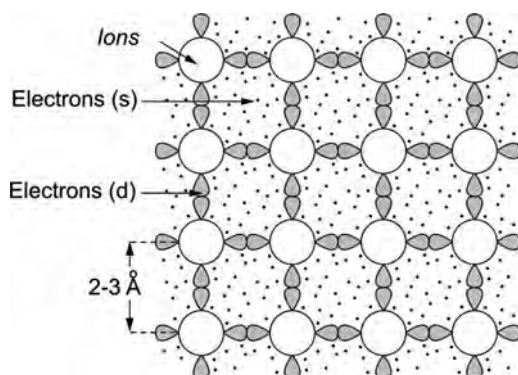


Fig. 3.2. Schematic presentation of the distribution of s and d valence electrons in transition metals. Ions are also shown

3.2.2 Transition Metals and Rare Earths

In these metals, besides the external shell s electrons (which behave as in the simple metals), d electrons of the highest occupied subshell also participate in the bonding (for lanthanides and actinides, f electrons also participate) (Fig. 3.2).

These d (and f) electrons, because of being closer to the nucleus, remain to a considerable degree localized around the parent atom along preferred directions; furthermore, they reduce the bond length and make the binding energy larger.

The ions form usually close-packed periodic structures such as *fcc* and *hcp* (see Sect. 3.3). Typical values are as follows:

Cohesive energy, U_c : Very large (e.g., 4.28 eV/atom for Fe and up to 8.90 eV/atom for W).

Bulk modulus, B : Very large (e.g., 1.68 Mbar for Fe, 3.23 Mbar for W).

Shear modulus, μ_s : Very large (e.g., 0.82 Mbar for Fe, 1.67 Mbar for W).

Electrical resistivity, ρ_e , (at $T = 295$ K) (in $\mu\Omega\text{cm}$): 43.1 for Ti, 9.8 for Fe, and 5.3 for Mo, while for the noble metals³ Cu, Ag, and Au the value is 1.7, 1.61, and 2.20 respectively, i.e., the lowest among all elemental solids.

Magnetic behavior: Only in this group of elemental solids, ferromagnetic (Fe, Co, Ni, Gd, Dy) and antiferromagnetic (Cr, Mn) behavior is found.

Mechanical properties: Ductile and hard.

3.2.3 Covalent Solids

In these solids, the electrons in the highest occupied s and p orbitals detach themselves from the parent atom and spread out over the volume of the solid

³ Noble metals, because of their fully occupied atomic d levels, behave like simple alkalis as far as most transport properties are concerned. On the other hand, their bonding properties are more like the other transition metals.

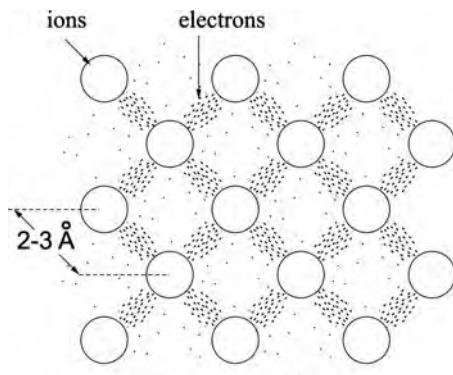


Fig. 3.3. Schematic presentation of electronic distribution and ionic location in covalent solids

not in a uniform manner but mainly along the direction of bonds among nearest ions. The latter form open, i.e., nondense, crystalline periodic structures quite often of tetrahedral nature with four nearest neighbors as in diamond and silicon. Their main properties are as follows (Fig. 3.3):

Cohesive energy, U_c : Very large (7.37 eV/atom for diamond, 4.63 eV/atom for Si).

Bulk modulus, B : Large (4.43 Mbar for diamond, 0.99 Mbar for Si).

Shear modulus, μ_s : Very large (4.8 Mbar for diamond, 0.67 Mbar for Si).

Electrical resistivity, ρ_e : Practically infinite; (covalent solids are insulators or semiconductors).

Magnetic behavior: Diamagnetic ($\chi_m < 0$ or $\mu_r < 1$).

Mechanical properties: Brittle, hard.

3.2.4 Ionic Solids

These are compounds consisting usually of the combination of an alkali element and a halogen element (e.g., NaCl, the common salt). In this case, an electron has been transferred from an alkali atom to a halogen atom creating thus a positive ion (cation) and a negative ion (anion). This transfer of electron costs energy, which is more than recovered, because of the mutual Coulomb attraction, of oppositely charged ions. In these solids, the crystalline structure is usually cubic with one anion surrounded by cations and vice versa. Their main properties are as follows (Fig. 3.4):

Cohesive energy, U_c : Large, e.g., 6.5 eV/per pair in NaCl.

Bulk modulus, B : Medium, e.g., 0.24 Mbar for NaCl.

Shear modulus, μ_s : Relatively large, e.g., 0.18 Mbar for NaCl.

Electrical resistivity, ρ_e : Practically infinite (they are insulators).

Magnetic response: Diamagnetic ($\chi_m < 0$ or $\mu_r < 1$).

Mechanical properties: Brittle.

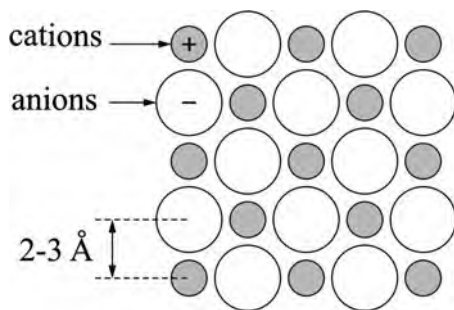


Fig. 3.4. Relative size and placement of cations and anions in typical ionic solids

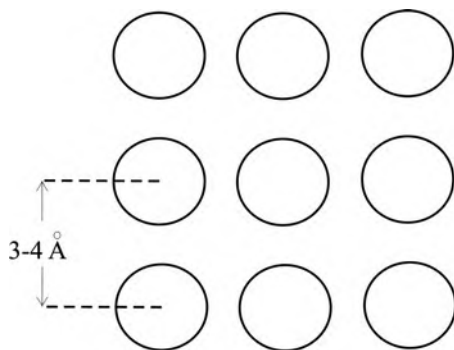


Fig. 3.5. In elemental van der Waals solids electrons remain within their parent atoms rearranging themselves as to produce mutually induced attractive dipole interactions

3.2.5 Van der Waals Bonded Solids

These are made of atoms or molecules that have completed shells only; as a result, no detachment of electrons from the parent atom or molecule takes place (as in metallic, covalent, or ionic solids) (Fig. 3.5).

The needed attraction for the solid state formation is provided by intra-atomic or intramolecular rearrangement of electrons, i.e., by induced mutual polarization giving rise to the weak van der Waals force. The crystal structure is usually the close-packed *fcc*. Because of the weak binding force, these solids melt and boil at very low temperatures. (Actually He remains liquid even at $T = 0\text{ K}$ for $P = 1\text{ bar}$ as a result of the very weak binding and the small atomic mass, which boosts the minimum atomic kinetic energy). Their main properties are as follows:

Cohesive energy, U_c : Very small (0.02 eV/atom for Ne 0.17 eV/atom for Xe).

Bulk modulus, B : Very small (0.01 Mbar for Ne, 0.018 Mbar for Kr).

Shear modulus, μ_s : Very small.

Electric resistivity, ρ_e : Practically infinite (these solids are insulators).

Magnetic response: Diamagnetic ($\chi_m < 0$ or $\mu_r < 1$).

Mechanical properties: Brittle.

3.2.6 Hydrogen Bonded Solids

These are molecular solids the molecules of which contain hydrogen(s); this (these) hydrogen(s) acts (act) as a bridge to bind the molecules together into a solid (ice is a typical example). It is the combination of *two unique* hydrogenic properties that is responsible for the uniqueness of the hydrogen bond: First, hydrogen cannot form an additional covalent bond with a nearby molecule, because its valence is only one; second, neither can it form an ionic bond with a nearby molecule because its large ionization energy does not favor the transfer of electron from hydrogen to a nearby molecule. As a result, there is no detachment of electrons from the hydrogen possessing molecule, but only an internal rearrangement within the molecule as in the van der Waals bond. However, because of its small size and its partial ionization (within the molecule), the hydrogen can come much closer to the neighboring molecule and exercise a stronger force than that of the van der Waals. Thus, the strength of the hydrogen bond is intermediate between the strong bonds (metallic, covalent, ionic) and the weak van der Waals bond. Typical values for the strength of a hydrogen bond are 0.1–0.3 eV per bond. This intermediate strength makes the hydrogen bond extremely important for biological structures and functions (Fig. 3.6). (Think of the two strands of DNA, which are held together by hydrogen bonds.)

In concluding this section, we mention that most of the elemental solids are metals (see Fig. 3.7), usually of gray silver color (gold and copper are well-known exceptions). Phosphorus (P), arsenic (As), sulfur (S), selenium (Se), tellurium (Te), chlorine (Cl), and bromine (Br) in their solid phase crystallize in complicated structures. For example, in the chalcogenides S, Se, and Te atoms held together by covalent bonds form chains; these chains folded and intertwined are connected to each other by weak van der Waals forces.

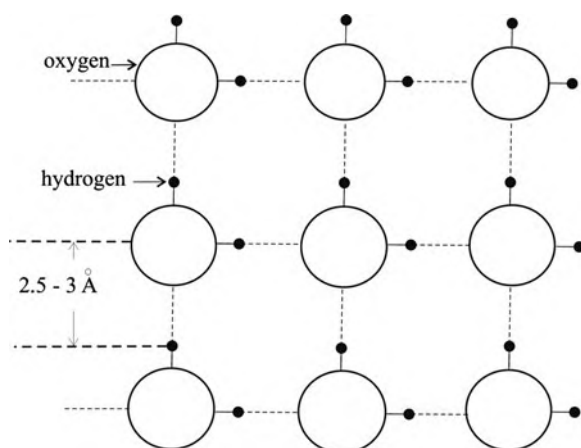


Fig. 3.6. Schematic, 2-D, presentation of ice, where each hydrogen of the H_2O molecule forms an extra bond (hydrogen bond, *dashed line*) with a nearby oxygen

PERIODIC TABLE OF THE ELEMENTS

* Estimates
** Argilum
*** Cassiopium

* LANTHANIDES

** ACTINIDES

Fig. 3.7. Most of the elemental solids are either simple (columns 1, 2 and 13, 14, 15 to the left of the heavy line) or transition (columns 3–12) metals; the upper right part of the periodic table consists of non-metals (columns 14–18 to the right of the shaded region); on both sides of the dividing line the solids are called metalloids (shaded region)

3.3 A Short Introduction to Crystal Structures

3.3.1 Some Basic Definitions

Before presenting the most common crystal structures, we need to give some definitions and introduce some concepts.

Three-dimensional Bravais lattice: It is the set of points in 3D space coinciding with the tips of the vectors

$$\mathbf{R}_n = n_1\boldsymbol{\alpha}_1 + n_2\boldsymbol{\alpha}_2 + n_3\boldsymbol{\alpha}_3, \quad (3.4)$$

where $\boldsymbol{\alpha}_1, \boldsymbol{\alpha}_2, \boldsymbol{\alpha}_3$ are three non-coplanar vectors, called *primitive vectors*, and n_1, n_2 , and n_3 take all integer values. Notice that different triads of vectors $\boldsymbol{\alpha}_1, \boldsymbol{\alpha}_2, \boldsymbol{\alpha}_3$ may correspond to the same Bravais lattice. For example, the triad $\boldsymbol{\alpha}_1, \boldsymbol{\alpha}_2, \boldsymbol{\alpha}_3$ and the triad $\boldsymbol{\alpha}_1, \boldsymbol{\alpha}_2, \boldsymbol{\alpha}'_3$, where $\boldsymbol{\alpha}'_3 = \boldsymbol{\alpha}_3 + \boldsymbol{\alpha}_1$, produce the same Bravais lattice. Bravais lattices can be defined not only in three-dimensional Euclidean space, but in any space of any dimensionality; For example, in Fig. 3.8 we show a portion of the general 2-D Bravais lattice such that $|\boldsymbol{\alpha}_1| \neq |\boldsymbol{\alpha}_2|$ and $\phi \neq \pi/2$ and $\phi \neq \phi_0$, where $\phi_0 = \cos^{-1}(|\boldsymbol{\alpha}_1/2|\boldsymbol{\alpha}_2|)$. (If $\phi = \phi_0$, the resulting lattice is centered rectangular, see Fig. 3.9).

Bravais lattices are classified into several *systems* according to their invariance under the operations of *translation*, *inversion* (with respect to a lattice point), *rotation* (with respect to an axis passing through a lattice point),

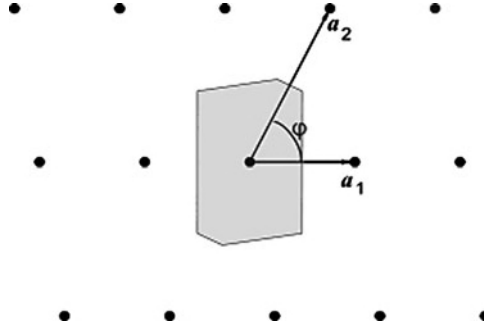


Fig. 3.8. The general type, called *oblique*, of the two dimensional Bravais lattice for which $|\alpha_1| \neq |\alpha_2|$ and $\phi \neq \pi/2$ and $\phi \neq \phi_0$ (see text). The shaded polygon is the so-called Wigner-Seitz primitive cell (see text)

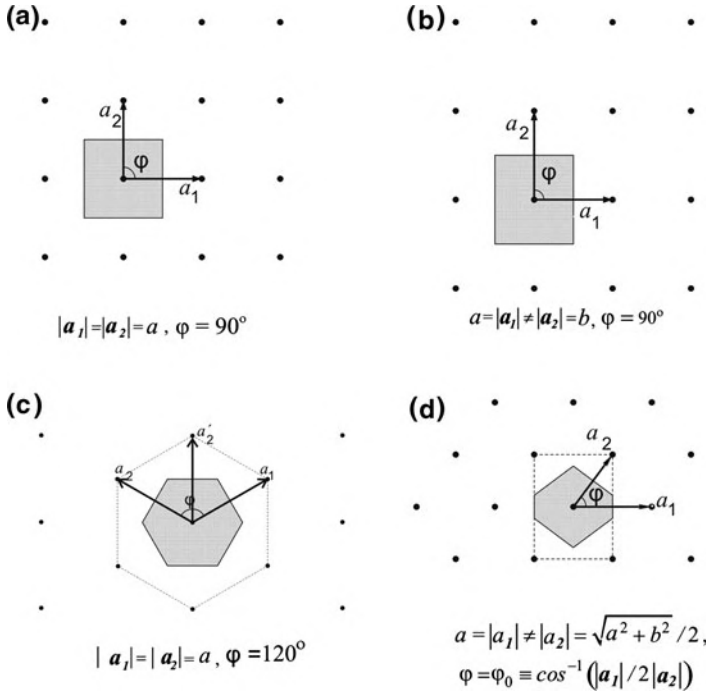


Fig. 3.9. The four special 2D types of Bravais lattices and the corresponding Wigner-Seitz primitive cells: (a) Square lattice (b) Rectangular lattice (c) Hexagonal lattice, and (d) Centered rectangular lattice. For the hexagonal lattice $\mathbf{a}_1 = (\sqrt{3}/2)a\mathbf{i} + (a/2)\mathbf{j}$ and $\mathbf{a}_2 = -(\sqrt{3}/2)a\mathbf{i} + (a/2)\mathbf{j}$. For case (d) $\mathbf{a}_1 = a\mathbf{i}$ and $\mathbf{a}_2 = (a/2)\mathbf{i} + (b/2)\mathbf{j}$

Table 3.1. The seven crystal systems and 14 Bravais lattices in three dimensions

	Simple	Base Centered	Body Centered	Face Centered
Cubic $a = b = c$ $\alpha = \beta = \gamma = 90^\circ$				
Tetragonal $a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$				
Orthorhombic $a \neq b \neq c \neq a$ $\alpha = \beta = \gamma = 90^\circ$				
Monoclinic $a \neq b \neq c \neq a$ $\alpha = \gamma = 90^\circ \neq \beta$				
Triclinic $a \neq b \neq c \neq a$ $\alpha, \beta, \gamma \neq 90^\circ$ $\alpha \neq \beta \neq \gamma \neq \alpha$				
Hexagonal $a = b \neq c$ $\alpha = \gamma = 90^\circ \neq \beta$ $\beta = 120^\circ$				
Rhombohedral $a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$				

reflection (with respect to a plane passing through a lattice point), and combinations of these.

For 2D Bravais lattices, there are four *systems* (the oblique one shown in Fig. 3.8, the square, the hexagonal, and the two *types* of rectangular all shown in Fig. 3.9) and five *types*; the two different types of rectangular lattice belong to the same system.

In three dimensions, there are *seven systems* and *14 types* of Bravais lattices (see Table 3.1).

Primitive cell: *It is a volume of space that, if translated by all vectors, $\mathbf{R}_n$, fills up completely all space without any overlap.*

Every primitive cell contains one and only one Bravais lattice point. Hence, its volume, V_p , equals one over the concentration, n_B , of lattice points.

$$V_p = \frac{1}{n_B} = |(\boldsymbol{\alpha}_1 \times \boldsymbol{\alpha}_2) \cdot \boldsymbol{\alpha}_3|. \quad (3.5)$$

The last expression in (3.5) is the volume of the parallelepiped defined by the three vectors $\boldsymbol{\alpha}_1$, $\boldsymbol{\alpha}_2$, $\boldsymbol{\alpha}_3$. Notice that this definition of primitive cell does not determine its shape. Besides the obvious choice of the parallelepiped determined by the primitive vectors $\boldsymbol{\alpha}_1$, $\boldsymbol{\alpha}_2$, $\boldsymbol{\alpha}_3$, there is another more symmetric choice widely used and called Wigner–Seitz cell.

Wigner–Seitz cell: *It is a primitive cell such that the distance of all its points from a central lattice point is smaller than (or equal to) the distance from any other lattice point.*

It follows from this definition that the Wigner–Seitz cell in 3-D is a polyhedron defined by the planes that bisect perpendicularly the vectors joining the central lattice point with all its neighboring lattice points.

The Wigner–Seitz cells for the five types of 2D Bravais lattice are shown in Figs. 3.8 and 3.9.

Unit cell: *It is a volume of space that, if translated by an infinite subset of the vectors $\mathbf{R}_n$, fills up completely all space without any overlap. The unit cell is chosen in such a way that on the one hand to have minimum volume and on the other hand to display simply and directly the full symmetry of the lattice. In some cases, the unit cell coincide with the primitive cell, i.e., the subset of $\mathbf{R}_n$ coincides with the whole set of $\mathbf{R}_n$.*

In the case of centered rectangular lattice shown in Fig. 3.9d, the unit cell is the rectangular defined by the dashed lines, while the primitive Wigner–Seitz cell is the enclosed hexagon. In all other cases shown in Figs. 3.8 and 3.9, the area of the primitive cell is the same as the area of the unit cell; hence, the latter is a primitive cell as well.

In general, the volume of the unit cell is equal to the volume of the primitive cell times a positive integer; the latter coincides with the number of lattice points belonging to the unit cell. For example, in the centered rectangular lattice, two lattice points belong to each unit cell (one at the center and $1/4$ at each of the four corners; the $1/4$ at each corner, because the point there is equally shared by four unit cells). Hence, the area of the unit cell in this case is twice the area of the primitive cell. Notice that it is easier to find the volume (or the area in 2D) of the primitive cell by finding first the volume of the unit cell and then dividing it by the number of lattice points belonging to the unit cell. The length (or the lengths) that defines (define) the size of the *unit cell* is (are) called *lattice constant* (s). For example, for the centered rectangular lattice shown in Fig. 3.9d, the lattice constants are $a = |\boldsymbol{\alpha}_1|$ and $b = 2\boldsymbol{\alpha}_2 \cdot \mathbf{j}$.

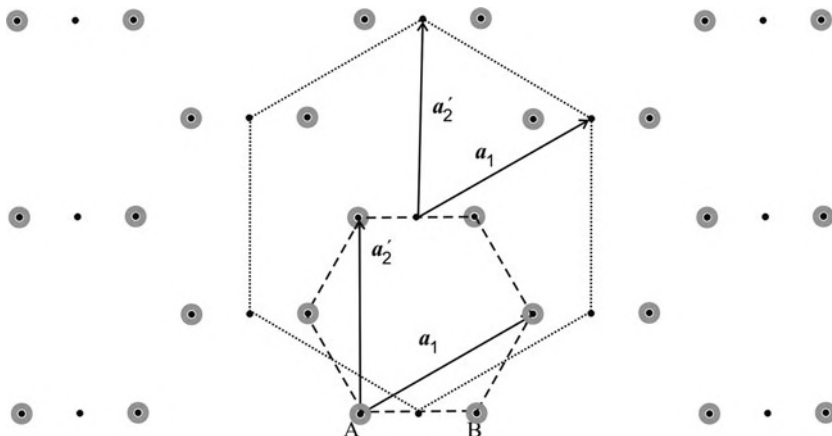


Fig. 3.10. The 2D honeycomb crystal structure (atoms are denoted by coated dots) results from the Bravais hexagonal lattice (*bare dots*) by placing at *each bare dot* two atoms (*coated dots*) as shown. The primitive vectors of the honeycomb structure are the same as those of the hexagonal lattice. The honeycomb lattice has two atoms (e.g., A and B) per primitive cell ($\mathbf{a}'_2 = \mathbf{a}_1 + \mathbf{a}_2$)

Simple crystal structures arise by placing the same type of atom (or the same type of molecule with the same orientation) at each point of a Bravais lattice.

Composite crystal structures arise by placing at each point of a Bravais lattice the same group of atoms in an identical manner so that the structures possess exactly the same translational symmetry, i.e., the same primitive vectors, as the underlined Bravais lattice.

An example of a composite crystal structure arises, if at each point of the hexagonal Bravais lattice shown in Fig. 3.9c we place symmetrically and parallel to the vector $\alpha_1 - \alpha_2$ two similar atoms at a distance $\alpha/\sqrt{3}$. The readers may verify that the resulting crystal structure is the honeycomb shown in Fig. 3.10. It must be pointed out that placing a group of atoms at each point of a Bravais lattice does not necessarily produce a composite crystal structure. For example, if at each point, $\mathbf{R}_n = (n_1\mathbf{i} + n_2\mathbf{j})\alpha$, of the square lattice in Fig. 3.9a we place a group of two identical atoms one at $\mathbf{R}_n$ and the other at $\mathbf{R}_n + (\mathbf{i} + \mathbf{j})\alpha/2$, we simply produce a square simple crystal structure with half lattice constant, i.e., with $\mathbf{R}_n = (n'_1\mathbf{i} + n'_2\mathbf{j})\alpha/2$ and not a composite crystal structure.

To avoid the creation of a new simple crystal structure in the process of placing a group of atoms at each lattice point, we must make sure that none of the vectors connecting *similar* atoms of the group is a primitive vector of the resulting structure. Groups having this property are called basis. Thus

$$\text{Composite crystal structure} = \text{Bravais lattice} + \text{Basis.} \quad (3.6)$$

3.3.2 Unit and Primitive Cells of Some Commonly Occurring 3-D Crystal Structures

Below the unit and the primitive cells of some common lattices are shown. In Figs. 3.11–3.14, pp. 64–66 some simple and/or commonly occurring (in metals) lattice structures are presented. In Table 3.2, p. 68 their basic properties are summarized. Some other lattice structures commonly occurring in semiconductors and ionic insulators are presented in Figs. 3.16–3.18, pp. 69–70; their properties are summarized in Table 3.3, p. 71.

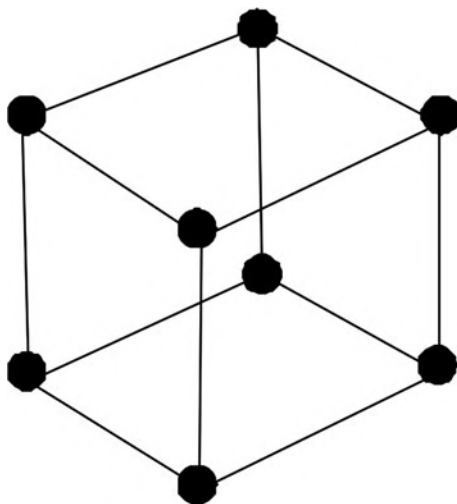


Fig. 3.11. Simple cubic, *sc*. The unit and the primitive cells coincide

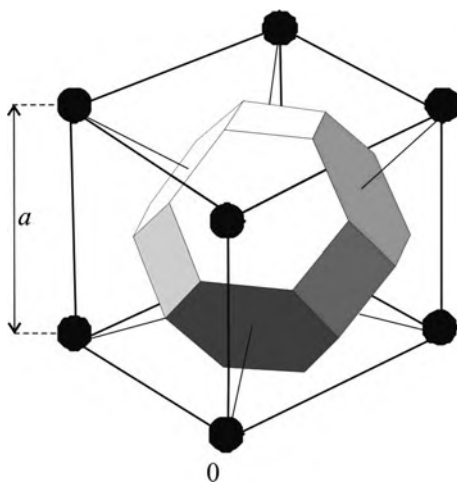


Fig. 3.12. Body centered cubic, *bcc*. The unit and the primitive cells are shown [SS75]

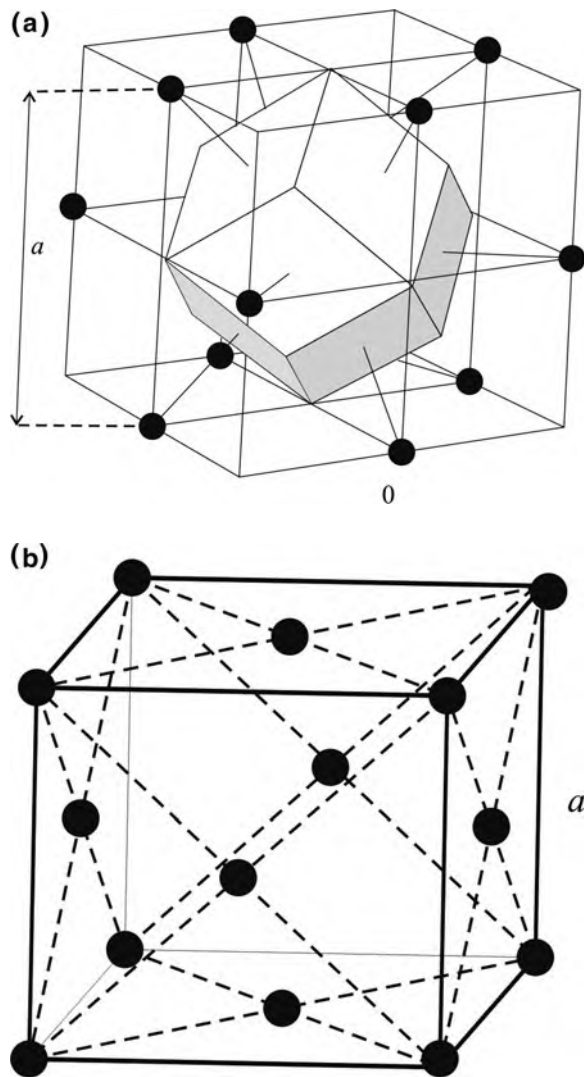


Fig. 3.13. (a) Face centered cubic, *fcc*. The unit and the primitive cells are shown [SS75]. (b) Another view of the *fcc* unit cell

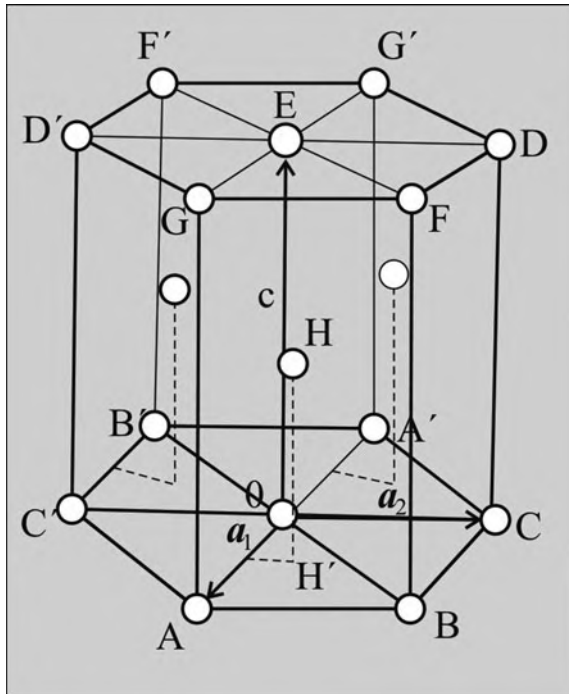


Fig. 3.14. Hexagonal close packed, *hcp*. In the ideal case $OE \equiv c$ is equal to $\sqrt{8/3}a$. $AB \equiv a$

The unit cell of the hexagonal close packed structure, *hcp*, is the regular hexagonal prism with the base $ABCA'B'C'$ and height, $c = \sqrt{8/3}a$, where $a = |\mathbf{a}_1| = |\mathbf{a}_2| = |\mathbf{AB}|$. In actual materials the ratio c/a may differ from the ideal value of $\sqrt{8/3} = 1.633$. A primitive cell of the *hcp* structure is the parallelepiped $OABCEGF$ the volume of which is $1/3$ of the volume of the unit cell. The *hcp* structure is a composite one with two atoms per *primitive* cell, one from the end points ($1/6$ at the points O , B , E , and F , and $1/12$ at the points A , C , D , and G), and the other at the point H with a projection H' at the center of the equilateral triangle OAB . $(HH') = c/2$ and $(OH') = a/\sqrt{3}$ (Fig. 3.14).

Both the *fcc* and *hcp* lattices can be constructed in a layer-by-layer manner by employing equal spheres, as shown in Fig. 3.15.

We mention also the *wurtzite structure*, which consists of two interpenetrating *hcp* sublattices displaced along the c -axis by an amount $u \cdot c$; one of the two sublattices is occupied by one type of atoms, e.g. Zn , while the other by another type, e.g. O . (See [SS82], p. 28). Each atom has four nearest neighbors of the opposite type; when $u = 3/8$ and $c/a = \sqrt{8/3}$, each atom is at equal distance from its four neighbors. Important materials such as AlN , SiC , and

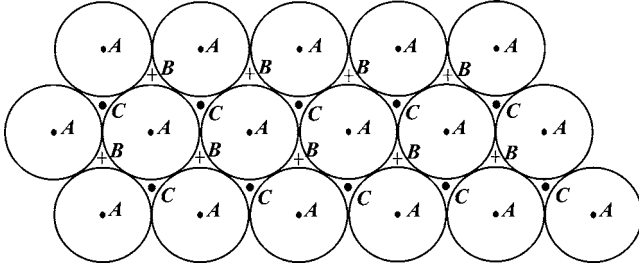


Fig. 3.15. Layer by layer construction of *fcc* or *hcp* lattices: The first layer consists of touching spheres centered at points A forming an hexagonal lattice; the spheres of the second layer are centered at points B (denoted by *crosses*). For the third layer there are two possibilities: (a) The spheres to be centered at points C; then the sequence is ABC which, if repeated periodically, ABCABCABC..., gives rise to an *fcc* lattice with the layers being normal to the direction (1, 1, 1). (b) The third layer of spheres to be centered above points A; then the sequence, if repeated, is ABABAB... and the resulting structure is *hcp* with the layers being normal to the *c*-axis

diluted magnetic semiconductors (see Sect. 20.6, pp. 590–591) crystallize in the wurtzite structure.

3.3.3 Systems and Types of 3D Bravais Lattices

See Table 3.1, p. 61

3.3.4 Crystal Planes and Miller Indices

A crystal plane is one that it is defined by three noncollinear lattice points. Any such plane includes an infinite number of lattice points. The three points defining a crystal plane can be chosen as the intersections of this plane with the three axes passing through the point (0, 0, 0) and parallel to the primitive vectors, $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$. Let us call these intersections $n_1\mathbf{a}_1$, $n_2\mathbf{a}_2$, and $n_3\mathbf{a}_3$. The *Miller indices* (hkl) of a crystal plane with respect to the primitive vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ are defined by the following relations:

$$h = \frac{C}{n_1}, \quad k = \frac{C}{n_2}, \quad \text{and} \quad \ell = \frac{C}{n_3}, \quad (3.7)$$

where the common constant C is such that h, k, ℓ are integers, usually the smallest (in absolute value) integers.

For cubic lattices $\mathbf{a}_1 = a\mathbf{i}$, $\mathbf{a}_2 = a\mathbf{j}$, $\mathbf{a}_3 = a\mathbf{k}$; for hexagonal lattices, a four Miller indices notation is used, ($hklm$), where $h = C/n_1$, $k = C/n_2$, $\ell = C/n_3$, $m = C/n_4$ and $n_1\mathbf{a}_1$, $n_2\mathbf{a}_2$, $-n'(\mathbf{a}_1 + \mathbf{a}_2)$, $n_3\mathbf{a}_3$ are the intersections of the crystal plane with the axes $\mathbf{a}_1$, $\mathbf{a}_2$, $-(\mathbf{a}_1 + \mathbf{a}_2)$, $\mathbf{a}_3$ defined in Table 3.2 (last column, fourth row). Simple geometry implies that $\ell = -(h + k)$.

Table 3.2. Properties of some common crystal structures

Features	Crystal structures			
	sc	bcc	fcc	Ideal hcp
Bravais lattice?	Yes	Yes	Yes	No
Similar atoms?	Yes	Yes	Yes	Yes or No
Lattice constant(s)	a	a	a	$c = \sqrt{\frac{8}{3}}a^a$
Primitive vectors	$\mathbf{a}_1 = a\mathbf{i}$	$\mathbf{a}_1 = \frac{a}{2}(\mathbf{j} + \mathbf{k} - \mathbf{i})$	$\mathbf{a}_1 = \frac{a}{2}(\mathbf{j} + \mathbf{k})$	$\mathbf{a}_1 = \frac{\sqrt{3}a}{2}\mathbf{i} + \frac{a}{2}\mathbf{j}$
	$\mathbf{a}_2 = a\mathbf{j}$	$\mathbf{a}_2 = \frac{a}{2}(\mathbf{k} + \mathbf{i} - \mathbf{j})$	$\mathbf{a}_2 = \frac{a}{2}(\mathbf{k} + \mathbf{i})$	$\mathbf{a}_2 = -\frac{\sqrt{3}a}{2}\mathbf{i} + \frac{a}{2}\mathbf{j}$
	$\mathbf{a}_3 = a\mathbf{k}$	$\mathbf{a}_3 = \frac{a}{2}(\mathbf{i} + \mathbf{j} - \mathbf{k})$	$\mathbf{a}_3 = \frac{a}{2}(\mathbf{i} + \mathbf{j})$	$\mathbf{a}_3 = c\mathbf{k}$
Basis of more than one atoms	–	–	–	$\mathbf{r}_1 = 0$ $\mathbf{r}_2 = \frac{2}{3}\mathbf{a}_1 + \frac{1}{3}\mathbf{a}_2 + \frac{1}{2}\mathbf{a}_3$
Wigner–Seitz primitive cell	cube	Truncated octahedron (14 faces) (see Fig. 3.12)	Regular rhombic dodecahedron (see Fig. 3.13)	Regular rhombic prism
Unit cell	Cube	Cube	Cube	Regular hexagonal prism
V_p	a^3	$a^3/2$	$a^3/4$	$\frac{\sqrt{3}}{2}a^2c = \sqrt{2}a^{3a}$
V_u/V_p	1	2	4	3
No of first nearest neighbors	6	8	12	12
No of second nearest neighbors	12	6	6	6
Distance of first neighbors, d	a	$\frac{\sqrt{3}}{2}a$	$\frac{\sqrt{2}}{2}a$	a^a
Distance of second neighbors, d_2	$\sqrt{2}a$	a	a	$\sqrt{2}a^a$
Volume fraction of touching spheres	$\pi/6 \approx 0.52$	$\sqrt{3}\pi/8 \approx 0.68$	$\sqrt{2}\pi/6 \approx 0.74$	$\sqrt{2}\pi/6 \approx 0.74$
Radius, r_α , of a sphere of volume V/N_α	$(3/4\pi)^{1/3}d \approx 0.62d$	$(1/\sqrt{3}\pi)^{1/3}d \approx 0.569d$	$(3\sqrt{2}/8\pi)^{1/3}d \approx 0.553d$	$(3\sqrt{2}/8\pi)^{1/3}d \approx 0.553d$

^aThis equality may be violated in real *hcp* lattices
 V_p the volume of primitive cell, V_u the volume of unit cell

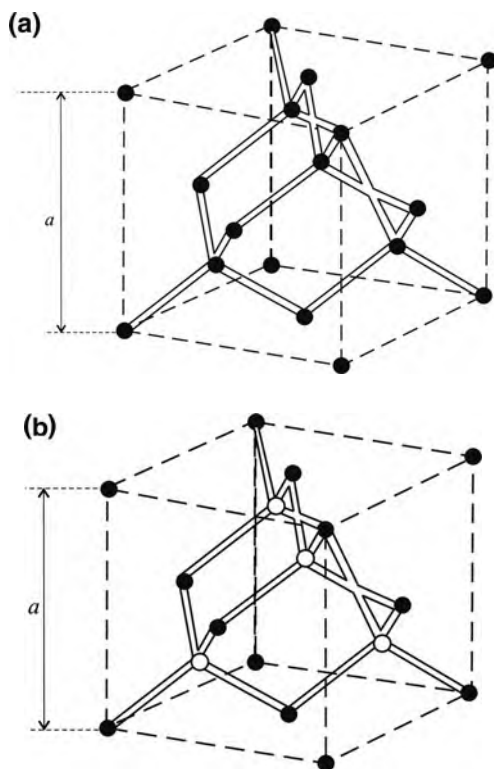


Fig. 3.16. (a) The crystal structure of *diamond*. It is a composite one consisting of an fcc Bravais lattice with two similar atoms per primitive cell one at the origin and the other at the point, $(\frac{a}{4}, \frac{a}{4}, \frac{a}{4})$. (b) The crystal structure of cubic *zinc sulfide* (ZnS , zinc blende) is as in diamond with the only difference that the basis of the two atoms consists of different atoms (one could be Zn and the other S)

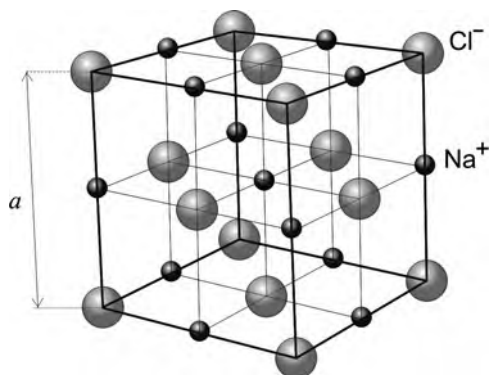


Fig. 3.17. The *sodium chloride* structure is created by placing Na^+ and Cl^- ions alternately in a simple cubic structure so that each Na^+ is surrounded by six Cl^- and vice versa. The Bravais lattice is fcc and the basis consists of two different ions per primitive cell one at the origin and the other at $(\frac{a}{2}, \frac{a}{2}, \frac{a}{2})$. One cubic unit cell is shown which contains a total of eight ions

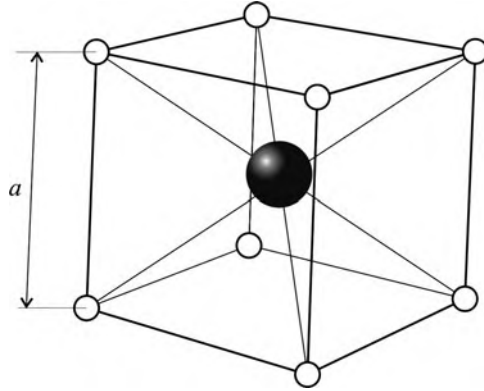


Fig. 3.18. The *cesium chloride* structure is created by placing a Cl^- ion in the central position of a *bcc* lattice; the eight corners of the *bcc* unit cell are occupied by Cs^+ . The Bravais lattice is *sc* and the basis consists of two different ions per primitive cell, one at the origin and the other at $(\mathbf{i} + \mathbf{j} + \mathbf{k})a/2$. One cubic unit cell is shown which contains in total two ions

Theorem. *The equation of the set of parallel crystal planes corresponding to the Miller indices (h, k, ℓ) with respect to the coordinate system defined by the primitive vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ is as follows:*

$$hx + ky + \ell z = \text{constant}, \quad (3.8)$$

where the constant is an integer (since for any lattice point on the crystal plane, x, y, z are integers). For two consecutive parallel planes, the constant in (3.8) changes by the least possible amount, i.e., by one.

Problem 3.1t. Prove (3.8)

Hint: Show that $\mathbf{R} - \mathbf{R}_1$ is perpendicular to $(\mathbf{R}_1 - \mathbf{R}_2) \times (\mathbf{R}_1 - \mathbf{R}_3)$, where $\mathbf{R} = x\mathbf{a}_1 + y\mathbf{a}_2 + z\mathbf{a}_3$, $\mathbf{R}_1 = (C/h)\mathbf{a}_1$, $\mathbf{R}_2 = (C/k)\mathbf{a}_2$, and $\mathbf{R}_3 = (C/\ell)\mathbf{a}_3$.

3.4 Bloch Theorem, Reciprocal Lattice, Bragg Planes, and Brillouin Zones

3.4.1 Bloch Theorem

All the solutions of a wave equation in a *homogeneous medium* can have the form of an exponential *plane wave* of spatial part, $\psi_{\mathbf{k}}(\mathbf{r}) = A \exp(i\mathbf{k} \cdot \mathbf{r})$; A is a normalization constant, $\mathbf{k}$ is the wavevector, and $\hbar\mathbf{k}$ is the momentum of the quantum of this wave. For such a solution, we have the relation

$$\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k} \cdot \mathbf{R}} \psi_{\mathbf{k}}(\mathbf{r}), \quad (3.9)$$

Table 3.3. Properties of some common crystal structures

Features	Crystal structures			
	Diamond crystal structure	Zinc sulfide or Zinc blende structure	NaCl structure	CsCl structure
Bravais lattice?	No	No	No	No
Similar atoms?	Yes	No	No	No
Lattice constant(s)	a	a	a	a
Primitive vectors	As in fcc	As in fcc	As in fcc	As in sc
Basis of more than one atoms	$\mathbf{r}_1 = 0$	$\mathbf{r}_{Zn} = 0$	$\mathbf{r}_{Na} = 0$	$\mathbf{r}_{Cs} = 0$
	$\mathbf{r}_2 = \frac{a}{4}(\boldsymbol{\iota} + \boldsymbol{j} + \boldsymbol{k})$	$\mathbf{r}_S = \frac{a}{4}(\boldsymbol{\iota} + \boldsymbol{j} + \boldsymbol{k})$	$\mathbf{r}_{Cl} = \frac{a}{2}(\boldsymbol{\iota} + \boldsymbol{j} + \boldsymbol{k})$	$\mathbf{r}_{Cl} = \frac{a}{2}(\boldsymbol{\iota} + \boldsymbol{j} + \boldsymbol{k})$
Wigner-Seitz primitive cell	As in fcc	As in fcc	As in fcc	As in sc
Unit cell	Cube	Cube	Cube	Cube
V_p	$a^3/4$	$a^3/4$	$a^3/4$	a^3
V_u/V_p	4	4	4	1
No of first nearest neighbors	4	4	6	8
No of second nearest neighbors	12	12	12	6
Distance of first neighbors, d	$\frac{\sqrt{3}}{4}a$	$\frac{\sqrt{3}}{4}a$	$a/2$	$\frac{\sqrt{3}}{2}a$
Distance of second neighbors, d_2	$\frac{\sqrt{2}}{2}a$	$\frac{\sqrt{2}}{2}a$	$\frac{\sqrt{2}}{2}a$	a
Volume fraction of touching spheres	$\sqrt{3}\pi/16 \approx 0.34$	$\sqrt{3}\pi/16 \approx 0.34$	$\pi/6 \approx 0.52$	$3\pi/8 \approx 0.68$
Radius, r_α , of a sphere of volume V/N_α	$(2/\sqrt{3}\pi)^{1/3}d \simeq 0.716d$	$(2/\sqrt{3}\pi)^{1/3}d \approx 0.716d$	$(3/4\pi)^{1/3}d \simeq 0.62d$	$(1/\sqrt{3}\pi)^{1/3}d \simeq 0.569d$
V_p the volume of primitive cell, V_u volume of unit cell				

where $\mathbf{R}$ is any vector in real space. In words, (3.9) says that in homogeneous media, there is a complete set of solutions having the following property:

Any translation in real space from $\mathbf{r}$ to $\mathbf{r}' = \mathbf{r} + \mathbf{R}$, where $\mathbf{R}$ is *arbitrary*, multiplies the solution by a factor $\exp(i\mathbf{k} \cdot \mathbf{R})$. This property stems from the fact that in a homogeneous medium, *any* translation from $\mathbf{r}$ to $\mathbf{r}' = \mathbf{r} + \mathbf{R}$ leaves the wave equation invariant.

This feature can be generalized to waves propagating in periodic media (the periodicity of the latter is always characterized by a Bravais lattice): In periodic media, there is a complete set of wave equation solutions having the following property: *Any* translation connecting *equivalent points* in space from $\mathbf{r}$ to $\mathbf{r}' = \mathbf{r} + \mathbf{R}_n$ (where, now, $\mathbf{R}_n$ is not completely arbitrary, but it is restricted to any of the Bravais lattice vectors characterizing the periodicity of the medium) multiplies the solution by $\exp(i\mathbf{k} \cdot \mathbf{R}_n)$:

$$\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}_n) = e^{i\mathbf{k} \cdot \mathbf{R}_n} \psi_{\mathbf{k}}(\mathbf{r}), \quad (3.10)$$

where $\mathbf{k}$ is called *crystal wavevector* and $\hbar\mathbf{k}$ is called *crystal momentum*.⁴ Again, this property stems from the fact that any translation by a vector of the Bravais lattice leaves the wave equation invariant. Equation (3.10) is called Bloch's theorem⁵; it can be recast in an equivalent form

$$\psi_{\mathbf{k}}(\mathbf{r}) = w_{\mathbf{k}}(\mathbf{r}) e^{i\mathbf{k} \cdot \mathbf{r}}, \quad (3.11)$$

where $w_{\mathbf{k}}(\mathbf{r})$ is a periodic function with the same periodicity as that of the medium, i.e.,

$$w_{\mathbf{k}}(\mathbf{r} + \mathbf{R}_n) = w_{\mathbf{k}}(\mathbf{r}). \quad (3.12)$$

The proof of Bloch theorem is given in Chap. 11. In Problem (3.10), the readers are asked to show how (3.12) follows from (3.10) and the definition (3.11). In Table 3.4 we compare the Bloch waves with plane waves and we point out the similarities and the differences. It must be stressed that propagation in a perfect periodic medium is free-like (since the average velocity of a Bloch wave is in general non-zero), and as a result, the mobility is in general infinite as in the case of zero force.

3.4.2 Reciprocal Lattice

The need to introduce the concept of the reciprocal lattice stems from Bloch's theorem as expressed in (3.10). Indeed, if $\mathbf{k}$ is replaced by $\mathbf{k}' = \mathbf{k} + \mathbf{G}_m$ where $\mathbf{G}_m$ is such that $\mathbf{R}_n \cdot \mathbf{G}_m = 2\pi \times \text{integer}$ (for any $\mathbf{R}_n$), then

$$e^{i\mathbf{k} \cdot \mathbf{R}_n} = e^{i\mathbf{k}' \cdot \mathbf{R}_n}, \quad (3.13)$$

which implies that $\mathbf{k}$ and $\mathbf{k}'$ correspond to the same solution.

⁴ Notice that the $\psi_{\mathbf{k}}(\mathbf{r})$ in a periodic medium (in contrast to the case of a homogeneous medium) is *not* an eigefunction of the momentum.

⁵ Floquet has proved this theorem in the 1-D case before Bloch.

Table 3.4. Comparison of plane and Bloch electronic waves

Property	Plane wave	Bloch wave
Force	Zero	Non zero; periodic function of $\mathbf{r}$
Potential $\mathcal{V}(\mathbf{r})$	Constant, independent of $\mathbf{r}$	Periodic function of $\mathbf{r}$
Wave form	$A \exp(i\mathbf{k} \cdot \mathbf{r})$	$w_{n,\mathbf{k}}(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r})$
Amplitude	A is constant, independent of $\mathbf{r}$	$w_{n,\mathbf{k}}(\mathbf{r})$ is a periodic function of $\mathbf{r}$ with the same periodicity as $\mathcal{V}(\mathbf{r})$
$\mathbf{k}$ varies over	The whole $\mathbf{k}$ space	A Brillouin zone, usually the first one
Other parameter characterizing the wave	None	The natural number $n = 1, 2, 3, \dots$ called band index. It compensates for the restriction of $\mathbf{k}$ in a single BZ.
Relation of $\mathbf{k}$ to the momentum $\mathbf{p}$ and the velocity $\mathbf{v}$	$\mathbf{p} = \hbar\mathbf{k}$, $\mathbf{v} = \hbar\mathbf{k}/m_e$	The quantity, $\hbar\mathbf{k}$, in spite of being called crystal momentum, is not the momentum and $\hbar\mathbf{k}/m_e$ is not the velocity. Bloch waves are not eigenfunctions of either $\hat{\mathbf{p}}$ or $\hat{\mathbf{v}}$.
Translation property	$\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = \exp(i\mathbf{k} \cdot \mathbf{R}) \psi_{\mathbf{k}}(\mathbf{r})$ for any $\mathbf{R}$	$\psi_{n,\mathbf{k}}(\mathbf{r} + \mathbf{R}_l) = \exp(i\mathbf{k} \cdot \mathbf{R}_l) \cdot \psi_{n,\mathbf{k}}(\mathbf{r})$ only for vectors $\mathbf{R}_l$ of the direct Bravais lattice
Dispersion relation connecting energy and $\mathbf{k}$	$\varepsilon = \frac{\hbar^2 k^2}{2m_e}$	$\varepsilon_n(\mathbf{k})$ is, in general, a complicated function of $\mathbf{k}$ for each n , to be determined by solving Schrödinger's equation.
Average velocity	$\langle \mathbf{v} \rangle = \mathbf{v} = \hbar\mathbf{k}/m_e$	$\langle \mathbf{v}_n \rangle = \frac{1}{\hbar} \frac{\partial \varepsilon_n(\mathbf{k})}{\partial(\mathbf{k})}$
Density of states	$\rho(\varepsilon) \sim \varepsilon^{1/2}$	$\rho(\varepsilon)$ is, in general, a complicated, nonmonotonic function of ε , with gaps and van Hove singularities different for each solid.
Finding the amplitude of the wave	$A = \frac{1}{\sqrt{V}}$	To find $w_{n,\mathbf{k}}(\mathbf{r})$ one has to solve the PDE resulting from Schrödinger's equation by substituting $\psi_{n,\mathbf{k}}(\mathbf{r}) = w_{n,\mathbf{k}}(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r})$.
Metal or insulator?	Always metal	Metal when the number of valence electrons per primitive cell is odd; otherwise either metal, or insulator or semiconductor depending on the particular solid.
Number of states (per spin) in the $\mathbf{k}$ -space volume element $\Delta^3 k$	$\frac{V \Delta^3 k}{(2\pi)^3}$	$\frac{V \Delta^3 k}{(2\pi)^3}$
Equation of motion	$\hbar \frac{d\mathbf{k}}{dt} = \mathbf{F}_{\text{tot}}$	$\hbar \frac{d\mathbf{k}}{dt} = \mathbf{F}_{\text{addit}}$
Mobility	Infinite	Infinite

Definition. *The set of vectors, $\mathbf{G}_m$, in $\mathbf{k}$ -space that satisfies the relation*

$$\mathbf{G}_m \cdot \mathbf{R}_n = 2\pi \times \text{integer}, \quad (3.14)$$

for every vector $\mathbf{R}_n = n_1\boldsymbol{\alpha}_1 + n_2\boldsymbol{\alpha}_2 + n_3\boldsymbol{\alpha}_3$ of a Bravais lattice is called the *reciprocal lattice of this Bravais lattice* $\{\mathbf{R}_n\}$; the latter is referred to as the *direct lattice* to be distinguished from the reciprocal.

Theorem. *The reciprocal lattice of a Bravais lattice is also a Bravais lattice, of the form*

$$\mathbf{G}_m = m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + m_3\mathbf{b}_3, \quad (3.15)$$

where m_1, m_2, m_3 are any integers and the basic vectors $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ can be expressed in terms of $\boldsymbol{\alpha}_1, \boldsymbol{\alpha}_2, \boldsymbol{\alpha}_3$ of the direct lattice as follows

$$\mathbf{b}_1 = 2\pi \frac{\boldsymbol{\alpha}_2 \times \boldsymbol{\alpha}_3}{(\boldsymbol{\alpha}_1 \boldsymbol{\alpha}_2 \boldsymbol{\alpha}_3)}, \quad \mathbf{b}_2 = 2\pi \frac{\boldsymbol{\alpha}_3 \times \boldsymbol{\alpha}_1}{(\boldsymbol{\alpha}_1 \boldsymbol{\alpha}_2 \boldsymbol{\alpha}_3)}, \quad \mathbf{b}_3 = 2\pi \frac{\boldsymbol{\alpha}_1 \times \boldsymbol{\alpha}_2}{(\boldsymbol{\alpha}_1 \boldsymbol{\alpha}_2 \boldsymbol{\alpha}_3)}, \quad (3.16)$$

where $(\boldsymbol{\alpha}_1 \boldsymbol{\alpha}_2 \boldsymbol{\alpha}_3) \equiv \boldsymbol{\alpha}_1 \cdot (\boldsymbol{\alpha}_2 \times \boldsymbol{\alpha}_3) = \boldsymbol{\alpha}_2 \cdot (\boldsymbol{\alpha}_3 \times \boldsymbol{\alpha}_1) = \boldsymbol{\alpha}_3 \cdot (\boldsymbol{\alpha}_1 \times \boldsymbol{\alpha}_2)$.

The proof of this theorem is based on the rather obvious relation

$$\boldsymbol{\alpha}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij}, \quad (3.17)$$

from which it follows that $\mathbf{R}_n \cdot \mathbf{G}_m = 2\pi (n_1 m_1 + n_2 m_2 + n_3 m_3) = 2\pi \times \text{integer}$, since n_1, n_2, n_3 and m_1, m_2, m_3 are any integers; thus for integers m_1, m_2, m_3 , (3.14) is satisfied; while it is not satisfied for any non-integer choice of m_1, m_2, m_3 (e.g., if m_i is a noninteger, we can choose for $\mathbf{R}_n = \boldsymbol{\alpha}_i$; then $\mathbf{G}_m \cdot \mathbf{R}_n = 2\pi m_i$, which does not satisfy the defining relation (3.14)), if m_i is non-integer.

Theorem. *The reciprocal of the reciprocal is the direct lattice.*

This is obvious from the defining equation (3.14), which implies that by taking $\{\mathbf{G}_m\}$ as the original lattice, $\{\mathbf{R}_n\}$ would be its reciprocal.

Theorem. *The product of the volumes $V_p V_p^{(r)}$ of the primitive cells of the direct and the reciprocal lattice is equal to $(2\pi)^3$.*

$$V_p V_p^{(r)} = (2\pi)^3. \quad (3.18)$$

This follows immediately from the relations $V_p = (\boldsymbol{\alpha}_1 \boldsymbol{\alpha}_2 \boldsymbol{\alpha}_3)$, $V_p^{(r)} = (\mathbf{b}_1 \mathbf{b}_2 \mathbf{b}_3)$, (3.16), and $(\mathbf{A} \times \mathbf{B}) \times (\mathbf{B} \times \mathbf{C}) = \mathbf{B}(\mathbf{A} \cdot \mathbf{C})$ for any vectors $\mathbf{A}, \mathbf{B}, \mathbf{C}$.

Combining (3.18) with the general relation $R(E) = V V_\kappa / (2\pi)^3$ for the number of states, we find that the number of states, R_p , (more accurately, the number of $\mathbf{k}$ -points) in any primitive cell of the reciprocal lattice is equal to the total number, N_p , of primitive cells in the crystal (since $V = N_p V_p$).

We conclude by pointing out that every perfect crystal is rigidly associated with two lattices: the direct in real space and the reciprocal in $\mathbf{k}$ -space. If the crystal is rigidly rotated, so do the two lattices.

Theorem. *The reciprocal of a bcc lattice is an fcc lattice and vice versa.*

The proof is left to the readers.

Theorem. *The vector $\mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$ of the reciprocal lattice is perpendicular to the crystal planes of the direct lattice characterized by the Miller indices (hkl) .*

Proof. Three non-collinear points on one of these parallel planes are as follows: $\mathbf{R}_1 = (n/h)\mathbf{a}_1$, $\mathbf{R}_2 = (n/k)\mathbf{a}_2$, and $\mathbf{R}_3 = (n/l)\mathbf{a}_3$. Hence, the vector $\mathbf{R}_1 - \mathbf{R}_2$ and $\mathbf{R}_1 - \mathbf{R}_3$ are two vectors on one of the (hkl) planes. However, $\mathbf{G} \cdot (\mathbf{R}_1 - \mathbf{R}_2) = 0$ and $\mathbf{G} \cdot (\mathbf{R}_1 - \mathbf{R}_3) = 0$ on account of (3.17) and $\mathbf{G}$ being $h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$. It follows that $\mathbf{G}$ is perpendicular to the planes (hkl) .

3.4.3 Bragg Planes

The concept of Bragg planes is necessitated, as we shall see later, when we analyze the scattering of a plane wave by a crystalline solid. It is also needed in order to define the so-called Brillouin zones (BZs).

Definition. *Bragg planes are all those that bisect perpendicularly the vectors $\mathbf{G}_m$ of the reciprocal lattice.*

Thus, the points $\mathbf{k}$ on the Bragg plane corresponding to the reciprocal vector $\mathbf{G}_m$ satisfy the relation

$$\frac{\mathbf{k} \cdot \mathbf{G}_m}{|\mathbf{G}_m|} = \frac{|\mathbf{G}_m|}{2}, \quad (3.19)$$

or equivalently

$$2\mathbf{k} \cdot \mathbf{G}_m = G_m^2. \quad (3.20)$$

3.4.4 Brillouin Zones

Definition. *The 1st BZ is the Wigner–Seitz primitive cell of the reciprocal lattice, or equivalently, it is the set of points in $\mathbf{k}$ -space that can be reached from the origin ($\mathbf{k} = 0$) without crossing any Bragg plane.*

In Fig. 3.19 we show the first BZs for some common 2D direct lattices; in Fig. 3.20 the 1st BZs for the direct lattices *sc*, *bcc*, *fcc*, and *hcp* are displayed. The capital letters denote specific high symmetry points on the boundary of the first BZ following a standardized notation (the origin, $\mathbf{k} = 0$ is denoted by Γ); similarly, Greek capital letters are used to denote specific straight segments in the 1st BZ for each lattice.

In Fig. 3.21 we show the first, the second, the third, and the fourth BZs of a square direct lattice. Notice that the BZs (except the first one) consist of disjoint pieces, which through translations by appropriate vectors of the reciprocal lattice can fully cover without overlaps the first BZ.

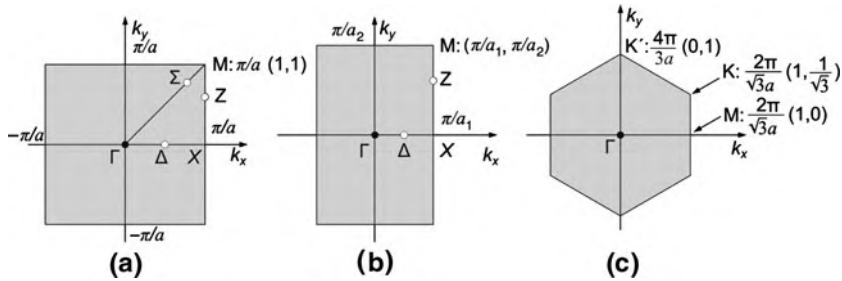


Fig. 3.19. First Brillouin Zones (BZs) for the following 2D direct lattices: (a) square of lattice constant a ; (b) rectangular of lattice constants, a_1, a_2 ; and (c) hexagonal of lattice constant a . The axes, k_x, k_y are parallel to the axes, x, y of the direct lattice. (See Fig. 3.9.)

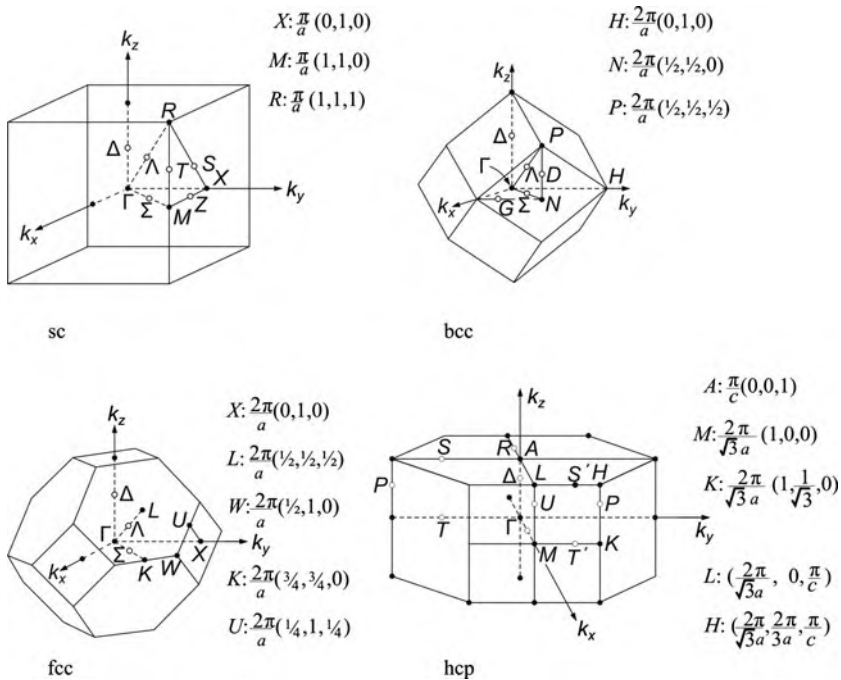


Fig. 3.20. The first BZs for the following 3D direct lattices: *sc*, *bcc*, *fcc*, and *hcp*. The axes, k_x, k_y, k_z are parallel to the axes x, y, z of the corresponding direct lattices. The coordinates of various points identified by capital letters are shown

Definition. The n th BZ is the set of points in $\mathbf{k}$ -space that can be reached from the origin ($\mathbf{k} = 0$) by crossing a minimum of $n - 1$ Bragg planes, or equivalently, the n th BZ is the set of points in $\mathbf{k}$ -space, that do not belong to the $(n - 2)$ th BZ and they can be reached from $(n - 1)$ th BZ by crossing a minimum of one Bragg plane.

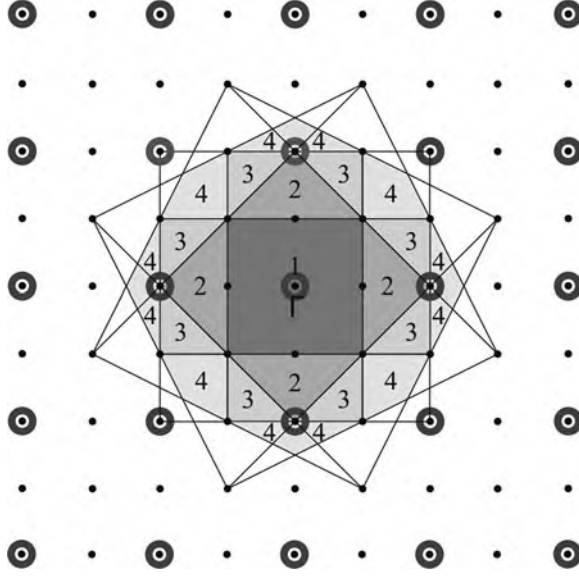


Fig. 3.21. Construction of the first four BZs for a square direct lattice. The steps for this construction are: (a) Find the basic vectors, $\mathbf{b}_1, \mathbf{b}_2$ of the reciprocal lattice. (b) Draw the vectors $\mathbf{G}_m = m_1\mathbf{b}_1 + m_2\mathbf{b}_2$ ($m_1, m_2 = 0, \pm 1, \pm 2, \dots$); the tips of these vectors are denoted by a coated dot. (c) Draw straight lines bisecting the vectors $\mathbf{G}_m$ perpendicularly. By 2, 3, 4 we denote the polygons which make up the second (four triangles), the third (eight triangles), and the fourth (eight triangles and four tetragons) BZs. The first BZ is the central square

A practical way to find out to which BZ an arbitrary chosen point $\mathbf{k}$ belongs is as follows: Consider all spheres (circles in 2-D) of radius $|\mathbf{k}|$ and centers at the tips of the reciprocal vectors $\mathbf{G}_m$ (except $\mathbf{G}_m = 0$). Then, if $\mathbf{k}$ is in the interior of exactly $n - 1$ spheres, $\mathbf{k}$ belongs to the interior of the n th BZ; if $\mathbf{k}$ is in the interior of exactly $n - 1$ spheres and at the surface of m additional spheres, then $\mathbf{k}$ belongs to the boundaries of the n th, $(n + 1)$ th, $\dots$, $(n + m)$ th BZs.

3.5 Key Points

- The rich variety of various types of solids can be classified in two main categories: hard matter and soft matter.
- Solids employ one or more of five elementary bonds to keep their atoms together: (a) metallic bond; (b) covalent bond; (c) ionic bond; (d) van der Waals bond; and (e) hydrogen bond. The origin of all these bonds is the electrostatic forces in combination with the quantum kinetic energy of electrons.

- The periodic arrangement of atoms in solids involves certain concepts such as Bravais lattice, primitive cell, unit cell, Wigner-Seitz cell, and classification of lattices according to their symmetries.
- The characteristics of some simple and common lattices (*bcc*, *fcc*, *hcp*, diamond, zincblende, sodium chloride, caesium chloride) are tabulated.
- The Bloch theorem states that a complete set of solutions of the wave equation in a periodic medium can always have the following basic translational property:

$$\psi(\mathbf{r} + \mathbf{R}_n) = \exp(i\mathbf{k} \cdot \mathbf{R}_n) \psi(\mathbf{r}),$$

where $\mathbf{R}_n$ is any vector of the Bravais lattice. Similarities and differences between the Bloch waves and plane waves are presented in Table 3.4.

- Bloch waves remain invariant if $\mathbf{k}$ is replaced by $\mathbf{k} + \mathbf{G}_m$, where $\mathbf{G}_m$ is any vector satisfying the following relation:

$$\mathbf{G}_m \cdot \mathbf{R}_n = 2\pi \times \text{integer, for any } \mathbf{R}_n.$$

The vectors $\mathbf{G}_m$ form a Bravais lattice called the reciprocal of the lattice $\{\mathbf{R}_n\}$. In the reciprocal lattice we define the concepts of Bragg planes and BZs, especially the first BZ.

3.6 Questions and Problems

- 3.1s Estimate the viscosity of water under normal conditions by using (3.1). The experimental value is 0.001 kg/ms
- 3.2s Consider two molecular solids: ice (H_2O) and dry ice (CO_2). Which one has larger cohesive energy? Why?
- 3.3 For the lattices in Tables 3.2 and 3.3, calculate in terms of a and d :
- The volume, V_p , of the primitive cell
 - The nearest neighbor distance, d
 - The volume fraction of touching spheres
 - The quantity r_a
- 3.4 Consider a periodic one-dimensional potential of period a consisting of equally-spaced delta functions (Dirac comb):

$$V(x) = \frac{\hbar^2}{mb} \sum_{n=-\infty}^{+\infty} \delta(x + na).$$

Each eigenstate of a particle of mass m moving in this potential is characterized by its eigenenergy, E , written for convenience as $E \equiv \hbar^2 k_0^2 / 2m$, and its crystal momentum (over $\hbar$) k . Using Bloch's theorem, show that the E vs. k relation is given implicitly by the following equation

$$\cos ka = \cos k_0 a + \frac{1}{bk_0} \sin k_0 a, \quad k_0 \equiv \sqrt{2mE/\hbar^2}. \quad (3.21)$$

Choose $b = a/5$ and plot the rhs of (3.21) as a function of $k_0 a$. For the values of $k_0 a$ for which this rhs is larger than one, there are no solutions satisfying the boundary conditions at both $\pm\infty$ (because, then, k is a complex number). Thus there are energy regions (gaps) where no solution exists. (See the book by Flügge, pp. 66–67.

- 3.5 Prove (3.17)
- 3.6 Prove that the reciprocal lattice of the reciprocal is the direct lattice by repeated use of (3.16)
- 3.7 Prove (3.18)
- 3.8 Prove that the reciprocal of a *bcc* is an *fcc* lattice and vice versa
- 3.9 Verify the coordinates of the points of the first Brillouin zones shown in Fig. 3.20
- 3.10 Show (3.12) by employing the relation (3.10) and the definition (3.11)
- 3.11 Show from Schrödinger's equation and (3.9) that the equation satisfied by w_{nk} is as follows

$$\hat{H}_{\mathbf{k}} w_{nk} = \varepsilon_{nk} w_{nk},$$

where

$$\hat{H}_{\mathbf{k}} = \frac{\hbar^2}{2m} [-\nabla^2 - 2i\mathbf{k} \cdot \nabla + k^2 + \mathcal{V}] \quad (3.22)$$

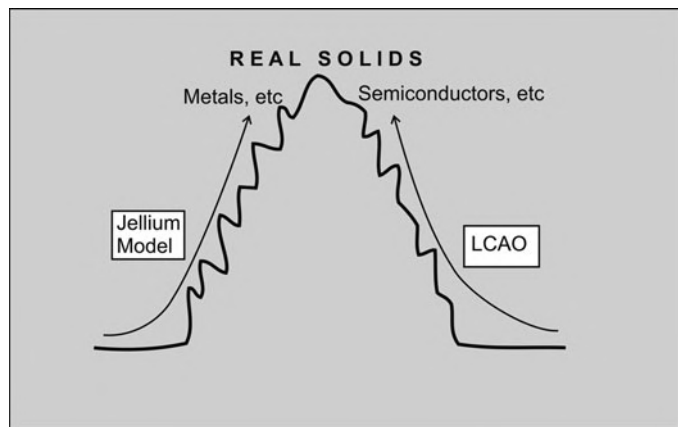
- 3.12s Show that translational symmetry implies that the only possible rotations compatible with this symmetry are $2\pi/n$ where $n = 1, 2, 3, 4, 6$

Further Reading

- R. A. L. Jones, *Soft condensed matter*, [M68].
- W. Hamley, *Introduction to Soft Matter: Polymer, Colloids, Amphiphiles, and Liquid Crystals*, [M69] and [M72].
- G. Strobl, *The Physics of Polymers*, [M70].
- P.G. de Gennes, *The physics of Liquid Crystals*, [M71].

Most of the Solid State books cover the topics of crystal lattices, reciprocal lattices, and Brillouin zones. Especially, the symmetry notation and classification of lattices are given in more detail than here.

Two Simple Models for Solids



The Jellium Model and Metals I: Equilibrium Properties

Summary. The simple Jellium Model (JM) for a solid, according to which valence electrons are detached from each atom and the resulting ions are replaced by a uniform background, is presented. The valence electrons, being free of force, spread themselves uniformly over the whole volume of the solid. Kinetic and potential energies as well as other relevant quantities, such as densities of electronic and phononic states, are obtained within this model. Based on these results, several thermodynamic quantities such as bulk modulus, specific heats, and thermal expansion coefficients are calculated and compared with the experimental data.

Comments

In this chapter, to a large extent, we rederive in a more detailed way (yielding more realistic values for the numerical factors left out before) the results we have already obtained in Chaps. 1 and 2 (there we employed a few general principles and dimensional analysis). Thus, within the simplistic Jellium Model (JM), we recalculate the electronic kinetic and potential energy, the corresponding pressures, the bulk modulus, the ionic eigenmodes of oscillation (which are the acoustic waves), the specific heat and the thermal expansion coefficient. Justifications for this rather lengthy rederivation of relations (obtained before by a simpler and physically more transparent way) are: (a) Material-specific, and hence, more realistic values for these quantities; and (b) the introduction of some concepts the usefulness and the applicability of which extends beyond the JM. Among them are the number, $R(E)$, and the density, $\rho(E)$, of single-electron eigenstates; the Fermi wavenumber, k_F , the Fermi Surface, S_F , and the density of states (DOS), $\rho_F = \rho(E_F)$ at E_F ; the number, $\tilde{\Phi}(\omega)$, and the density, $\tilde{\phi}(\omega)$, of ionic eigenmodes; the phonon concept, and the Debye temperature, Θ_D .

4.1 Introduction

The Jellium model (JM), the simplest possible model for a solid, assumes that *solid formation is associated with the splitting of each atom to ζ electrons and to a cation of charge ζ , where ζ is the bonding atomic valence;*¹ *each cation is assumed to be mashed, as to cover uniformly the volume per atom, ν_a , associated with it (see (2.20)); as a result of this last assumption we end up with a uniform ionic background (a jelly) of mass density*

$$\rho_M = m_a/\nu_a, \quad (4.1)$$

and charge density

$$\rho_e = \zeta e/\nu_a, \quad (4.2)$$

(instead of the actual discrete ions). This positive uniform ionic charge density is fully compensated by the negative charge density of the valence electrons, which, being assumed free of any force, spread themselves uniformly over the whole volume, V , of the solid.

For every atom the atomic number Z , the mass² $m_a = A_w m_u$, and the bonding valence ζ are assumed known. It remains to find the volume per atom, ν_a , by minimizing the total energy. Having determined ν_a we can obtain immediately the concentration of atoms

$$n_a \equiv \frac{N_a}{V} \equiv \frac{1}{\nu_a}, \quad (4.3)$$

the radius per atom

$$r_a \equiv (3\nu_a/4\pi)^{1/3}, \quad (4.4)$$

and the density ρ_M given by (4.1). In many books instead of ν_a , n_a , and r_a , the quantities volume per valence electron, ν_e , concentration of valence electrons, n_e , and the radius per valence electron, r_s , are introduced; they are directly related to ν_a , n_a , and r_a as follows

$$\nu_e = \frac{\nu_a}{\zeta}, \quad (4.5)$$

$$n_e = \zeta n_a, \quad (4.6)$$

$$r_s = r_a/\zeta^{1/3}. \quad (4.7)$$

The *dimensionless quantities* $\bar{r}_a \equiv r_a/a_B$ and $\bar{r}_s \equiv r_s/a_B$ are also widely used.

Is the JM capable of accounting approximately for some properties of solids? Or, is it so oversimplified as to be irrelevant? The answer is “yes” to the first question and “no” to the second, in spite of the drastic omission of the force experienced by each (detached) electron due to the ions and the other

¹ For the value of ζ for each atom and related comments see Table 4.1 at p. 85.

² The atomic weight A_w is almost equal to A , the mass number, (if there is only one stable isotope); $m_u \simeq 1823 m_e$ is defined as the 1/12 of the mass of carbon-12.

Table 4.1. Bonding valence, transport valence (if available), and nominal valence (s) for the atoms of the periodic table. The noninteger bonding valence has been determined by J.H. Rose and H.B. Shore (Phys. Rev. **B49**, 11588 [1994]) based on the electronic concentration at the middle of the nearest neighbor distance in the corresponding elemental solids; a noninteger valence indicates that the ionic electrons participate to some degree in the bond formation

Cu 29		2.57 ← bonding valence, ξ 1 ← transport valence 1.2 ← nominal valence, s																	
Li 3	Be 4	Sc 21	Ti 27	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36		
1.09	1.99	2.22	3.20	3.45	3.53	3.41	3.32	3.09	2.83	2.57	2.40	2.43							
1	2	2	3	4	2, 3, 4, 5	2, 3, 6	2, 3	2, 3	2, 3	1, 2	2	3							
1	2	2	3	4	2, 3, 4, 5	2, 3, 4, 6, 7	2, 3	2, 3	2, 3	1, 2	2	3							
Na 11	Mg 12	K 19	Ca 20	Sc 21	Ti 27	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
1.11	2.08	1.21	2.22	2.85	3.20	3.45	3.53	3.41	3.32	3.09	2.83	2.57	2.40	2.43					
1	2	1	2	3	3, 4	2, 3, 4, 5	2, 3, 6	2, 3, 4, 6, 7	2, 3	2, 3	2, 3	1, 2	2	3					
1	2	1	2	3	3, 4	2, 3, 4, 5	2, 3, 6	2, 3, 4, 6, 7	2, 3	2, 3	2, 3	1, 2	2	3					
Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54		
1.24	2.32	3.21	3.15	4.14	4.42	4.24	4.05	3.67	3.15	2.70	2.48	2.51	(w)						
1	2	2	4	3, 5	2, 3, 4, 5, 6	4, 7	2, 3, 4, 6, 8	2, 3, 4	2, 4	1	3	2	3	4	3				
1	2	3	4	3, 5	2, 3, 4, 5, 6	4, 7	2, 3, 4, 6, 8	2, 3, 4	2, 4	3	2	3	4	3					
Cs 55	Ba 56	La 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86		
1.28	2.58	3.50	3.97	4.51	4.29	4.79	4.72	4.36	3.90	3.26	(a) 2.52	2.38	3.5						
2	2	2	4	5	6	6	6	4	3	1	2	3	4	3					
2	2	3	4	5	6	6	6	4	3	3	2	3	4	3					
Fr 87	Ra 88	Ac 89																	
			Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71			
		3	3	3	3	3	3	2	3	3	3	3	3	3	3	2	3		
			Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103			
			4	4	4	4	4	4	4										

electrons. The reason for this surprising answer (from a classical point of view which ignores the wave character of the electrons) is that the actual force on each electron is, to a first approximation, periodic and as such allows free-like propagation (for eigenenergies inside a band) and *in this respect resembles no force at all*. This is the reason that the JM is a reasonable first approximation for metals, where the Fermi level is inside a band. On the other hand, for semiconductors and insulators, where the Fermi energy is inside a gap, the JM is expected to fail. The reason is that zero force produces no gaps, and hence, it is incapable of accounting for semiconducting or insulating properties.

4.2 Electronic Eigenfunctions, Eigenenergies, Number of States, and Density of States

In the JM the state of each electron, being free of force, is characterized by its momentum, $\mathbf{p} = \hbar\mathbf{k}$, and its spin component, $s_z = \pm 1/2$; the corresponding eigenenergy, ε_k , is given in terms of $\mathbf{p}$ and ε_G as follows:

$$\varepsilon_k = \frac{p^2}{2m} + \varepsilon_G = \frac{\hbar^2 k^2}{2m} + \varepsilon_G, \quad (4.8)$$

where ε_G is the energy per electron, if all electrons had zero kinetic energy; the corresponding to $\mathbf{k}$ eigenfunction is a plane wave according to (B.16)

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k} \cdot \mathbf{r}}. \quad (4.9)$$

The *number of states*, $R(E)$ (for a given orientation of spin, i.e., per spin), with energy ε_k less than E is given by

$$R(E) = \sum'_{\mathbf{k}} = \int d^3r \int \frac{d^3k}{(2\pi)^3}, \quad (4.10)$$

where the prime denotes that the summation over $\mathbf{k}$, or the integration over d^3k is subject to the restriction $\varepsilon_k \leq E$. The last relation in (4.10) was obtained by employing the basic formula (B.19). Equation (4.10) can be written equivalently as

$$R(E) = \frac{V V_{k(E)}}{(2\pi)^3}. \quad (4.11)$$

where $V_{k(E)}$ is a volume in $\mathbf{k}$ -space such that all of its points satisfy the inequality $\varepsilon_k \leq E$; this volume, in view of (4.8), is the volume of a sphere of radius $k(E) \equiv \sqrt{2m(E - \varepsilon_G)/\hbar^2}$. Thus,

$$R(E) = \frac{V}{(2\pi)^3} \frac{4\pi}{3} k(E)^3 = \frac{\sqrt{2} V m^{3/2}}{3\pi^2 \hbar^3} (E - \varepsilon_G)^{3/2}. \quad (4.12)$$

Notice that $R(E)$, as demanded from a number, is actually dimensionless.

The *density of states* (DOS), $\rho(E)$ (per spin), is defined as the number of states with corresponding eigenenergies between E and $E + dE$ divided by dE :

$$\rho(E) \equiv \frac{R(E + dE) - R(E)}{dE} \equiv R'(E). \quad (4.13)$$

Within the JM, and in view of (4.12) and (4.13), the DOS (per spin) is given by

$$\rho(E) = \frac{3}{2(E - \varepsilon_G)} R(E), \quad (4.14)$$

$$\rho(E) = \frac{Vm^{3/2}}{\sqrt{2\pi^2\hbar^3}} (E - \varepsilon_G)^{1/2} \sim (E - \varepsilon_G)^{1/2}, \quad E \geq \varepsilon_G. \quad (4.15)$$

It is advisable to reexpress the DOS in terms of the velocity $v(E)$ and the area, $S_{k(E)}$, of the surface enclosing the volume $V_{k(E)}$. Within the framework of the JM, $S_{k(E)} = 4\pi k^2(E)$ and $v(E) = \hbar k(E)/m$; hence, $V_{k(E)} = mS_{k(E)}v(E)/3\hbar$. Combining this last relation with (4.11) and (4.13) and taking into account that $dR/dE = (dR/dk)/(dE/dk)$, we obtain for the DOS per spin

$$\rho(E) = \frac{V}{(2\pi)^3} \frac{S_{k(E)}}{\hbar v(E)}. \quad (4.16)$$

Equation (4.16) is important, because it is valid for Bloch waves as well with a proper reinterpretation for the velocity v . More explicitly, for a periodic system, we have in analogy with (4.16):

$$\rho_n(E) = \frac{V}{(2\pi)^3} \int_{S_n} \frac{dS_n}{\hbar |\langle \mathbf{v}_n \rangle|}, \quad \rho(E) = \sum_n \rho_n(E), \quad (4.17)$$

where $\hbar \langle \mathbf{v}_n \rangle = \nabla \varepsilon_n(\mathbf{k})$ (see Table 3.3), the integration extends over the surface S_n defined by the equation $\varepsilon_n(\mathbf{k}) = E$, and dS_n is the elementary area of this surface; the summation over n extends over all the bands for which the equation $\varepsilon_n(\mathbf{k}) = E$ has solutions.

Problem 4.1t. Prove (4.17) by taking into account that the volume, dV_k , between the surfaces defined by the equations $\varepsilon_n(\mathbf{k}) = E$ and $\varepsilon_n(\mathbf{k} + d\mathbf{k}) = E + dE$ is given by $dV_k = \int dS_{k(E)} dk_\perp$; and $dE = \nabla \varepsilon_n \cdot d\mathbf{k} = |\nabla \varepsilon_n(k)| dk_\perp$.

The DOS and the number of states are very important concepts, because the calculation and interpretation of almost all physical quantities of interest involve $\rho(\varepsilon)$, or $R(\varepsilon)$. For example, the determination of the Fermi energy, E_F , proceeds through the number of states $R(E)$. Indeed, if within the total volume V (to be determined) of the solid there are $N_e = \zeta N_a$ free electrons, the minimum total energy (i.e., the ground state energy of the solid) is obtained when the N_e electrons occupy the $N_e/2$ lowest energy eigenstates (two electrons per state, one with spin up and the other with spin down) spanning the

range from the minimum energy, $E = \varepsilon_G$, to the maximum occupied state of energy E_F (the so-called *Fermi energy*, see Fig. 1.2, p. 13). Hence, the number of states per spin with E less than E_F , $R(E_F)$, is equal to $N_e/2$,

$$\frac{N_e}{2} = R(E_F). \quad (4.18)$$

Substituting (4.12) for $R(E_F)$ and solving for E_F , we obtain

$$E_F = \frac{\hbar^2}{2m_e} (3\pi^2 n_e)^{2/3} + \varepsilon_G, \quad (4.19)$$

which coincides with the expression quoted in the footnote 17, p. 12 by taking $\varepsilon_G = 0$.

From now on we shall take $\varepsilon_G = 0$. Notice, however, that ε_G is the contribution to the Fermi energy due to the potential energy E_P of the particles of the system: $\varepsilon_G = \partial E_P / \partial N_e$. Thus, E_F , without the ε_G , is actually the kinetic energy contribution to the Fermi energy.

Since E_F is the maximum occupied eigenenergy (when the solid is in its ground state, or equivalently, when the absolute temperature, $T = 0$ K) the maximum electron wavenumber, k_F , and the maximum electron velocity, v_F , are given respectively by

$$E_F = \frac{\hbar^2}{2m} k_F^2 = \frac{1}{2} m v_F^2. \quad (4.20)$$

Comparison of (4.19) (with $\varepsilon_G = 0$) and (4.20) gives for k_F the expression

$$k_F = (3\pi^2 n_e)^{1/3}. \quad (4.21)$$

The quantities, k_F , $p_F = \hbar k_F$, v_F , and $T_F = E_F/k_B$ are called *Fermi wavenumber*, Fermi momentum, Fermi velocity, and Fermi temperature respectively; the latter indicates a temperature that must be exceeded, if the classical limit is to be approached. For numerical values, see Table 4.2 (at p. 89).

Problem 4.2t. Show that E_F , k_F , p_F , v_F , and $T_F = E_F/k_B$ can be expressed in terms of $\bar{r}_s \equiv r_s/a_B$ or $\bar{r}_a \equiv r_a/a_B$ as follows³

$$\frac{E_F}{E_0} = \frac{T_F}{T_0} = \frac{1}{2} \left(\frac{9\pi}{4} \right)^{2/3} \frac{1}{\bar{r}_s^2} \simeq \frac{1.842}{\bar{r}_s^2} = \frac{1.842\zeta^{2/3}}{\bar{r}_a^2}, \quad (4.22)$$

$$\frac{k_F}{k_0} = \frac{p_F}{p_0} = \frac{v_F}{v_0} = \left(\frac{9\pi}{4} \right)^{1/3} \frac{1}{\bar{r}_s} = \frac{1.919}{\bar{r}_s} = \frac{1.919\zeta^{1/3}}{\bar{r}_a}. \quad (4.23)$$

³ $E_0 = \hbar^2/ma_B^2 = 27, 2 \text{ eV}$, $T_0 = \hbar^2/k_B ma_B^2 \simeq 3, 16 \times 10^5 \text{ K}$, $k_0 = a_B^{-1} = 1.89 \times 10^8 \text{ cm}^{-1}$, $v_0 = \hbar/ma_B = c/137$, and $p_0 = mv_0 = \hbar k_0$ are the units of the corresponding quantities in the atomic system where $\hbar = 1$, $m = m_e = 1$, $e^2 = 1$.

Table 4.2. Fermi parameters for the JM based on the experimental value of $\bar{\tau}_a$ and an integer choice for ζ .

H	He																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																					
Li	1	Be	2																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																			
3.25	1.88	3.93																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																				
1.11	1.93	0.92																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																				
1.29	2.23	0.92																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																				
4.74	14.18	1.07																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																				
55	165	3.24																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																				
Na	1	Mg	2																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																			
3.93	2.65	3.93																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																				
0.92	1.37	0.92																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																				
1.07	1.58	1.07																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																				
3.24	7.13	3.24																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																				
37.6	82.7	37.6																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																				
K	1	Ca	2	Sc*	3	Ti*	4	V*	5	Cr*	6	Mn*	7	Fe*	8	Co*	9	Ni*	10	Cu	11	Zn	12	Ga	13	Ge	14	As	15	Se	16	Br	17	Kr	18	Xe	19	Rn	20	Lu*	21	Yb*	22	La*	23	Ce*	24	Pr*	25	Nd*	26	Pm*	27	Sm*	28	Eu*	29	Gd*	30	Tb*	31	Dy*	32	Ho*	33	Er*	34	Tm*	35	Y*	36	Zr*	37	Nb*	38	Mo*	39	Tc*	40	Ru*	41	Rh*	42	Pd*	43	Ag	44	Cd	45	In	46	Sn (a)	47	Sb*	48	Te	49	I	50	Xe	51	Rn	52	Lu*	53	Yb*	54	La*	55	Ce*	56	Pr*	57	Nd*	58	Pm*	59	Sm*	60	Eu*	61	Gd*	62	Tb*	63	Dy*	64	Ho*	65	Er*	66	Tm*	67	Y*	68	Zr*	69	Nb*	70	Mo*	71	Tc*	72	Ru*	73	Rh*	74	Pd*	75	Ag	76	Cd	77	In	78	Sn (a)	79	Sb*	80	Te	81	I	82	Xe	83	Rn	84	Lu*	85	Yb*	86	La*	87	Ce*	88	Pr*	89	Nd*	90	Pm*	91	Sm*	92	Eu*	93	Gd*	94	Tb*	95	Dy*	96	Ho*	97	Er*	98	Tm*	99	Y*	100	Zr*	101	Nb*	102	Mo*	103	Tc*	104	Ru*	105	Rh*	106	Pd*	107	Ag	108	Cd	109	In	110	Sn (a)	111	Sb*	112	Te	113	I	114	Xe	115	Rn	116	Lu*	117	Yb*	118	La*	119	Ce*	120	Pr*	121	Nd*	122	Pm*	123	Sm*	124	Eu*	125	Gd*	126	Tb*	127	Dy*	128	Ho*	129	Er*	130	Tm*	131	Y*	132	Zr*	133	Nb*	134	Mo*	135	Tc*	136	Ru*	137	Rh*	138	Pd*	139	Ag	140	Cd	141	In	142	Sn (a)	143	Sb*	144	Te	145	I	146	Xe	147	Rn	148	Lu*	149	Yb*	150	La*	151	Ce*	152	Pr*	153	Nd*	154	Pm*	155	Sm*	156	Eu*	157	Gd*	158	Tb*	159	Dy*	160	Ho*	161	Er*	162	Tm*	163	Y*	164	Zr*	165	Nb*	166	Mo*	167	Tc*	168	Ru*	169	Rh*	170	Pd*	171	Ag	172	Cd	173	In	174	Sn (a)	175	Sb*	176	Te	177	I	178	Xe	179	Rn	180	Lu*	181	Yb*	182	La*	183	Ce*	184	Pr*	185	Nd*	186	Pm*	187	Sm*	188	Eu*	189	Gd*	190	Tb*	191	Dy*	192	Ho*	193	Er*	194	Tm*	195	Y*	196	Zr*	197	Nb*	198	Mo*	199	Tc*	200	Ru*	201	Rh*	202	Pd*	203	Ag	204	Cd	205	In	206	Sn (a)	207	Sb*	208	Te	209	I	210	Xe	211	Rn	212	Lu*	213	Yb*	214	La*	215	Ce*	216	Pr*	217	Nd*	218	Pm*	219	Sm*	220	Eu*	221	Gd*	222	Tb*	223	Dy*	224	Ho*	225	Er*	226	Tm*	227	Y*	228	Zr*	229	Nb*	230	Mo*	231	Tc*	232	Ru*	233	Rh*	234	Pd*	235	Ag	236	Cd	237	In	238	Sn (a)	239	Sb*	240	Te	241	I	242	Xe	243	Rn	244	Lu*	245	Yb*	246	La*	247	Ce*	248	Pr*	249	Nd*	250	Pm*	251	Sm*	252	Eu*	253	Gd*	254	Tb*	255	Dy*	256	Ho*	257	Er*	258	Tm*	259	Y*	260	Zr*	261	Nb*	262	Mo*	263	Tc*	264	Ru*	265	Rh*	266	Pd*	267	Ag	268	Cd	269	In	270	Sn (a)	271	Sb*	272	Te	273	I	274	Xe	275	Rn	276	Lu*	277	Yb*	278	La*	279	Ce*	280	Pr*	281	Nd*	282	Pm*	283	Sm*	284	Eu*	285	Gd*	286	Tb*	287	Dy*	288	Ho*	289	Er*	290	Tm*	291	Y*	292	Zr*	293	Nb*	294	Mo*	295	Tc*	296	Ru*	297	Rh*	298	Pd*	299	Ag	300	Cd	301	In	302	Sn (a)	303	Sb*	304	Te	305	I	306	Xe	307	Rn	308	Lu*	309	Yb*	310	La*	311	Ce*	312	Pr*	313	Nd*	314	Pm*	315	Sm*	316	Eu*	317	Gd*	318	Tb*	319	Dy*	320	Ho*	321	Er*	322	Tm*	323	Y*	324	Zr*	325	Nb*	326	Mo*	327	Tc*	328	Ru*	329	Rh*	330	Pd*	331	Ag	332	Cd	333	In	334	Sn (a)	335	Sb*	336	Te	337	I	338	Xe	339	Rn	340	Lu*	341	Yb*	342	La*	343	Ce*	344	Pr*	345	Nd*	346	Pm*	347	Sm*	348	Eu*	349	Gd*	350	Tb*	351	Dy*	352	Ho*	353	Er*	354	Tm*	355	Y*	356	Zr*	357	Nb*	358	Mo*	359	Tc*	360	Ru*	361	Rh*	362	Pd*	363	Ag	364	Cd	365	In	366	Sn (a)	367	Sb*	368	Te	369	I	370	Xe	371	Rn	372	Lu*	373	Yb*	374	La*	375	Ce*	376	Pr*	377	Nd*	378	Pm*	379	Sm*	380	Eu*	381	Gd*	382	Tb*	383	Dy*	384	Ho*	385	Er*	386	Tm*	387	Y*	388	Zr*	389	Nb*	390	Mo*	391	Tc*	392	Ru*	393	Rh*	394	Pd*	395	Ag	396	Cd	397	In	398	Sn (a)	399	Sb*	400	Te	401	I	402	Xe	403	Rn	404	Lu*	405	Yb*	406	La*	407	Ce*	408	Pr*	409	Nd*	410	Pm*	411	Sm*	412	Eu*	413	Gd*	414	Tb*	415	Dy*	416	Ho*	417	Er*	418	Tm*	419	Y*	420	Zr*	421	Nb*	422	Mo*	423	Tc*	424	Ru*	425	Rh*	426	Pd*	427	Ag	428	Cd	429	In	430	Sn (a)	431	Sb*	432	Te	433	I	434	Xe	435	Rn	436	Lu*	437	Yb*	438	La*	439	Ce*	440	Pr*	441	Nd*	442	Pm*	443	Sm*	444	Eu*	445	Gd*	446	Tb*	447	Dy*	448	Ho*	449	Er*	450	Tm*	451	Y*	452	Zr*	453	Nb*	454	Mo*	455	Tc*	456	Ru*	457	Rh*	458	Pd*	459	Ag	460	Cd	461	In	462	Sn (a)	463	Sb*	464	Te	465	I	466	Xe	467	Rn	468	Lu*	469	Yb*	470	La*	471	Ce*	472	Pr*	473	Nd*	474	Pm*	475	Sm*	476	Eu*	477	Gd*	478	Tb*	479	Dy*	480	Ho*	481	Er*	482	Tm*	483	Y*	484	Zr*	485	Nb*	486	Mo*	487	Tc*	488	Ru*	489	Rh*	490	Pd*	491	Ag	492	Cd	493	In	494	Sn (a)	495	Sb*	496	Te	497	I	498	Xe	499	Rn	500	Lu*	501	Yb*	502	La*	503	Ce*	504	Pr*	505	Nd*	506	Pm*	507	Sm*	508	Eu*	509	Gd*	510	Tb*	511	Dy*	512	Ho*	513	Er*	514	Tm*	515	Y*	516	Zr*	517	Nb*	518	Mo*	519	Tc*	520	Ru*	521	Rh*	522	Pd*	523	Ag	524	Cd	525	In	526	Sn (a)	527	Sb*	528	Te	529	I	530	Xe	531	Rn	532	Lu*	533	Yb*	534	La*	535	Ce*	536	Pr*	537	Nd*	538	Pm*	539	Sm*	540	Eu*	541	Gd*	542	Tb*	543	Dy*	544	Ho*	545	Er*	546	Tm*	547	Y*	548	Zr*	549	Nb*	550	Mo*	551	Tc*	552	Ru*	553	Rh*	554	Pd*	555	Ag	556	Cd	557	In	558	Sn (a)	559	Sb*	560	Te	561	I	562	Xe	563	Rn	564	Lu*	565	Yb*	566	La*	567	Ce*	568	Pr*	569	Nd*	570	Pm*	571	Sm*	572	Eu*	573	Gd*	574	Tb*	575	Dy*	576	Ho*	577	Er*	578	Tm*	579	Y*	580	Zr*	581	Nb*	582	Mo*	583	Tc*	584	Ru*	585	Rh*	586	Pd*	587	Ag	588	Cd	589	In	590	Sn (a)	591	Sb*	592	Te	593	I	594	Xe	595	Rn	596	Lu*	597	Yb*	598	La*	599	Ce*	600	Pr*	601	Nd*	602	Pm*	603	Sm*	604	Eu*	605	Gd*	606	Tb*	607	Dy*	608	Ho*	609	Er*	610	Tm*	611	Y*	612	Zr*	613	Nb*	614	Mo*	615	Tc*	616	Ru*	617	Rh*	618	Pd*	619	Ag	620	Cd	621	In	622	Sn (a)	623	Sb*	624	Te	625	I	626	Xe	627	Rn	628	Lu*	629	Yb*	630	La*	631	Ce*	632	Pr*	633	Nd*	634	Pm*	635	Sm*	636	Eu*	637	Gd*	638	Tb*	639	Dy*	640	Ho*	641	Er*	642	Tm*	643	Y*	644	Zr*	645	Nb*	646	Mo*	647	Tc*	648	Ru*	649	Rh*	650	Pd*	651	Ag	652	Cd	653	In	654	Sn (a)	655	Sb*	656	Te	657	I	658	Xe	659	Rn	660	Lu*	661	Yb*	662	La*	663	Ce*	664	Pr*	665	Nd*	666	Pm*	667	Sm*	668	Eu*	669	Gd*	670	Tb*	671	Dy*	672	Ho*	673	Er*	674	Tm*	675	Y*	676	Zr*	677	Nb*	678	Mo*	679	Tc*	680	Ru*	681	Rh*	682	Pd*	683	Ag	684	Cd	685	In	686	Sn (a)	687	Sb*	688	Te	689	I	690	Xe	691	Rn	692	Lu*	693	Yb*	694	La*	695	Ce*	696	Pr*	697	Nd*	698	Pm*	699	Sm*	700	Eu*	701	Gd*	702	Tb*	703	Dy*	704	Ho*	705	Er*	706	Tm*	707	Y*	708	Zr*	709	Nb*	710	Mo*	711	Tc*	712	Ru*	713	Rh*	714	Pd*	715	Ag	716	Cd	717	In	718	Sn (a)	719	Sb*	720	Te	721	I	722	Xe	723	Rn	724	Lu*	725	Yb*	726	La*	727	Ce*	728	Pr*	729	Nd*	730	Pm*	731	Sm*	732	Eu*	733	Gd*	734	Tb*	735	Dy*	736	Ho*	737	Er*	738	Tm*	739	Y*	740	Zr*	741	Nb*	742	Mo*	743	Tc*	744	Ru*	745	Rh*	746	Pd*	747	Ag	748	Cd	749	In	750	Sn (a)	751	Sb*	752	Te	753	I	754	Xe	755	Rn	756	Lu*	757	Yb*	758	La*	759	Ce*	760	Pr*	761	Nd*	762	Pm*	763	Sm*	764	Eu*	765	Gd*	766	Tb*	767	Dy*	768	Ho*	769	Er*	770	Tm*	771	Y*	772	Zr*	773	Nb*	774	Mo*	775	Tc*	776	Ru*	777	Rh*	778	Pd*	779	Ag	780	Cd	781	In	782	Sn (a)	783	Sb*	784	Te	785	I	786	Xe	787	Rn	788	Lu*	789	Yb*	790	La*	791	Ce*	792	Pr*	793	Nd*	794	Pm*	795	Sm*	796	Eu*	797	Gd*	798	Tb*	799	Dy*	800	Ho*	801	Er*	802	Tm*	803	Y*	804	Zr*	805	Nb*	806	Mo*	807	Tc*	808	Ru*	809	Rh*	810	Pd*	811	Ag	812	Cd	813	In	814	Sn (a)	815	Sb*	816	Te	817	I	818	Xe	819	Rn	820	Lu*	821	Yb*	822	La*	823	Ce*	824	Pr*	825	Nd*	826	Pm*	827	Sm*	828	Eu*	829	Gd*	830	Tb*	831	Dy*	832	Ho*	833	Er*	834	Tm*	835	</

The quantity $\bar{r}_a$ can be determined experimentally either from the density (see (2.23)) or from the lattice structure and the lattice constant; typical values of $\bar{r}_a$ are around 3. Calculate the numerical values of E_F , T_F , k_F , and v_F for copper (Cu) assuming that $\zeta = 1$.

The DOS per spin at the Fermi energy, $\rho(E_F) \equiv \rho_F$ is obtained by combining (4.14) ($\rho(E) = 3R(E)/2E$) with (4.18).

$$\rho_F = \frac{3N_e}{4E_F}. \quad (4.24)$$

Equations (4.12), (4.14), (4.19), and (4.21)–(4.24) are valid for a three-dimensional JM. For a D -dimensional JM, we have:

$$R(E) \sim k^D \sim E^{D/2}, \quad (4.25)$$

$$\rho(E) = \frac{D}{2E} R(E) \sim E^{(D-2)/2}, \quad (4.26)$$

$$\rho(E) = \frac{L^D}{(2\pi)^D} \frac{S_{k(E)}}{\hbar v}, \quad (4.27)$$

$$k_F \sim n_e^{1/D}, n_e = N_e/L^D, \quad (4.28)$$

$$E_F = \frac{\hbar^2 k_F^2}{2m}, \quad (4.29)$$

$$\rho_F = \frac{D}{4E_F} N_e. \quad (4.30)$$

Calculate explicitly the quantities, k_F , E_F , ρ_F for $D = 1$ and $D = 2$. See also Problem 4.4 at the end of this chapter.

In Fig. 4.1 a schematic plot of the DOS for a D -dimensional JM is given ($D = 1, 2, 3$).

In Table 4.2 at p. 89 we give the values of the Fermi parameters based on the experimental value of n_a and an integer choice for ζ .

Notice that $R(E)$ and the DOS $\rho(E)$ for free particles depend on two factors: The dimensionality D and the dispersion relation, $E \sim k^s$. In this more general case, $R(E) \sim k^D \sim E^{D/s}$. Hence, $\rho(E) \sim E^a$, $a = (D - s)/s$.

4.3 Kinetic and Potential Energy, Pressures, and Elastic Moduli

In Chap. 1 we have shown that the combination of Heisenberg and Pauli's principles makes the minimum kinetic energy of N_e free electrons confined to a three-dimensional volume V proportional to $N_e^{5/3}/V^{2/3}$ (see (1.11) and the footnote 18, p. 12). Hence, $E_F \equiv \partial E_{K, \min}/\partial N_e = (5/3)(E_{K, \min}/N_e)$ or

$$E_{K, \min} = \frac{3}{5} N_e E_F. \quad (4.31)$$

Combining (4.19) and (4.31), we obtain (remembering that $N_e = \zeta N_a$ and $\nu_e = \nu_a/\zeta$) the following expression for $E_{K, \min}$:

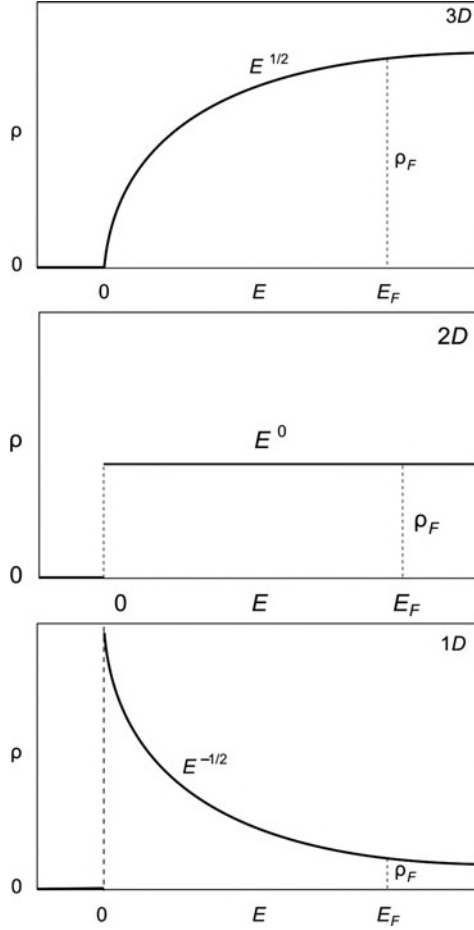


Fig. 4.1. Electronic DOS vs. energy for a 3-, 2-, 1-dimensional JM

$$E_{K, \min} = \frac{3}{5} N_e \frac{\hbar^2}{2m} (3\pi^2/\nu_e)^{2/3} \simeq 2.87 N_e \frac{\hbar^2}{m} \frac{1}{\nu_e^{2/3}} = 2.87 N_a \zeta^{5/3} \frac{\hbar^2}{m} \frac{1}{\nu_a^{2/3}}, \quad (4.32)$$

which coincides with (1.11) and (2.11) by recalling that $\nu_i \equiv V/N_i$ ($i = e, a$). Taking into account that $\nu_e = (4\pi/3)r_s^3 = (4\pi/3)a_B^3 r_s^3$ and $\bar{r}_s = \bar{r}_a/\zeta^{1/3}$, we can rewrite $E_{K, \min}$ as follows:

$$E_{K, \min} = 1.105 N_e \frac{\hbar^2}{ma_B^2} \frac{1}{\bar{r}_s^2} = 1.105 N_a \zeta^{5/3} \frac{E_0}{\bar{r}_a^2} = N_a \frac{30.07 \zeta^{5/3}}{\bar{r}_a^2} \text{ eV}, \quad (4.33)$$

where we have introduced the unit of energy $E_0 \equiv \hbar^2/ma_B^2 = 27.2 \text{ eV}$.

Problem 4.3t. Obtain $E_{K, \min}$ by summing directly the doubly occupied $N_e/2$ lowest energy levels

$$E_{K, \min} = 2 \sum_{|\mathbf{k}| < k_F} \frac{\hbar^2 k^2}{2m} = 2V \int_{|\mathbf{k}| < k_F} \frac{d^3 k}{(2\pi)^3} \frac{\hbar^2 k^2}{2m} = 2 \frac{4\pi V}{(2\pi)^3} \int_0^{k_F} dk k^2 \frac{\hbar^2 k^2}{2m}, \quad (4.34)$$

and show that your result coincides with (4.31).

Problem 4.4t. Obtain (4.31) by employing the free electron DOS, $\rho(\varepsilon) = C\varepsilon^{1/2}$ (where C does not depend on ε) and the relations

$$E_{K, \min} = 2 \int_0^{E_F} d\varepsilon \rho(\varepsilon) \varepsilon, \quad (4.35)$$

$$N_e = 2 \int_0^{E_F} d\varepsilon \rho(\varepsilon).$$

Problem 4.5t. Show that for a D -dimensional JM the minimum kinetic energy of free electrons is given by

$$E_{K, \min} = \frac{D}{2+D} N_e E_F. \quad (4.36)$$

Hint: Follow the arguments of Sects. 1.4.1 and 1.4.2 to conclude that $E_{K, \min}$ is proportional to $N_e \times N_e^{2/D}$.

We repeat that in every one of the relations seen earlier, the Fermi energy is actually the kinetic energy contribution to the total Fermi energy.

To calculate the JM *potential energy*, which has not yet been dealt with up to now, we have to first define a reference state for which the potential energy shall be taken as zero. The natural choice for the JM is the one for which the N_a ions and the $N_e = \zeta N_a$ free electrons are at their ground state and at infinite distance from each other. With this choice of reference state, the potential energy, E_p , is given approximately by (*see problem 4.6*)

$$\frac{E_p}{E_0} \equiv \bar{E}_p = -N_e \frac{c_p}{\bar{r}_s} = -N_a \frac{c_p \zeta^{4/3}}{\bar{r}_a}, \quad (4.37)$$

where

$$c_p = 0.56 + 0.6\zeta^{2/3}. \quad (4.38)$$

The $1/\bar{r}_s$ (or $1/\bar{r}_a$, or $v_a^{-1/3}$) dependence of E_p on $\bar{r}_s$ (or $\bar{r}_a$, or v_a) is to be expected, since, as it was pointed out in Sect. 2.2, the potential energy is of coulombic nature; furthermore, E_p has to be negative, since, otherwise, the formation of a solid would be energetically unfavorable. As it is explained in Problem 4.6, the $0.6\zeta^{2/3}$ contribution in (4.38) is the result of the difference of the electron–ion Coulomb attraction minus the *uncorrelated* electron–electron and ion–ion Coulomb repulsion; the 0.56 contribution is due to the correlated motion of the electrons, which makes their average pairwise distance

larger than in the absence of correlations. This increase in the average pairwise distance lowers the uncorrelated Coulomb electron–electron repulsion, by approximately $0.56N_e/\bar{r}_s$. Combining (4.33) and (4.37), we have the following expression for the total ground state energy^{4,5} of the JM.

$$\frac{\bar{U}}{N_a} \equiv \frac{U}{N_a E_0} = \frac{1.105\zeta^{5/3}}{\bar{r}_a^2} - \frac{c_p\zeta^{4/3}}{\bar{r}_a}, \quad (4.39)$$

where c_p is given by (4.38) and $E_0 \equiv \hbar^2/ma_B^2 = 27.2\text{ eV}$. An equivalent equation to (4.39) (without explicit expression for c_p) has been obtained in Sect. 2.2, (2.12); there, instead of r_a , the volume ν_a has been used denoted by ν for its equilibrium value and by ν' for any other value. There are several attempts to improve the result (4.39) for the JM; their common characteristic is the reintroduction of the discrete character of the ions as spherical particles of radius⁶ r_c , while the valence electrons are still treated as free. Here we introduce a version of improved JM, called *revised* JM (RJM), which assumes that the volume $4\pi r_c^3/3$ of each ion is inaccessible to the free electrons and it involves some other approximations as well (see Problem 4.7s). Within the framework of RJM the binding energy is given by

$$\frac{U}{N_a E_0} = \frac{\alpha}{\bar{r}_a^2} - \frac{\gamma}{\bar{r}_a}, \quad \text{RJM}, \quad (4.40)$$

where

$$\alpha = 1.3\zeta^{5/3} + \eta\bar{r}_c\zeta^2, \quad (4.41)$$

$$\gamma = 0.56\zeta^{4/3} + 0.9\zeta^2, \quad (4.42)$$

$\bar{r}_c = r_c/a_B$ and η varies from 0.4 to 0.9; the smaller value is associated with *ions* of half-filled shells and the larger with completed cells; η is given by the following linear interpolation formula

$$\eta = 0.4 + 0.5 \left| \frac{|\zeta_0 - \zeta|}{\zeta_1} - 1 \right|, \quad (4.43)$$

where ζ_0 is the number of electrons in the external shell of the *atom* and $\zeta_1 = 1$ for the first three rows of the Periodic Table of the elements (which do not have d-electrons) and $\zeta_1 = 6$ for the rest.

⁴ The kinetic and the elastic energy due to the oscillating motion of the ions is not included in (4.39).

⁵ The energy U , which is defined as the minimum energy required to split the solid to isolated $N_e = \zeta N_a$ electrons and N_a ions, is called *binding energy* and it is different from the *cohesive energy*, U_c , defined as the minimum energy required to split the solid to isolated N_a atoms (see Sect. 2.6.4, p. 33). Obviously the difference $U - U_c$ equals to the minimum energy required to extract ζ electrons from each of the N_a atoms. Thus, $U = U_c + N_a \sum_{i=1}^{\zeta} I_i$, where I_i is the i th ionization potential.

⁶ The radius r_c is smaller than the atomic radius, R_a , which in turn is smaller than the radius per atom, r_a .

By minimizing the energy U with respect to the free parameter $\bar{r}_\alpha$, we obtain its equilibrium value,⁷

$$\bar{r}_\alpha = \frac{2\alpha}{\gamma} = \frac{2.6\zeta^{1/3} + 2\eta\bar{r}_c\zeta^{2/3}}{0.56 + 0.9\zeta^{2/3}}, \quad \text{RJM}, \quad (4.44)$$

in terms of the known quantities ζ , $\bar{r}_c$, ζ_0 . This is an explicit version of (2.13) of Chap. 2. The equilibrium binding energy is given by

$$\frac{U}{N_a E_0} = -\frac{1}{2} \frac{\gamma}{\bar{r}_a}, \quad (4.45)$$

where $\bar{r}_a$ is the equilibrium value of the radius per atom. Having obtained $\bar{r}_a$ theoretically, we can immediately determine ν_a , n_a and the mass density ρ_M according to (2.23). In Fig. 4.2 we compare the theoretical result for $\bar{r}_a$ with the corresponding experimental result for each of the 70 elemental metals of the Periodic Table. In Table 4.3 we compare results based on (4.44) with experimental data for some nonmetallic elemental solids, the most severe test for the JM. Analysis of the results of Fig. 4.2 and Table 4.3 shows what one should have expected from the very beginning: The JM or the RJM is reasonable for simple metals (since their electronic behavior is matching the basic assumption of the model), is more or less acceptable for transition metals, and it becomes more and more inadequate as we move to semiconductors and insulators.

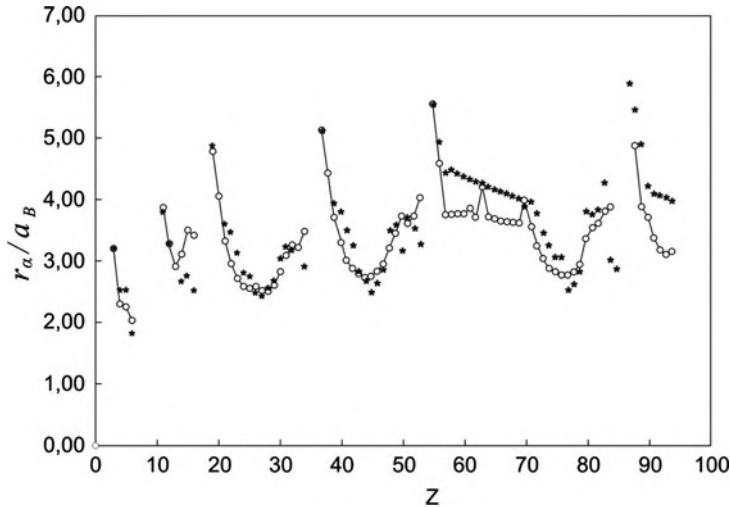


Fig. 4.2. Comparison of the theoretical value of $\bar{r}_a$ (asterisks) based on (4.44) with the corresponding experimental data (open circles) for all metallic elemental solids. The solid lines is a guide to the eye through the experimental values of $\bar{r}_a$. Notice the nonmonotonic variations with Z and connect it with the data of Fig. 2.1

⁷ Here we used the same symbol, $\bar{r}_a$, for both the equilibrium and any other value of the radius per atom.

Table 4.3. Comparison of theoretical results for $\bar{r}_a$ and B (based on (4.59)) with the corresponding experimental data for some nonmetallic elemental solids

Solid/ Z	ζ	$\bar{r}_c$	η	$a/\zeta^{5/3}$	$\bar{r}_s$	r_a		B (Mbar)	
						Theory	Exp.	Theory	Exp.
B/5	1,000	0.662	0.900	1,896	2,597	2,597	2,310	0.250	1,780
C/6	4,000	0.302	0.900	1,731	1,187	1,943	2,090	9,819	4,43
Si/14	4,000	0.794	0.900	2,434	1,722	2,733	3,180	2,512	0.998
P/15	3,000	0.832	0.900	2,380	1,957	2,832	3,570	1,294	0.304
S/16	4,000	0.699	0.900	2,299	1,626	2,581	3,460	3,159	0.178
As/33	3,000	1,096	0.900	2,723	2,239	3,229	3,270	0.755	0.394
Se/34	4,000	0.945	0.900	2,650	1,874	2,975	3,530	1,788	0.091
Te/52	4,000	1,323	0.900	3,190	2,256	3,582	3,800	0.852	0.230
I/53	5,000	1,172	0.900	3,104	1,945	3,326	4,100	1,741	–
Po/84	6,000	1,267	0.733	2,988	1,692	3,075	3,920	3,361	0.260
At/85	7,000	1,172	0.733	2,944	1,528	2,923	–	5,516	–

As was pointed out in Chap.1 (Sect.1.2) the *pressures* at $T = 0$ K associated with the kinetic and the potential energy are given respectively by

$$P_K = -\frac{\partial E_K}{\partial V}, P_P = -\frac{\partial E_P}{\partial V}, \quad (4.46)$$

while the bulk modulus, B , is given by (see p. 26)

$$B = -V \left(\frac{\partial P}{\partial V} \right) = V \left(\frac{\partial^2 U}{\partial V^2} \right), \quad (4.47)$$

where $P = P_K + P_P$. Equations (4.46) and (4.47) are valid for $T = 0$ K (see also (C.10) and (C.11)). Obviously, it is more convenient for the calculation of derivatives to express U in terms of V instead of $\bar{r}_a$. Hence, we write

$$E_K = \frac{N_a E_0 \alpha}{\bar{r}_a^2} = \frac{A}{V^{2/3}} \quad \text{and} \quad E_P = -\frac{N_a E_0 \gamma}{\bar{r}_a} = -\frac{\Gamma}{V^{1/3}}, \quad (4.48)$$

where the quantities A and Γ will not be calculated explicitly (there is no need for that). Recalling that $V \equiv N_a (4\pi/3) a_B^3 \bar{r}_a^3$, and $E_0/a_B^3 \equiv P_0 = 294$ Mbar, and using (4.46) and (4.47), we have

$$P_K = \frac{2}{3V} \frac{A}{V^{2/3}} = \frac{2}{3V} \frac{N_a E_0 \alpha}{\bar{r}_a^2} = \frac{P_0}{2\pi} \frac{\alpha}{\bar{r}_a^5}, \quad (4.49)$$

$$P_P = -\frac{1}{3V} \frac{\Gamma}{V^{1/3}} = -\frac{1}{3V} \frac{N_a E_0 \gamma}{\bar{r}_a} = -\frac{P_0}{4\pi} \frac{\gamma}{\bar{r}_a^4}, \quad (4.50)$$

$$B = \frac{5}{3} \frac{2}{3V} \frac{A}{V^{2/3}} - \frac{4}{3} \frac{1}{3V} \frac{\Gamma}{V^{1/3}} = \frac{1}{3} P_K = \frac{P_0}{6\pi} \frac{\alpha}{\bar{r}_a^5}. \quad (4.51)$$

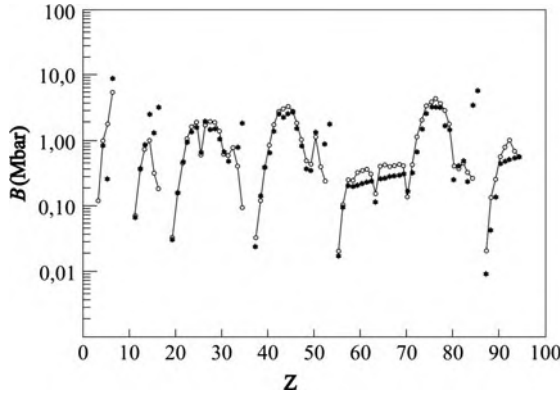


Fig. 4.3. Theoretical results (*asterisks*) for B based on (4.51) compared with the corresponding experimental data (*open circles*) for all the elemental solids. The solid line through the data is a guide to the eye

In deriving the last two relations in (4.51), it was assumed that the total pressure P is equal to zero (i.e., $|P_P| = P_K$; use of (4.49) and (4.50) was also made). The relation $B = P_K/3$ is consistent with (2.14) (although the value of α is different). In Fig. 4.3 we compare our theoretical result for B with the corresponding experimental value for all the elemental metals.

Problem 4.6t. Show that in the presence of a nonzero total pressure P , such that $|P| \ll B$, we have

$$B = B_{P=0} + 3|P|. \quad (4.52)$$

Hint: Take into account the relation $|P| = P_K - |P_P|$ (see (1.3)) as well as that the pressure P would reduce slightly the equilibrium volume.

Problem 4.7ts. Show that for copper and for $P = 0$

$$P_K = |P_P| = 3.48 \text{ Mbar}, \quad (4.53)$$

$$B = 1.16 \times 10^{11} \text{ N/m}^2, \quad (4.54)$$

while the experimental value of B is $1.37 \times 10^{11} \text{ N/m}^2$

The results of Problem 4.7ts confirms the fact that the equilibrium volume of a solid is established by the balance of two huge pressures (of the order of Mbar)—the expansive one stemming from the quantum kinetic energy of the electrons and the compressive one coming from the attractive Coulomb interactions. An external pressure P of a few bars hardly influences this balance: its effect on the relative change of equilibrium volume $|\Delta V|/V$ is equal to⁸ P/B , i.e., about 10^{-6} .

⁸ This follows from the definition of $B = -V(\partial P/\partial V)$; since for $P \ll B$, $\partial P/\partial V = P/\Delta V$.

We conclude this section by pointing out that the JM or the RJM is unable to calculate the shear modulus μ_s (see Sect. E.3 of Appendix E): the theoretical determination of the latter requires the calculation of the energy difference between the equilibrium lattice structure and a properly deformed one. However, the very concept of lattice structure is absent in the JM.

4.4 Acoustic Waves are the Ionic Eigenoscillations in the JM

We pointed out in Sect. 2.3 (p. 27) that the ions in a solid undergo small oscillations around their equilibrium positions; because of the small amplitude, the restoring forces, to a good approximation, are linear functions of the displacements. As a result, there are special solutions to the equations of motion, called eigenoscillations or normal modes of oscillation, or eigenmodes, such that all ions oscillate with the same frequency, ω_ν , for each eigenoscillation ν ($\nu = 1, 2, 3, \dots, 3N_a - 6$; $3N_a - 6 \simeq 3N_a$).

For the JM, where the ions have been replaced by a uniform continuum of mass density, ρ_M , of bulk modulus, B , and of shear modulus, μ_s , (if we go phenomenologically beyond the JM), the eigenoscillations, as it was shown in Appendix E, are plane acoustic waves characterized by the wavevector $\mathbf{q}$, and the polarization index s ($s = 1$ for longitudinal waves, $s = 2, 3$ for transverse or shear waves) of the form

$$\mathbf{u}_\nu(\mathbf{r}, t) = N_\nu^* \boldsymbol{\varepsilon}_\nu e^{i(\omega_\nu t - \mathbf{q} \cdot \mathbf{r})} + \mathbf{N}_\nu \boldsymbol{\varepsilon}_\nu e^{-i(\omega_\nu t - \mathbf{q} \cdot \mathbf{r})}, \quad \nu \equiv \mathbf{q}, s, \quad (4.55)$$

where the eigenfrequency $\omega_\nu = \omega_{\mathbf{q},s}$ is given by

$$\omega_{\mathbf{q},s} = c_s q, \quad s = 1, 2, 3. \quad (4.56)$$

In (4.55), (4.56), $\boldsymbol{\varepsilon}_\nu \equiv \boldsymbol{\varepsilon}_{\mathbf{q},s}$ is a unit vector parallel to $\mathbf{q}$ for $s = 1$ and perpendicular to $\mathbf{q}$ for $s = 2, 3$; $\boldsymbol{\varepsilon}_{\mathbf{q},3}$ is also perpendicular to $\boldsymbol{\varepsilon}_{\mathbf{q},2}$. N_ν^* and N_ν are the amplitudes of the eigenoscillation with dimensions of length. The sound velocities c_s are given by (2.33–2.36), which we repeat here.

$$c_1 \equiv c_\ell = c_0 \sqrt{1 + \frac{4}{3}x}, \quad x = \frac{\mu_s}{B}, \quad (4.57)$$

$$c_2 = c_3 = c_t = c_0 \sqrt{x}, \quad (4.58)$$

and

$$c_0 = \sqrt{\frac{B}{\rho_M}} = \frac{\sqrt{2}v_0}{3\bar{r}_a} \sqrt{\frac{\alpha m}{A_w m_u}} = \frac{24.15}{\bar{r}_a} \sqrt{\frac{\alpha}{A_w}} \text{ Km/s}, \quad v_0 = \frac{\hbar}{ma_B} = \frac{c}{137}, \quad (4.59)$$

and α is given by (4.41). Equation (4.59) is almost the same as the results (2.31), (2.32) of the dimensional analysis.

Table 4.4. Comparison of theoretical (based on (4.59)) and experimental value of c_0 , for several elemental solids

Solid	ζ	$\bar{r}_s$	A_w	c_0 (m/sec)		x	c_l (m/sec)	c_t (m/sec)
				Theory	Exp.			
Be	1.99	2.06	9.012	7,885	7,875	1.33	13,113	9,080
Mg	2.07	2.61	24.31	4,396	4,571	0.445	5,770	3,050
Ti	4	2.22	47.90	5,573	4,881	0.41	6,070	3,125
Mo	6	1.82	95.94	5,956	5,119	0.428	6,416	3,350
W	6	1.82	183.85	4,303	4,014	0.518	5,220	2,890
Fe	3	1.76	55.85	4,654	4,627	0.49	5,950	3,240
Ni	2.76	1.87	58.70	4,137	4,256	0.494	5,480	2,990
Cu	2.49	2.02	63.546	3,545	3,930	0.35	4,760	2,325
Ag	2.55	2.16	107.87	2,679	3,141	0.263	3,650	1,610
Au	3.3	1.93	196.97	2,544	3,041	0.166	3,361	1,239
Zn	2.44	2.30	65.38	3,225	3,128	0.608	4,210	2,440
Al	2.76	2.15	26.98	5,698	5,675	0.325	6,794	3,235
Pb	3.5	2.56	207.2	2,255	2,003	0.122	2,160	700
Si	4	1.722	28.086	8,269	6,479	0.680	8,945	5,341

^aThe experimental values are no more than 10% accurate

Problem 4.8t. Show that, if we keep only the JM kinetic energy $3N_e E_F/5$ in the total energy (see (4.31)), then the resulting expression for $c'_0 = (B/\rho_M)^{1/2}$ would be

$$c'_0 = \sqrt{\frac{10}{9} \frac{\zeta}{m_a} \frac{E_K}{N_e}} = v_F \sqrt{\frac{\zeta}{3} \frac{m}{m_a}}. \quad (4.60)$$

Equation (4.60) is known as the **Bohm–Staver relation**.

In Table 4.4, we compare the theoretical value of c_0 based on (4.59) with the corresponding experimental value for several solids.

For a given polarization, s , the number of eigenoscillations, $\tilde{\Phi}_s(\omega)$, with $\omega_{\mathbf{q},s} < \omega$, is equal to the number of $\mathbf{q}$'s with $|\mathbf{q}| < q(\omega) \equiv \omega/c_s$; but this number is given by the basic equation (4.11)

$$\tilde{\Phi}_s(\omega) = \frac{V}{(2\pi)^3} \frac{4\pi}{3} [q(\omega)]^3 = \frac{V}{6\pi^2} \frac{\omega^3}{c_s^3}. \quad (4.61)$$

The total number of eigenoscillations, $\tilde{\Phi}(\omega)$, with eigenfrequency less than ω , is obtained by summing $\tilde{\Phi}_s(\omega)$ over the three polarizations

$$\tilde{\Phi}(\omega) = \frac{V}{6\pi^2} \left(\frac{1}{c_l^3} + \frac{2}{c_t^3} \right) \omega^3 = \frac{V}{2\pi^2} \frac{\omega^3}{\tilde{c}^3}, \quad (4.62)$$

where we have introduced for convenience the appropriately averaged sound velocity $\tilde{c}$:

$$\frac{3}{\tilde{c}^3} \equiv \frac{1}{c_\ell^3} + \frac{2}{c_t^3}. \quad (4.63)$$

Notice that $\tilde{\Phi}_s(\omega)$ ($s = 1, 2, 3$) and $\tilde{\Phi}(\omega)$ grow without limit as ω becomes larger and larger; this is an artifact of the JM, which treats the discrete ions as a continuum and allows, thus, very large (without limit) wavevectors $\mathbf{q}$ and hence, very large (without limit), $\omega = \tilde{c}q$. Arbitrary large q 's correspond to arbitrary small wavelengths, $\lambda \equiv 2\pi/q$, which, of course, have no meaning for a discrete lattice, since the discreteness implies that $\lambda \gtrsim d$ where d is the nearest neighbor distance. To remedy this defect of the JM we introduce an upper cut off frequency, ω_D , such that the total number of eigenoscillations with $\omega < \omega_D$, $\tilde{\Phi}(\omega_D)$, to coincide with the actual total number of eigenoscillations, $3N_a - 6 \simeq 3N_a$. Hence

$$\frac{V}{2\pi^2} \frac{\omega_D^3}{\tilde{c}^3} = 3N_a \Rightarrow \omega_D = \tilde{c} (6\pi^2 n_a)^{1/3}. \quad (4.64)$$

Equation (4.62) together with the upper cutoff, ω_D , is called the **Debye Model** (DM) for ionic vibrations, and ω_D , the highest frequency within the DM, is called the **Debye frequency**. Besides ω_D , we define the Debye wavenumber $q_D = \omega_D/\tilde{c}$, the Debye energy $\varepsilon_D = \hbar\omega_D$, and the **Debye temperature**, $\Theta_D = \hbar\omega_D/k_B$. We have, taking into account (4.64),

$$q_D = (6\pi^2 n_a)^{1/3} = \left(\frac{6\pi^2}{\zeta} n_e \right)^{1/3} = \left(\frac{2}{\zeta} \right)^{1/3} k_F, \quad (4.65)$$

and

$$\Theta_D = \frac{\hbar \tilde{c} q_D}{k_B} = 8426 \left(\frac{\alpha}{A_w} \right)^{1/2} \frac{f}{\bar{r}_a^2} \text{ K}, \quad (4.66)$$

where

$$f \equiv \frac{\tilde{c}}{c_0} = 3^{1/3} \left[\frac{1}{(1 + \frac{4}{3}x)^{3/2}} + \frac{2}{x^{3/2}} \right]^{-1/3}, \quad x = \frac{\mu_s}{B}. \quad (4.67)$$

The total number of eigenoscillations, $\tilde{\Phi}(\omega)$ can be expressed in terms of ω_D in an easier to remember formula

$$\begin{aligned} \tilde{\Phi}(\omega) &= 3N_a \frac{\omega^3}{\omega_D^3}, \quad 0 \leq \omega \leq \omega_D, \\ &= 3N_a, \quad \omega_D < \omega, \end{aligned} \quad (4.68)$$

and the density of eigenoscillations, $\tilde{\phi}(\omega)$, per unit frequency is $\tilde{\phi}(\omega) = d\tilde{\Phi}/d\omega$, i.e.,

$$\begin{aligned} \tilde{\phi}(\omega) &= 9N_a \frac{\omega^2}{\omega_D^3}, \quad 0 \leq \omega \leq \omega_D \\ &= 0, \quad \omega_D < \omega \end{aligned} \quad (4.69)$$

Problem 4.9t. Show that the **Debye** wavelength $\lambda_D \equiv 2\pi/q_D$ for an **fcc** crystal is related to the lattice constant a and the nearest neighbor distance $d = a/\sqrt{2}$ as follows

$$\lambda_D = \left(\frac{\pi}{3}\right)^{1/3} a = 1.015a = \sqrt{2} \left(\frac{\pi}{3}\right)^{1/3} d = 1.436d.$$

As it was pointed out in Sect. 2.2, to each eigenoscillation corresponds a linear harmonic oscillator. The proof of this statement is based upon the fact that the total ionic Hamiltonian can be written as a sum of independent linear harmonic oscillators.

Proof. Within the framework of the JM (including, phenomenologically, the shear modulus μ_s) the total ionic Hamiltonian $\hat{H}$ is $\int \frac{\hat{\pi}^2}{2\rho_M} dV + \int \Delta dV$, where $\boldsymbol{\pi} = \rho_M \dot{\mathbf{u}}$ is the momentum density and Δ is the elastic deformation-energy density, see (E.11–E.13). Taking into account that the most general form of $\mathbf{u}(\mathbf{r}, t)$ is a sum of the eigenoscillations $\mathbf{u}_\nu(\mathbf{r}, t)$ with arbitrary coefficients N_ν (see (4.55)), we can transform $\hat{H}$ to

$$\hat{H} = \sum_{\nu} \hat{H}_{\nu}, \quad \nu \equiv \mathbf{q}, s, \quad (4.70)$$

where

$$\hat{H}_{\nu} = V \rho_M \omega_{\nu}^2 (N_{\nu}^* N_{\nu} + N_{\nu} N_{\nu}^*). \quad (4.71)$$

Quantum mechanically $\hat{\mathbf{u}}(\mathbf{r}, t)$ and $\hat{\pi}(\mathbf{r}, t)$ are operators that obey the familiar commutation relations $[\hat{u}_{\ell}(\mathbf{r}, t), \hat{u}_{\ell'}(\mathbf{r}', t)] = [\hat{\pi}_{\ell}(\mathbf{r}, t), \hat{\pi}_{\ell'}(\mathbf{r}', t)] = 0$, and $[\hat{u}_{\ell}(\mathbf{r}, t), \hat{\pi}_{\ell'}(\mathbf{r}', t)] = i\hbar \delta_{\ell, \ell'} \delta(\mathbf{r} - \mathbf{r}')$, $\ell, \ell' = x, y, z$. As a result of this, as we shall show in Sect. 9.3 and Problem 9.7s, $\hat{N}_{\nu}$ and $\hat{N}_{\nu}^*$ are also operators obeying the commutation relation $[\hat{N}_{\nu}, \hat{N}_{\nu'}] = [\hat{N}_{\nu}^*, \hat{N}_{\nu'}^*] = 0$ and $[\hat{N}_{\nu}, \hat{N}_{\nu'}^*] = \delta_{\nu, \nu'} \hbar / 2V \rho_M \omega_{\nu}$. Substituting in (4.71), we find

$$\hat{H}_{\nu} = 2V \rho_M \omega_{\nu}^2 \hat{N}_{\nu}^* \hat{N}_{\nu} + \frac{\hbar \omega_{\nu}}{2}. \quad (4.72)$$

Based on the commutation relations between $\hat{N}_{\nu}, \hat{N}_{\nu'}, \hat{N}_{\nu}^*, \hat{N}_{\nu'}^*$, we show in Problem 9.7s that the eigenvalues of the product operator $\hat{N}_{\nu}^* \hat{N}_{\nu}$ are $n_{\nu} \hbar / 2V \rho_M \omega_{\nu}$ where $n_{\nu} = 0, 1, 2, \dots$. Thus, the eigenvalues of $\hat{H}_{\nu}$ are

$$E_{\nu}(n_{\nu}) = \hbar \omega_{\nu} \left(n_{\nu} + \frac{1}{2} \right), \quad n_{\nu} = 0, 1, 2, \dots \quad (4.73)$$

It follows from (4.70) to (4.73) above that the eigenenergies of $\hat{H}$ are

$$E(\{n_{\mathbf{q}, s}\}) = \sum_{\mathbf{q}, s} \hbar \omega_{\mathbf{q}, s} \left(n_{\mathbf{q}, s} + \frac{1}{2} \right), \quad n_{\mathbf{q}, s} = 0, 1, 2, \dots, \quad (4.74)$$

and the ground state ionic energy, known as *zero point energy*, is

$$U_i^{(0)} = \frac{1}{2} \sum_{\mathbf{q},s} \hbar \omega_{\mathbf{q},s}. \quad (4.75)$$

This ionic energy should have been added to the energy U (see (4.40)) to obtain the total ground state energy of the solid. However, the omission of $U_i^{(0)}$ hardly influences the equilibrium values of $\bar{r}_a$, P_K , P_P , B because $U_i^{(0)}/U \simeq 0.01$. The quanta of ionic eigenoscillations, $\hbar \omega_{\mathbf{q},s}$, are called **phonons**. Their thermodynamic average number $\bar{n}_{\mathbf{q},s} \equiv \langle n_{\mathbf{q},s} \rangle$ is given by (C.71)

$$\bar{n}_{\mathbf{q},s} = \frac{1}{e^{\beta \hbar \omega_{\mathbf{q},s}} - 1}, \quad \beta = \frac{1}{k_B T}. \quad (4.76)$$

Hence, the thermodynamically average ionic energy is given by

$$E(\{\bar{n}_{\mathbf{q},s}\}) = U_i^{(0)} + U_{\text{ph}}(T) \quad \text{where} \quad U_{\text{ph}}(T) = \sum_{\mathbf{q},s} \hbar \omega_{\mathbf{q},s} \bar{n}_{\mathbf{q},s}. \quad (4.77)$$

Problem 4.10t. Using the phononic DOS (4.69) show that the ionic zero point energy is given by

$$U_i^{(0)} = \frac{9}{8} N_a \hbar \omega_D. \quad (4.78)$$

Problem 4.11t. The Debye phononic DOS coincides with the actual one for $\omega \ll \omega_D$. Give the physical argument justifying this statement.

Hint: Low ω implies small q , i.e., long wavelength λ , $\lambda \gg a$; a is the lattice constant.

In Fig. 4.4 we compare the Debye phononic DOS with the actual one for Al.

4.5 Thermodynamic Quantities

4.5.1 General Formulas

Each of the thermodynamic potentials (see Appendix C) within the JM can be written as a sum of three terms: the first one is its value at $T = 0$ K, the second is due to electron excitations above the Fermi energy E_F , and the third one is associated with the thermal creation of various phonons (i.e., the appearance of nonzero values of $\bar{n}_{\mathbf{q},s}$ in (4.76, 4.77)). Thus, we have for the total energy, $U(T)$, the total free energy, $F(T)$, and the grand thermodynamic potential, $\Omega = -P(T)V$

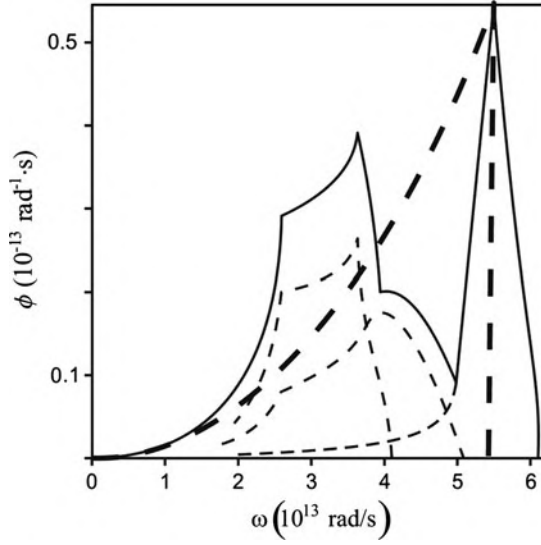


Fig. 4.4. Phononic DOS for *Al*: *Continuous line* is the experimental one, while the *heavy dashed line* is the DOS of the Debye model. The *light dashed lines* are the experimental contributions to the total DOS from the three polarizations, the two transverse and the one longitudinal. Can you tell which is which? The area under the actual and the Debye phononic DOS is the same and equal to $3N_a$

$$U(T) = U_0 + \Delta E_K(T) + U_{\text{ph}}(T), \quad (4.79)$$

$$F(T) = F_0 + \Delta F_K(T) + F_{\text{ph}}(T), \quad (4.80)$$

$$-\Omega(T) = P(T)V = P_0V - \Delta\Omega_K(T) - \Omega_{\text{ph}}(T), \quad (4.81)$$

where

$$U_0 = F_0 = \frac{A}{V^{2/3}} - \frac{\Gamma}{V^{1/3}} + \frac{9}{8}N_a\hbar\omega_D, \quad (4.82)$$

$$P^{(0)} = \frac{2}{3V} \frac{A}{V^{2/3}} - \frac{1}{3V} \frac{\Gamma}{V^{1/3}} - \frac{9}{8}N_a\hbar \frac{\partial\omega_D}{\partial V}, \quad (4.83)$$

$$\Delta E_K(T) = \frac{\pi^2}{3}\rho_F(k_B T)^2 = -\frac{3}{2}\Delta\Omega_K(T), \quad (4.84)$$

$$\begin{aligned} U_{\text{ph}}(T) &= \int d\omega \tilde{\phi}(\omega) \hbar\omega \langle n(\omega) \rangle = \frac{9N_a\hbar}{\omega_D^3} \int_0^{\omega_D} \frac{d\omega \omega^3}{e^{\beta\hbar\omega} - 1} \\ &= 9N_a \left(\frac{T}{\Theta_D} \right)^3 k_B T \int_0^{x_D} \frac{dx x^3}{e^x - 1}, \quad x_D = \frac{\Theta_D}{T}, \end{aligned} \quad (4.85)$$

$$F_{\text{ph}}(T) = -\hbar \int_0^\infty \frac{d\omega \tilde{\Phi}(\omega)}{e^{\beta\hbar\omega} - 1}, \quad (4.86)$$

$$\frac{\partial F_{\text{ph}}}{\partial V} = U_{\text{ph}}(T) \frac{1}{\omega_D} \frac{\partial \omega_D}{\partial V} = -P_{\text{ph}}(T) = \Omega_{\text{ph}}(T)/V, \quad (4.87)$$

$$P(T) = P^{(0)} + \frac{2\pi^2}{9} \frac{\rho_F}{V} (k_B T)^2 - U_{\text{ph}}(T) \frac{1}{\omega_D} \frac{\partial \omega_D}{\partial V}, \quad (4.88)$$

Equations (4.82–4.88) were derived as follows: Equation (4.82), by combining (4.48) and (4.78); (4.83), by taking into account (4.82) and the relation $P^{(0)} = -\partial U_0/\partial V$; (4.84), from (C.57) and by using the relation $\varepsilon\rho(\varepsilon) = \frac{3}{2}R(\varepsilon)$ valid for the JM and (C.46) and (C.47); (4.85), by replacing the sum over $\mathbf{q}$ and s in (4.77) by the integration over the DOS $\tilde{\phi}(\omega)$ and then using (4.69) and a change of variables from ω to $x = \beta\hbar\omega$; (4.86), from (C.65) by replacing ε by $\hbar\omega$; (4.87) by differentiating (4.86) with respect to V , taking into account, in view of (4.68), (4.69), that $\partial\tilde{\Phi}/\partial V = -\left(3\tilde{\Phi}/\omega_D\right)(\partial\omega_D/\partial V) = -\left(\tilde{\phi}(\omega)\omega/\omega_D\right)(\partial\omega_D/\partial V)$ ($0 \leq \omega \leq \omega_D$) and remembering the relations $P = -(\partial F/\partial V)_T = -\Omega/V$; finally (4.88) by combining (4.84) together with $\Delta\Omega_K = -P_K V$ and (4.87). Keep in mind that for constant pressure P the volume V becomes a function of T and P .

Problem 4.12t. Prove (4.85) and (4.87). Show that the limiting values of $U_{\text{ph}}(T, V)$ for low and high temperatures are

$$U_{\text{ph}}(T) \simeq \frac{3\pi^4}{5} N_a \left(\frac{T}{\Theta_D}\right)^3 k_B T, \quad T \lesssim \Theta_D/20, \quad (4.89)$$

$$U_{\text{ph}}(T) \simeq 3N_a k_B T - \frac{9}{8} N_a \hbar \omega_D, \quad \Theta_D \lesssim T. \quad (4.90)$$

Notice that the expression for $U_{\text{ph}}(T)$ in (4.90) plus $U_i^{(0)}$ gives for the ionic energy the Dulong–Petit result of $3N_a k_B T$. Following the argument in Sect. 2.4 explain why $U_{\text{ph}} \sim T^4$ as $T \rightarrow 0$ K.

To proceed with these formulae, we need the derivative, $\partial\omega_D/\partial V$. If the ionic vibrations were truly harmonic, the Debye frequency ω_D would be a constant independent of V and $\partial\omega_D/\partial V$ would be zero. Actually $\partial\omega_D/\partial V$ is different from zero and it is written as

$$\frac{\partial\omega_D}{\partial V} = -\gamma_G \frac{\omega_D}{V}, \quad (4.91)$$

where γ_G is taken approximately as a constant, called *Grüneisen constant*.

Problem 4.13t. Show that within the JM

$$\gamma_G = \frac{4}{3}. \quad (4.92)$$

Hints: Using (4.51) prove first that $dB/dV = -3B/V$ and then $d\rho_M/dV = -\rho_M/V$. Next show that the derivatives of $\tilde{c} = f c_0 = f \sqrt{B/\rho_M}$ with respect to V equals to $-\tilde{c}/V$ assuming that f is volume independent. Finally take into account that $\omega_D = \tilde{c} q_D$ and that q_D is given by (4.65).

4.5.2 Specific Heat, C_V

Using the relation $C_V = (\partial U / \partial T)_V$ together with (4.79), (4.84), and (4.85), we obtain for the C_V :

$$C_V = \frac{2\pi^2}{3} \rho_F k_B^2 T + \frac{9N_a \hbar}{\omega_D^3} \frac{\partial}{\partial T} \int_0^{\omega_D} \frac{d\omega \omega^3}{e^{\beta \hbar \omega} - 1}, \quad (4.93)$$

where the first term in the rhs of (4.93) is due to the excitation of the electrons just above the Fermi energy, and the second, which can be written as

$$C_{V\text{ph}} = 9N_a \left(\frac{T}{\Theta_D} \right)^3 k_B \int_0^{x_D} dx \frac{x^4 e^x}{(e^x - 1)^2}, \quad (4.94)$$

is coming from the thermal creation of phonons. Notice that, within the JM, $\rho_F = 3N_a/4E_F$, so that

$$C_{Ve} = \frac{3}{2} N_e k_B \left(\frac{\pi^2}{3} \frac{T}{T_F} \right), \quad (4.95)$$

where the physical origin of the factor $\pi^2 T / 3T_F$ (which is much smaller than one and multiplies the classical expression $\frac{3}{2} N_e k_B$ for C_{Ve}) has been explained in Sect. 2.4. Thus, for low temperatures ($T \lesssim \Theta_D/20$), the JM implies that $C_V \simeq \gamma_c T + C_1 T^3$ or $C_V/T \simeq \gamma_c + C_1 T^2$ where $\gamma_c = (2\pi^2/3) \rho_F k_B^2$ and $C_1 = (12\pi^4/5) N_a k_B / \Theta_D^3 = 1944 / \Theta_D^3$ (the expression for C_1 follows by differentiating (4.89) and the numerical value of 1944 is valid only for one mol, for which $N_a k_B = 8.3145 \text{ JK}^{-1} \text{ mol}^{-1}$).

Problem 4.14t. The experimental values of C_V/T vs. T^2 for copper are plotted below in Fig. 4.5. From these data and assuming the validity of the RJM determine for copper the DOS per spin at E_F , ρ_F , the radius per atom $\bar{r}_a$, the Debye temperature Θ_D , and the velocity of sound c_0 (assuming $\zeta = 2.57$ and $f = 0.665$). Compare the so-determined values of $\bar{r}_a$, Θ_D , and c_0 with the corresponding experimental values.

Problem 4.15t. Show that the JM expression for γ_c is

$$\gamma_c = 0.07 \zeta^{1/3} \bar{r}_a^2 \text{ mJ K}^{-2} \text{ mol}^{-1}. \quad (4.96)$$

Compare the experimental value of γ_c given in Table 4.5 p. 106, with that of (4.96). Whatever serious discrepancies between the theoretical results based on the jellium model (see (4.96)) and the corresponding experimental data for γ_c are due to two reasons. First the DOS $\rho(\varepsilon)$ in real solids (with the possible exception of simple metals) is a non monotonic function of ε with peaks, dips, and gaps (see Fig. 10.1 in p. 275). Depending on whether E_F coincides with peaks or dips, ρ_F could be much larger or much smaller than the JM-value of $3N_a/4E_F$; furthermore, if the Fermi energy lies within a gap, as in

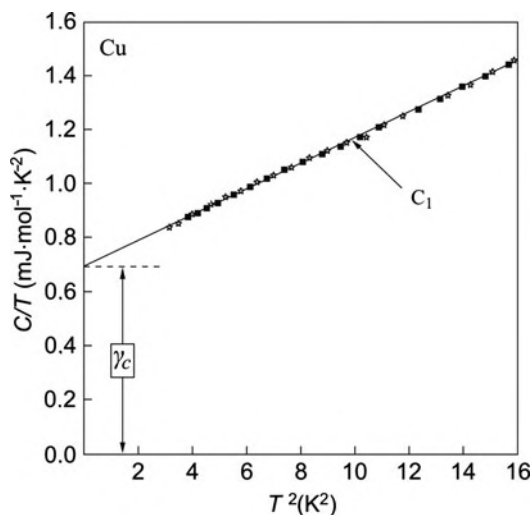


Fig. 4.5. The experimental data for the dependence of the specific heat C on the temperature T for copper are plotted as C/T vs. T^2 for very low temperatures ($2\text{ K} \lesssim T \lesssim 4\text{ K}$)

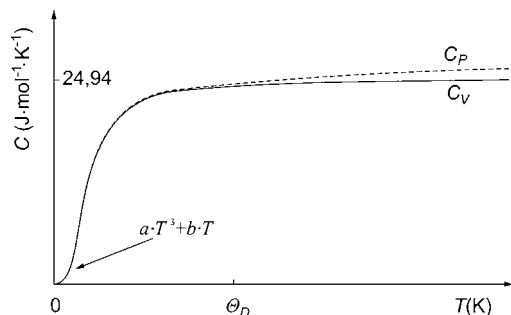


Fig. 4.6. Specific heat vs. temperature for a typical solid. For insulators and semiconductors, $b = 0$ and, hence, $C = C_{\text{ph}} \sim T^3$ at very low temperatures. For metals the $b \cdot T$ term is non-negligible only for very low temperatures, $T \lesssim 10\text{ K}$. Only for high temperatures ($T \gtrsim \Theta_D$) there is an appreciable difference between C_P and C_V

semiconductors and insulators, ρ_F is zero and there is no appreciable electronic contribution to the specific heat. Second, the electron–phonon interaction, to be presented later, multiplies the formula for γ_c by a factor $(1 + \lambda)$, where the dimensionless quantity λ varies from metal to metal from about 0.1 to almost 2. Taking into account the above remarks, we conclude that a realistic formula for γ_c is the following:

$$\gamma_c = \frac{2\pi^2}{3} \rho_F (1 + \lambda) k_B^2, \quad (4.97)$$

Table 4.5. Comparison of RJM based theoretical values of γ_c (in $\text{mJK}^{-2} \text{mol}^{-1}$) (4.96) with the corresponding experimental data for five different groups of elemental solids: I, simple metals; II, transition metals; III, semimetals; IV, semiconductors; and V, insulators

Group	Solid	Theory	Exp.	Group	Solid	Theory	Exp.
I	Li	0.64	1.63	II	Sc	1.16	10.7
	Na	0.91	1.38		Y	1.42	10.2
	K	1.50	2.08		La	1.75	10
	Rb	1.73	2.41		Ti	1.18	3.35
	Cs	2.05	3.20		Zr	1.41	2.80
	Cu	0.60	0.695		Hf	1.39	2.16
	Ag	0.71	0.646		V	0.97	9.26
	Au	0.74	0.729		Nb	1.28	7.79
	Be	0.51	0.17		Ta	1.26	5.9
	Mg	0.84	1.3		Cr	0.76	1.40
	Ca	1.39	2.9		Mo	1.19	2.0
	Sr	1.62	3.6		W	1.19	1.3
	Ba	2.06	2.7		Mn(a)	0.59	13.8
	Zn	0.77	0.64		Mn(γ)	0.59	9.20
	Cd	1.01	0.688		Re	1.05	2.3
	Hg(a)	1.19	1.79		Fe	0.56	4.98
	Al	0.76	1.35		Ru	0.72	3.3
	Ga	0.88	0.596		Os	1.06	2.4
	In	1.09	1.69		Co	0.52	4.73
	Tl	1.25	1.47		Rh	0.59	4.9
III	Sn(w)	0.98	1.78		Ir	0.63	3.1
	Pb	1.38	2.98		Ni	0.58	7.02
	As	0.90	0.19		Pd	0.62	9.42
IV	Sb	1.22	0.11		Pt	0.62	6.8
	Bi	1.62	0.008				
IV	Si	0.71	0				
	Ge	0.90	0				
V	Ne	0	0				
	Ar	0	0				

or

$$\gamma_c = 0.0866 (1 + \lambda) \bar{\rho}_{\text{Fa}} \text{ mJ mol}^{-1} \text{ K}^{-2}, \quad (4.98)$$

where ρ_F is the actual value of $\rho(E_F)$ per spin for each solid, $\bar{\rho}_{\text{Fa}} = 2\rho_F E_0/N_a$ is the dimensionless electronic DOS per atom for the two directions of spin, and $E_0 = \hbar^2/ma_B^2$.

At temperature $T = T_0 \simeq \Theta_D/100 \simeq 4\text{ K}$ and for simple metals, the electronic contribution C_{V_e} to the specific heat is about equal to the phononic contribution, $C_{V_{\text{ph}}}$. For $T \ll T_0$, $C_{V_e} \gg C_{V_{\text{ph}}}$, while for $T \gtrsim 10\text{ K}$ the specific heat is dominated by $C_{V_{\text{ph}}}$ as shown in Fig. 4.6.

4.5.3 Bulk Thermal Expansion Coefficient

The bulk thermal expansion coefficient, a_b , defined by $a_b \equiv (\partial V / \partial T)_P / V$, is equal to

$$a_b = \frac{1}{B_T} \left(\frac{\partial P}{\partial T} \right)_V, \quad (4.99)$$

(see (C.23) and its proof at the end of Sect. C.1). The derivative $(\partial P / \partial T)_V$ can be easily calculated from (4.88); furthermore, taking into account (4.93) for the electronic contribution to the specific heat (if any) and (4.91) for the derivative $\partial \omega_D / \partial V$, we have the following final formula for a_b :

$$a_b = \frac{1}{B_T V} \left(\frac{2}{3} C_{Ve} + \gamma_G C_{Vph} \right), \quad (4.100)$$

where, for the JM, $\gamma_G = 4/3$. For very low temperatures, $T \lesssim T_0$ ($T_0 \simeq 4$ K), and for metals only, C_{Ve} gives the main contribution to the thermal expansion coefficient; in all other cases C_{Vph} dominates. Especially for $T \gtrsim \Theta_D$, $C_{Vph} \simeq 3N_a k_B$ and (4.100) becomes

$$a_b \simeq \frac{4n_a k_B}{B(0)} = \frac{1.14 \times 10^{-4}}{0.56\zeta^{4/3} + 0.9\zeta^2} \bar{r}_a \text{ K}^{-1}, \quad T \gtrsim \Theta_D. \quad (4.101)$$

Problem 4.16t. Prove (4.101). Calculate a_b for Cu and Fe at room temperature and compare with the corresponding data of 4.95×10^{-5} and $3.54 \times 10^{-5} \text{ K}^{-1}$ respectively.

Thus, the bulk thermal expansion coefficient at room temperature is of the order of 10^{-4} K^{-1} and the linear thermal expansion coefficient, α_L , of the order of 10^{-5} .

4.6 Key Points

- The Jellium Model (JM), the simplest possible for solids, involves only one quantity to be determined by minimizing the free energy: the volume per atom, $\nu_a \equiv V/N_a$ (or, equivalently, the concentration $n_a = 1/\nu_a$, or $r_a = (3\nu_a/4\pi)^{1/3}$, or $r_s = r_a/\zeta^{1/3}$, where ζ is the valence).
- The number of states per spin $R(E)$ with energy below E is related to the density of states (DOS), $\rho(E)$: $\rho(E) = dR(E)/dE$. For the JM, the DOS ($\rho(E) \sim \sqrt{E}$), the Fermi energy, E_F , the Fermi momentum (over $\hbar$), $k_F = (3\pi^2 n_e)^{1/3}$, and the DOS at E_F , $\rho_F = 3N_e/4E_F$ are determined, where $n_e = \zeta n_a$.
- For the JM, the total ground state energy per atom $\bar{U}/N_a$, in atomic units, is given by

$$\frac{\bar{U}}{N_a} = \frac{\alpha}{\bar{r}_a^2} - \frac{\gamma}{\bar{r}_a},$$

where α , and γ are known (see (4.41) and (4.42)). By minimizing $\bar{U}$ with respect to $\bar{r}_a$, we find its equilibrium value: $\bar{r}_a = 2\alpha/\gamma$, as well as the bulk modulus, $B: \bar{B} = \alpha/6\pi\bar{r}_a^5$.

- The vibrations of the uniform ionic background are acoustic waves of wavevector $\mathbf{q}$ and frequency $\omega_s = c_s q$, where c_s is the sound velocity for longitudinal waves ($s = 1$) and for transverse waves ($s = 2, 3$).
- The number of eigenoscillations of type s with frequency below ω is given by $\tilde{\Phi}_s(\omega) \sim q^3 \sim \omega^3/c_s^3$; the total number below ω , $\tilde{\Phi}(\omega)$, is the sum over s . To preserve the total number of eigenoscillations $3N_a$, an upper cut off, ω_D , is introduced such that $\tilde{\Phi}(\omega_D) = 3N_a$. Hence, the DM results

$$\begin{aligned}\tilde{\Phi}(\omega) &= 3N_a \frac{\omega^3}{\omega_D^3}, \quad \omega \leq \omega_D \\ &= 3N_a, \quad \omega > \omega_D.\end{aligned}$$

The Debye temperature Θ_D is defined as $\hbar\omega_D/k_B$, where $\omega_D = \tilde{c}q_D$, and the Debye wave number is given $q_D = (6\pi^2 n_a)^{1/3}$.

- The thermodynamic quantities are due to the electronic excitations, plus the ionic excitations, plus the ground state contribution (if any). Expressions for the thermodynamic potentials (U , F , Ω), the pressure, the specific heat, and the thermal expansion coefficient have been obtained.

4.7 Problems

- 4.1s. For the elemental solids Na , K ($\zeta = 1$) Mg , Ca ($\zeta = 2$), Fe , Al ($\zeta = 3$), and Ti ($\zeta = 4$), calculate the binding energy per atom in eV and compare them with the corresponding experimental data. To obtain the latter, take into account that the binding energy per atom is the sum of the cohesive energy per atom plus the first ζ ionization potentials.
- 4.2s. For the elemental solids Al , Cu , Au , Fe , Pb , Mg , and Be calculate q_D , ω_D , ε_D , and Θ_D ; for the latter compare with the experimental values. (See Table 4.4)
- 4.3s. Starting from (C.25), show that

$$\frac{C_P - C_V}{C_V} = \gamma_G^2 \frac{TC_V}{B_T V}. \quad (4.102)$$

Hence, for low temperatures ($T \ll \Theta_D$) $C_P \simeq C_V$, while for $T \gtrsim \Theta_D$

$$\frac{C_P - C_V}{C_V} = x \frac{T}{\Theta_D},$$

where $x = 0.64 (1/\alpha A_w)^{1/2} \times f$ and α is given by (4.41). Calculate for Fe the value of x , the relative difference $(C_P - C_V)/C_V$, and the ratio B_s/B_T at room temperature (see (C.24)).

- 4.4 Show that the number of states per spin $R(E)$, the DOS per spin $\rho(E)$, the Fermi wavenumber k_F , the Fermi energy E_F , and the DOS per spin at $E = E_F$, ρ_F , for a D -dimensional JM of volume $V_D = L^D$ and number of free electrons, N_e , are given by:

$$R(E) = \frac{L^D}{(2\pi)^D} c_D k(E)^D, \quad k(E) = \sqrt{2mE/\hbar^2}, \quad (4.103)$$

$$\sim E^{D/2}$$

$$\rho(E) = \frac{D}{2E} R(E) \sim E^{(D-2)/2}, \quad (4.104)$$

$$\frac{L^D}{(2\pi)^D} c_D k_F^D = \frac{N_e}{2}, \quad (4.105)$$

$$E_F = \frac{\hbar^2 k_F^2}{2m}, \quad (4.106)$$

$$\rho_F = (D/4E_F) N_e, \quad (4.107)$$

where $c_D k_F^D$ is the volume of a D -dimensional sphere of radius k_F , and the quantity c_D is equal to $2\pi^{D/2}/\Gamma(D/2)$, where $\Gamma(x)$ is the Γ function for which $\Gamma(x+1) = x\Gamma(x)$, $\Gamma(x)\Gamma(1-x) = \pi/\sin \pi x$ and $\Gamma(n) = (n-1)!$, $n = 1, 2, 3, \dots$, $\Gamma(1) = 1$; $c_d = 2, \pi, 4\pi/3, \pi^2/2$ for $D = 1, 2, 3, 4$ respectively.

Show also that

$$k_F = \frac{2\pi}{(2c_D^2)^{1/D}} \frac{1}{r_s} = \frac{2\pi}{(2c_D^2)^{1/D}} \frac{\zeta^{1/D}}{r_a}, \quad (4.108)$$

where $\nu_e \equiv L^D/N_e = c_D r_s^D$. Prove also (4.27).

- 4.5 Calculate the coefficient γ_c for lead using both the simple JM formula (4.95) and formula (4.97) with $\rho_F = 0.252$ states per atom per eV and per spin, as calculated by a realistic method taking into account the periodic potential. The λ value for lead is given in Table 5.2, p. 126. Compare with the experimental value given in Table 4.5, p. 106.
- 4.6 The potential energy of the electron-ion system can be written as a sum of three terms: $E_p = E_H + E_x + E_c$ where E_H is the classical electrostatic term

$$E_H = \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{4\pi\epsilon_0|\mathbf{r}-\mathbf{r}'|} d^3r d^3r', \quad (4.109)$$

where $\rho(\mathbf{r}) = \sum_n \rho_n(\mathbf{r})$ is the total density of electric charge (both electronic and ionic) and $\rho_n(\mathbf{r})$ is the density within the W-S cell centered at the point $\mathbf{R}_n$ and zero outside it. Substitute $\rho = \sum_n \rho_n$ in (4.109); in the resulting double sum the terms $n \neq n'$, give a negligible contribution (because the total charge within the W-S cell is zero and the W-S

can be approximated by a sphere of equal volume). Within each W-S cell $\rho_n = \rho_{ne} + \rho_{ni}$. Thus,

$$E_H = \frac{1}{2} N_a \left[\int_{WS} \frac{d^3 r d^3 r'}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|} [2\rho_{ne}(\mathbf{r})\rho_{ni}(\mathbf{r}') + \rho_{ne}(\mathbf{r})\rho_{ne}(\mathbf{r}')] \right]. \quad (4.110)$$

In (4.110) we have not included the term $\rho_{ni}(\mathbf{r})\rho_{ni}(\mathbf{r}')$, since this is just the potential self-energy of each ion which by assumption does not change upon the formation of the solid. Taking into account that within the JM $|\rho_{ne}| = \rho_{ni} = \zeta e/\nu_a$, (4.110) becomes

$$E_H = -\frac{1}{2} N_a \rho_{ne}^2 \int_{WS} \frac{d^3 r d^3 r'}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|}. \quad (4.111)$$

The integral in (4.111) can be performed analytically (by approximating the W-S cell by a sphere). Show that the result is

$$E_H = -\frac{3}{5} N_a \frac{\zeta^2 e^2}{4\pi\epsilon_0 r_a}. \quad (4.112)$$

The term E_x is due to the fact that the antisymmetric nature of the electronic wave function $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_2)$ induces correlations that increase the average electronic distance $|\mathbf{r} - \mathbf{r}'|$ and, hence, reduces the size of the repulsive electron–electron interactions. This reduction is given by the following exact formula (assuming the validity of the JM; see [SS83], pp. 47–54)

$$E_x = -\frac{3}{4\pi} \left(\frac{9\pi}{4} \right)^{1/3} \frac{N_e e^2}{4\pi\epsilon_0 r_s} = -\frac{0.458}{\bar{r}_s} N_e E_0. \quad (4.113)$$

In reality, Coulomb interactions modify the electronic wave function $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_2)$. This modification further increases the average distance $|\mathbf{r} - \mathbf{r}'|$ between electrons and, as a result, reduces further the electron–electron interaction by an amount of the order of

$$E_c \simeq -\frac{0.1e^2}{4\pi\epsilon_0 \bar{r}_s} N_e E_0, \quad (4.114)$$

E_x and E_c are called exchange and correlation corrections respectively (see Chap. 8, Sect. 8.3)

- 4.7s Assume that each ion is a sphere of radius r_c at the centre of each W-S cell (which is approximated by a sphere of radius $r_a > r_c$). Assume further that the density of free electrons is uniform in the region $r_c < r < r_a$ and zero for $r < r_c$. Show, then that (4.109) of the previous problem gives the following result:

$$E_H = -N_a \frac{\zeta^2 e^2}{4\pi\epsilon_0 r_a} \left[1.5 \frac{1-x^2}{1-x^3} - 0.6 \frac{1-2.5x^3+1.5x^5}{(1-x^3)^2} \right],$$

where $x = r_c/r_a$. The quantity in brackets varies almost linearly from 0.9 when $x = 0$ to 0.5 when $x = 1$. What is the kinetic energy in view of the fact that the volume of the ions is inaccessible to the electrons? (For a numerical value chose $x = 0.6$).

- 4.8 Assume that a particle moves free of force in a D -dimensional space and that its eigenenergies ε_k are related to its wavenumber k by the relation, $\varepsilon_k = c_s k^s$. How are (4.30) and (4.36) generalized in this case?
- 4.9 Prove (4.70) and (4.71).
- 4.10 Consider a generalization of the DM by introducing two Debye energies (frequencies or temperatures)

$$\varepsilon_{D\ell} = \hbar c_\ell k_D \quad \text{and} \quad \varepsilon_{Dt} = \hbar c_t k_D.$$

Plot the phononic DOS, $\phi(\omega)$, for this model; chose the values for Al and compare with the results shown in Fig. 4.4.

- 4.11. Show that the temperature dependence of the bulk modulus is given by

$$\bar{B}(T) \simeq \bar{B}(0) + 16\bar{\varepsilon}_D/\bar{\nu}_a (e^{\beta\varepsilon_D} - 1) - (3\gamma_G + 4) \bar{U}_{\text{ph}}/\bar{V}$$

Hint: $B_T = -V(\partial P/\partial V)_T$, where $P(T)$ is given by (4.88) and $\bar{P}^{(0)} = (2\alpha/3\bar{\nu}_e \bar{r}_s^2) - (\gamma/3\bar{\nu}_e \bar{r}_s) + 3\bar{\varepsilon}_D/2\bar{\nu}_e$. Take into account that $\bar{\nu}_e$ and $\bar{r}_s$ depend on temperature as follows: $\nu_e = \nu_{e0} + \int_0^T a_b(T') \bar{\nu}_e(T') dT'$ and $a_b(T')$ is given by (4.100).

- 4.12. Show that by taking into account the temperature dependence of V in calculating C_V (as we did in Problem 4.11) the relative correction will be of the order P/B , i.e., negligible.

Further Reading

- Most books of Solid State Physics cover the material presented in this chapter. However, they usually omit the contribution of the potential energy and they restrict themselves to the simple JM. A notable exception is the book by Harrison [SS76], Chap. 15.

The Jellium Model and Metals II: Response to External Perturbations

Summary. The response of a solid to an external electric field is characterized by the dielectric function, ε , or the conductivity, σ , or the electric susceptibility, χ_e , of the solid. By relatively simple considerations, *different* expression for ε are obtained, depending mainly on whether $k \ll \omega/v_F$ or $k \gg \omega/v_F$. The static conductivity in metals depends on the area of the Fermi surface and the mean free path. The latter is strongly reduced by phonon scattering, and hence, by temperature increase. An external static magnetic field modifies the conductivity leading to the so-called magnetoresistance and the Hall effect; it induces additional excited states, which give rise to cyclotron, spin, and nuclear magnetic resonances; and it magnetizes the solid. Temperature gradients is another source that drives the material out of thermodynamic equilibrium in the presence or absence of electromagnetic fields.

5.1 Response to Electric Field

Before studying this chapter the readers are advised to refresh their memory by going over Appendix A, where a brief summary of the electrodynamics of continuous media is presented. In particular the readers must familiarize themselves with quantities such as the AC electrical conductivity, $\sigma(\mathbf{k}, \omega)$, the dielectric function,¹ $\varepsilon(\mathbf{k}, \omega)$, and the electrical susceptibility, $\chi_e(\mathbf{k}, \omega)$. All these quantities are related to each other so that the knowledge of one gives immediately the other two (see also (D.1) to (D.3) in Appendix D). It must be stressed that these quantities expressed as a function of the wavevector, $\mathbf{k}$, and the frequency, ω , relate the *Fourier transform* of the current density, or the electric induction, or the polarization to the *Fourier transform* of the electric field (see, e.g., (A.42) to (A.46) regarding this point).

¹ In SI, the dielectric function is the dimensionless ratio of the permittivity to the permittivity of the vacuum: $\hat{\varepsilon}_r = \hat{\varepsilon}/\epsilon_0$. Similarly the relative magnetic permeability is the dimensionless ratio of the permeability to the permeability of the vacuum: $\hat{\mu}_r = \mu/\mu_0$. In this chapter, for the sake of simplicity, we shall drop the subscript r .

In this and the next section, we shall assume that the relative magnetic permeability, μ_r , of our jellium model (JM) is equal to 1; this is a reasonable approximation, since in most solids $\mu_r \simeq 1$. Anyway, in Sect. 5.3, we shall return to the study of $\mu_r(\mathbf{k}, \omega)$. For the time being, we shall concentrate on the dielectric function, $\varepsilon(\mathbf{k}, \omega)$, and on the electrical conductivity, $\sigma(\mathbf{k}, \omega)$, which are related as follows.

$$\varepsilon(\mathbf{k}, \omega) - 1 = \frac{4\pi i}{4\pi\varepsilon_0\omega} \sigma(\mathbf{k}, \omega), \text{ SI.} \quad (5.1)$$

In G-CGS, $4\pi\varepsilon_0$ must be replaced by 1, i.e., it must be omitted. In the general case, ε and σ are tensors (see Appendix A). Then, (5.1) becomes

$$\varepsilon_{ij} - \delta_{ij} = 4\pi i \sigma_{ij} / 4\pi\varepsilon_0\omega. \quad (5.2)$$

5.2 The Dielectric Function

In Sect. D.1 of Appendix D, we have demonstrated the crucial importance of the dielectric function in various aspects of interactions of solids with electromagnetic fields and charged particles, as well as in extracting information about the properties of solids. More explicitly we have shown that:

- (a) The propagation, absorption, reflection, and transmission of electromagnetic waves (EM waves) in condensed matter depend mainly on the index of refraction, n , which by definition is equal to the square root of the dielectric function times the relative permeability

$$n = \sqrt{\varepsilon\mu_r} = \sqrt{\varepsilon}, \quad (5.3)$$

where the last relation follows from our assumption that $\mu_r = 1$. Indeed, the *phase velocity*, ω/k_1 , of EM waves in solids, and more generally of transverse waves, equals c/n_1 where c is the light velocity in vacuum and k_1 , n_1 are the real parts of the wavenumber, k , and the index of refraction, $n = \sqrt{\varepsilon}$, respectively. The *absorption coefficient*, α' is equal to $2\omega n_2/c = \omega\varepsilon_2/cn_1$ and, consequently, the other absorption coefficient $\alpha \equiv n_1\alpha'$ is given by $\omega\varepsilon_2/c$, where n_2 , ε_2 are the imaginary parts of n and ε respectively (see (D.8–D.10)).

- (b) If n_2 , ε_2 are considered negligible, i.e., $n_2 = \varepsilon_2 \simeq 0$, then the phase velocity of a transverse oscillation of the coupled system, material/EM field, is given by $\omega/k = c/n$ or

$$n^2 = \varepsilon(\mathbf{k}, \omega) = \frac{c^2 k^2}{\omega^2}, \quad (5.4)$$

If a solution of (5.4), $\omega = \omega(\mathbf{k})$, is such that $\omega(\mathbf{k})/k$ is much smaller than c , then, for such a solution, the rhs of (5.4) is huge and the electrostatic approximation of assuming instantaneous transmission of the electric forces (i.e., $c = \infty$) is a good one. Thus the solutions to

$$\varepsilon(\mathbf{k}, \omega) \simeq \infty, \quad (5.5)$$

give (to a very good approximation) the frequency-vs.- $\mathbf{k}$ relation, $\omega = \omega(\mathbf{k})$, of the *transverse* collective eigenoscillations, such as the transverse acoustic waves, for which the phase velocity is much smaller than c . The existence of solutions of (5.5) means that the electrostatic forces alone are capable of sustaining transverse collective eigenoscillations of the electric charges of the solid. However, these oscillations, being of transverse nature, will set up EM fields which in turn will act on the oscillating charges. Thus, a coupling of the eigenoscillations satisfying (5.5) and the EM field will take place, which will lead us back to (5.4). When $\omega/k \ll c$, the coupling is weak and, as a first approximation, it can be omitted.

- (c) Similarly the solutions to the equation

$$\varepsilon(\mathbf{k}, \omega) = 0, \quad (5.6)$$

give the exact frequency-vs.- $\mathbf{k}$ relation, $\omega = \omega(\mathbf{k})$, of the longitudinal collective eigenoscillations, such as longitudinal acoustic (LA) waves (for a proof see Sect. D.1c in Appendix).

- (d) We have also shown that the Fourier transform, $4\pi q_1 q_2 / 4\pi \varepsilon_0 k^2$, of the Coulomb interaction, $q_1 q_2 / 4\pi \varepsilon_0 r_{12}$, of two charges q_1, q_2 in vacuum, is simply connected to the Fourier transform, $\tilde{\mathcal{V}}_s(\mathbf{k}, \omega)$, of the screened Coulomb interaction, $\mathcal{V}_s(\mathbf{r}_{12})$, between two charges q_1, q_2 *inside* a solid:

$$\tilde{\mathcal{V}}_s(\mathbf{k}, \omega) = \frac{4\pi q_1 q_2}{4\pi \varepsilon_0 \varepsilon(\mathbf{k}, \omega) k^2}, \quad (5.7)$$

where $\varepsilon(\mathbf{k}, \omega)$ is the dielectric function of the solid (see Section D.1g in Appendix D). Thus, the dielectric function provides in general a dynamic (i.e., ω -dependent) screening of the bare Coulomb interaction. In the simple case, where the screened Coulomb interaction is assumed to have the familiar form,

$$\mathcal{V}_s(r_{12}) = \frac{q_1 q_2}{4\pi \varepsilon_0 r_{12}} e^{-k_s r_{12}}, \quad (5.8)$$

Its Fourier transform is equal to (see Problem 5.11s)

$$\tilde{\mathcal{V}}_s(k) = \frac{4\pi q_1 q_2}{4\pi \varepsilon_0 (k^2 + k_s^2)}, \quad (5.9)$$

where k_s is the inverse screening length. Hence, a screening of the form (5.9) corresponds (according to (5.7)) to a dielectric function of the form

$$\varepsilon(k) = 1 + (k_s^2/k^2), \quad \omega/v_F \ll k \ll k_F, \quad (5.10)$$

since the substitution of (5.10) in (5.7) produces (5.9). Notice that the more accurate expression given in (D.26)–(D.28) reduces to (5.10), when $k \ll k_F$.

Furthermore, the dielectric function gives the losses of an energetic charged particle of known trajectory inside a solid as well as the inelastic differential scattering cross-section of a charged particle by a solid. Finally, the potential energy of the JM can be expressed in terms of $\varepsilon(\mathbf{k}, \omega)$. For more information about the role of $\varepsilon(\mathbf{k}, \omega)$ in various physical quantities the readers are urged to read Sect. D.1 of Appendix D.

In Section D.3 of Appendix D, we employed a simple Newtonian equation of motion with a few phenomenological parameters and we obtained the following approximate expression for the dielectric function:

$$\varepsilon(\mathbf{k}, \omega) = 1 - \frac{\omega_{pf}^2}{\omega^2 + i\omega/\tau_f} - \sum_b \frac{\omega_{pb}^2}{\omega^2 - \omega_b^2 + i\omega/\tau_b} - \frac{\omega_{pi}^2}{\omega^2 - \omega_i^2 + i\omega/\tau_i}, \quad k \ll \frac{\omega}{v_F}. \quad (5.11)$$

The last term in the rhs of (5.11) is the contribution to ε due to the ionic motion (assuming a single ion per primitive cell and $k \ll \omega/v_i$, see (5.14)); the sum over b is due to the excitation of various groups of electrons not contributing to the DC conductivity (e.g., electrons bound to the ions); finally, the term $\omega_{pf}^2/(\omega^2 + i\omega/\tau_f)$ is the contribution of “free” electrons (i.e., electrons contributing to the DC conductivity). The frequencies ω_{pf} , ω_{pb} , ω_{pi} appearing in (5.11) are given in terms of the corresponding concentrations n_f , n_b , and $n_i = n_a$ as follows:

$$\omega_{pf}^2 = \frac{4\pi e^2 n_f}{4\pi \varepsilon_0 m_e}, \quad (5.12)$$

$$\omega_{pb}^2 = \frac{4\pi e^2 n_b}{4\pi \varepsilon_0 m_e}, \quad (5.13)$$

$$\omega_{pi}^2 = \frac{4\pi (\zeta e)^2 n_a}{4\pi \varepsilon_0 m_a}. \quad (5.14)$$

The parameters τ_f , τ_b , τ_i are phenomenological relaxation times for “free” electrons, “bound” electrons, and ions respectively; to the “free” -electron-relaxation time we shall return in the next two sections. Each of the bound electron resonance frequencies ω_b is related classically to a restoring force of the form $-\kappa_b \mathbf{u}$, according to the formula $\omega_b^2 = \kappa_b/m_e$, while, quantum mechanically, the various $\hbar\omega_b$ ’s are related to excitation energies; finally, the ionic quantity $\omega_i = c_t k$ has been included purely phenomenologically to take into account the existence of transverse ionic collective oscillation, i.e., transverse acoustic waves, as dictated by (5.5). Note that, strictly speaking, in the JM $\omega_i = 0$. In Fig. 5.1 we present data for the dielectric function of silver, which exhibits a free-electron-like behaviour $\varepsilon = \varepsilon_b - \omega_{pf}^2/(\omega^2 + i\omega/\tau_f)$. (Notice that $\varepsilon_b = 6.8$ instead of 1 because of “bound” electron contributions, when $\omega \ll \omega_b$ and $\omega \ll \omega_b^2 \tau_b$).

It must be stressed that (5.11) is an approximate expression valid only when $k \ll \omega/v_F$ and $k \ll \omega/v_i$. More explicitly, the free electron contribution

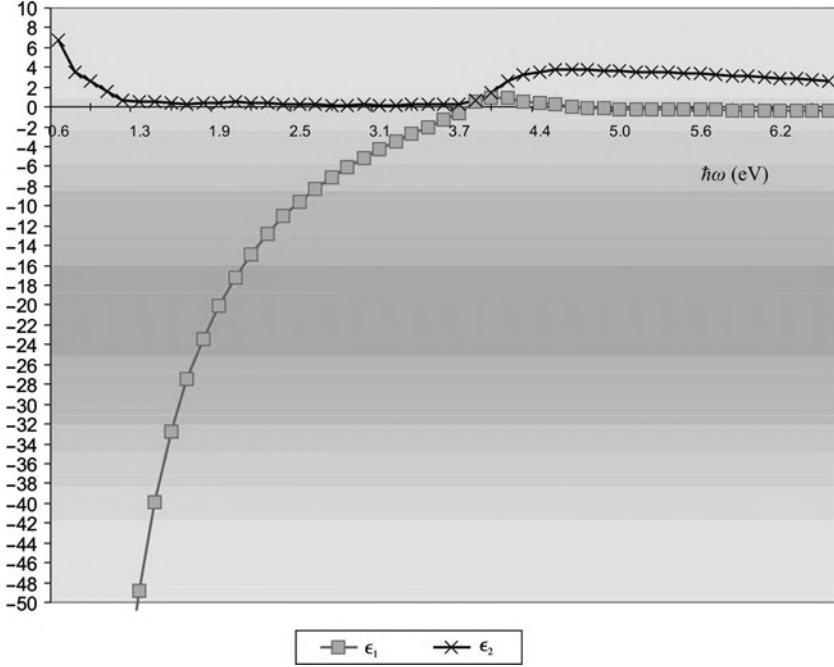


Fig. 5.1. The experimentally determined dielectric function of Ag ($\epsilon_1 = \text{Re}(\epsilon)$, $\epsilon_2 = \text{Im}(\epsilon)$), vs. $\hbar\omega$ (in eV). The experimental points follow very closely the JM-like formula $\epsilon/\epsilon_b = 1 - (\omega_p^2 / (\omega^2 + i\omega/\tau_f))$, known as the *Drude formula* with $\omega_p^2 = \omega_{pf}^2/\epsilon_b$ (for Ag $\epsilon_b = 6.8$, $\hbar\omega_p = 3.8$ eV, $1/\tau_f \simeq 0.04$ eV) (After B.P. Johnson and R. W. Christy, PRB 6, 4370 (1972))

to $\epsilon(\mathbf{k}, \omega)$, $\delta\epsilon_f(\mathbf{k}, \omega)$, is given by quite different expressions in the two limiting regimes, $k \ll \omega/v_F$, and $k \gg \omega/v_F$:

$$\delta\epsilon_f(\mathbf{k}, \omega) \simeq -\frac{\omega_{pf}^2}{\omega^2 + i\omega/\tau_f}, \quad k \ll \omega/v_F \quad (5.15)$$

$$\simeq \frac{k_s^2}{k^2}, \quad k \gg \omega/v_F. \quad (5.16)$$

The expression (5.15) follows from (5.11), while the expression (5.16) follows from (5.10) (or the more accurate (D.26), which is valid for $k > k_F$ as well, while the validity of (5.16) requires also that $k \ll k_F$).

Similarly the contribution $\delta\epsilon_i(\mathbf{k}, \omega)$ from the single ion per primitive cell is given by the following expressions in the two limiting regimes, $k \ll \omega/v_i$, and $k \gg \omega/v_i$:

$$\delta\epsilon_i(\mathbf{k}, \omega) \simeq -\frac{\omega_{pi}^2}{\omega^2 - \omega_i^2 + i\omega/\tau_i}, \quad k \ll \omega/v_i, \quad (5.17)$$

$$\simeq \text{constant} \ll 1, \quad k \gg \omega/v_i. \quad (5.18)$$

Notice that the characteristic ionic velocity v_i , which separates the two limiting regimes for the ionic contribution is determined by the relation $m_a v_i^2 \simeq \hbar \omega_D$; it is easy to show that v_i is of the order of $v_F (m_e/m_a)^{3/4}$. The typical value of v_F in metals is of the order of 10^8 cm/s, while the typical value of v_i is of the order of 10^4 cm/s (for $m_a \simeq 50 m_u$).

The bound electron contribution is not so sensitive to the ratio $\omega/v_F k$ and is expected to give a constant positive contribution, $\tilde{\chi}_b$, in the regime $\omega/v_F \ll k \ll \omega/v_i$ and for $\omega \ll \omega_b$; in this regime, the “free” electron contribution is given by (5.16), while the ionic contribution is given by (5.17). Thus,

$$\varepsilon(\mathbf{k}, \omega) \simeq 1 + \frac{k_s^2}{k^2} + \tilde{\chi}_b - \frac{\omega_{pi}^2}{\omega^2 - \omega_i^2 + i\omega/\tau_i}, \quad \omega/v_F \ll k \ll \omega/v_i \quad (5.19)$$

The vanishing of (5.19) gives, according to (5.6), the ω -vs.- k relation of longitudinal collective eigenoscillations; the resulting ω -vs.- k relation is the following (we omitted the lossy term $i\omega/\tau_i$ and we took into account that $\omega_i^2 = c_t^2 k^2$):

$$\omega_k^2 = \left[c_t^2 + \frac{\omega_{pi}^2}{(1 + \tilde{\chi}_b) k^2 + k_s^2} \right] k^2. \quad (5.20)$$

However, this is the ω -vs.- k relation for a LA wave the velocity c_ℓ of which (defined in the limit of small k , i.e., when $(1 + \tilde{\chi}_b) k^2 \ll k_s^2$) is

$$c_\ell^2 = c_t^2 + \frac{\omega_{pi}^2}{k_s^2}. \quad (5.21)$$

The readers may recall that c_ℓ is of the order of a few km/s, i.e., about 3×10^5 cm/s; hence, it satisfies the double inequality $v_i \ll c_\ell \ll v_F$, and hence, $k = \omega/c_\ell$ satisfies the conditions $\omega/v_F \ll k \ll \omega/v_i$, necessary for the validity of (5.19), on which both (5.20) and (5.21) are based. Strictly speaking, within the JM, $c_t = 0$ and $c_\ell^2 = c_0^2 = B/\rho_M$. Combining the last two relation with (5.21), we find the following expression for the inverse screening length, k_s :

$$k_s^2 = \frac{\omega_{pi}^2}{c_0^2} = \frac{\omega_{pi}^2}{B} \rho_M, \quad (5.22)$$

$$= \left(\frac{7.03 \zeta^{5/3} k_F}{\alpha a_B} \right)^{1/2}, \quad \text{RJM}, \quad (5.23)$$

$$= \left(\frac{4 k_F}{\pi a_B} \right)^{1/2} \equiv k_{TF}, \quad \text{JM}. \quad (5.24)$$

This last expression coincides with (D.27).

Problem 5.1t. Prove (5.23, 5.24), using for the first one (4.59) and for the second one (4.60); $k_{TF} \equiv (4k_F/\pi a_B)^{1/2}$ is known as the *Thomas-Fermi inverse screening length*.

The LA wave, which corresponds to $\varepsilon(k, \omega) = 0$ in the regime $(\omega/v_F) \ll k \ll (\omega/v_i)$ (i.e., when $\varepsilon(k, \omega)$ is given by (5.19)), is mainly a wavy *ionic* motion, where the resulting oscillating variations in the density of ionic charges are screened by the very mobile free electrons; the smaller k is, the more efficient the screening is and the weaker the restoring force is. This explains why $\omega(k) \rightarrow 0$ as $k \rightarrow 0$.

Besides LA waves, there is another kind of longitudinal collective eigenoscillations involving essentially only electrons and appearing in the opposite limit of $\omega \gg v_F k$ (i.e., when $\varepsilon(k, \omega)$ is given by (5.11)). For simplicity, we omit the lossy terms and we make the reasonable assumption that $\omega_i \ll \omega \ll \omega_b$; then the solution of the equation, $\varepsilon(k, \omega) = 0$, determining the eigenfrequency of this longitudinal oscillation, gives

$$\omega_p = \sqrt{(\omega_{pf}^2 + \omega_{pi}^2)/(1 + \tilde{\chi}_b)} \simeq \omega_{pf}/\sqrt{1 + \tilde{\chi}_b}, \quad (5.25)$$

where $\tilde{\chi}_b = \sum_b \omega_{pb}^2/\omega_b^2$. This so-called *plasma oscillation* is a wavy *collective free-electron* motion against the almost-immobile ions. The resulting oscillating variations in the electronic charges, which cannot be screened by the almost-immobile ions, set up long-range Coulomb fields providing the strong restoring force responsible for the high value of eigenfrequency, ω_p . The quantity $\hbar\omega_p$ can be determined experimentally by inelastic scattering of an external electronic beam. For simple metals, like the alkalis, where $\varepsilon(\omega)$ at UV is dominated by the free electron-contribution, ω_p can also be determined approximately as the frequency at which the metal becomes transparent to UV radiation. Indeed, for $\omega > \omega_p$, the dielectric function $\varepsilon(\omega) \simeq 1 + \tilde{\chi}_b - (\omega_{pf}^2/\omega^2)$ becomes positive, and, hence, $k = \omega\sqrt{\varepsilon}/c$ becomes positive indicating propagation. In Table 5.1 we present the experimental values of ω_p for some materials. In Fig. 5.2 we plot the ω -vs.- k relation for the quanta of the two longitudinal eigenoscillations, the LA phonon and the plasmon.

Problem 5.2t. Show that, in the simple JM, $\bar{\omega}_{pf} \equiv \omega_{pf}/\omega_0$, (where $\omega_0 = \hbar/m_e a_B^2$), is equal to

$$\bar{\omega}_{pf} = \frac{\sqrt{3}}{\bar{r}_s^{3/2}}, \quad (5.26)$$

Table 5.1. Experimental values for $\hbar\omega_p$ for various materials (in eV). In the upper line the data are from inelastic scattering, while in the lower they are from the transparency threshold

Li	Na	K	Rb	Mg	Al	Ag	Si ^a	Ge ^a
7.12	5.71	3.72	—	10.6	15.3	—	16.7	16.2
8.00	5.90	3.97	3.65	—	—	3.8	—	—

^aAt such high value of $\omega = \omega_p$, the valence electrons behave approximately as free (see p. 116, Eq. (5.11) because $\omega_p \gg \omega_b$).

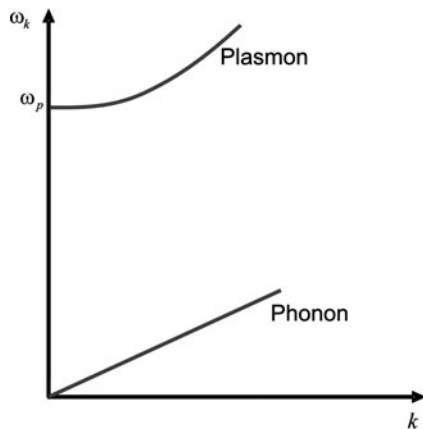


Fig. 5.2. Dispersion relation, ω_k vs. k , for longitudinal acoustic (LA) phonon and for plasmon in metals. Phonons and plasmons are examples of collective bosonic quasiparticles

or

$$\hbar\omega_{\text{pf}} = \frac{47.13}{r_s^{3/2}} \text{ eV}, \quad (5.27)$$

or

$$\omega_{\text{pf}} = \frac{7.16}{r_s^{3/2}} \times 10^{16} \text{ rad/s}. \quad (5.28)$$

Problem 5.3t. Show that ω_{pf} can be expressed in terms of the Fermi velocity, v_F and the electronic DOS at E_F per unit volume and per spin, $\rho_{\text{FV}} = \rho_F/V$, as follows:

$$\omega_{\text{pf}}^2 = \frac{4\pi}{4\pi\epsilon_0} \frac{2}{3} e^2 v_F^2 \rho_{\text{FV}}, \quad (5.29)$$

Equation (5.29) is important because its validity extends beyond the JM.

5.3 Static Electrical Conductivity

The JM always produces a single band of electronic eigenenergies extending from $E = 0$ to $E = \infty^2$. There are no gaps in the DOS within the framework of the JM; hence, this model fails completely to describe the DC conductivity of semiconductors and insulators; it exhibits always only metallic behavior. Thus, the results for transport quantities based on the JM are applicable only to metals (and even there they may fail quantitatively).

² More precisely, the lowest energy of this infinite band is $\mu_P = (\partial E_P / \partial N_e)_V$ where E_P is the potential energy. Usually, for simplicity, we choose the zero of energy at μ_P , i.e., we set $\mu_P = 0$.

In the DC limit, $\omega \rightarrow 0$, only the free electron part, σ_f , contributes to the electrical conductivity. The result, by combining (5.1) and (5.11), is

$$\sigma_f = \sigma = \frac{n_e e^2 \tau}{m} = 4\pi \varepsilon_0 \omega_{\text{pf}}^2 \tau / 4\pi. \quad (5.30)$$

In (5.30) and from now on we drop the index f, since we are dealing only with free electrons. The validity of the equation $\sigma = 4\pi \varepsilon_0 \omega_{\text{pf}}^2 \tau / 4\pi$ goes beyond the JM, if the realistic expression (5.29) for ω_{pf}^2 is used. Instead of τ , it is more convenient to introduce the mean free path ℓ (to the inverse of which both elastic and inelastic scatterings contribute (see (5.38) and Sect. 5.4 below as well as Sect. 9.4) through the relation

$$\ell = v_F \tau. \quad (5.31)$$

The Fermi velocity enters in ℓ , because only the electrons at E_F are capable of responding to the electric field (because of Pauli's principle). It is also useful to introduce the concept of the area of the *Fermi surface*, S_F ; this is the surface in $\mathbf{k}$ -space, the points of which satisfy the equation

$$\varepsilon_{\mathbf{k}} = E_F. \quad (5.32)$$

Within the JM, the Fermi surface is a sphere of radius $k_F = (2mE_F/\hbar^2)^{1/2}$; its area $S_F = 4\pi k_F^2 \sim n_e^{2/3}$, since $k_F = (3\pi^2 n_e)^{1/3}$. In more realistic models, the dependence of S_F on n_e is not so simple.

Problem 5.4t. Prove the following relations for the resistivity, ρ , or the conductivity, σ :

$$\rho \equiv \frac{1}{\sigma} = 92.5 \frac{\bar{r}_s^2}{\ell} \mu\Omega \text{ cm}, \quad \ell \text{ in } \text{\AA}, \quad (5.33)$$

$$\sigma = \frac{1}{12\pi^3} \frac{e^2}{\hbar} S_F \ell, \quad (5.34)$$

$$\sigma = \frac{2}{3} e^2 \rho_{\text{FV}} v_F \ell. \quad (5.35)$$

Hints: Start with (5.30), (5.31) and take into account (4.21), $n_e = k_F^3/3\pi^2$, $S_F = 4\pi k_F^2$, and (5.29).

Equations (5.34) and (5.35) are important because they are valid not only within the JM but also for more realistic models, provided that the actual area of the Fermi surface or the actual values of ρ_{FV} and v_F are employed.

To proceed with the theoretical calculation of σ (or ρ), we need to obtain the mean free path ℓ ; ℓ is related to the concentration of scatterers, n_s , and their transport scattering cross-section, σ_s ; the latter gives the area of the electron flow front intercepted by each scatterer. If the scattering is weak

and/or the concentration, n_s , of scatterers is low, the mean free path is given by the relation

$$\ell n_s \sigma_s = 1. \quad (5.36)$$

Equation (5.36) can be easily justified by considering a cylindrical volume parallel to the electron flow of length L and geometrical cross-section S ; the number of scatterers within this volume is $n_s SL$ and each one intercepts an area σ_s . Thus, the total area intercepted is equal to $n_s SL \sigma_s$. We define ℓ so that, when $L = \ell$, the whole flow through the cross-section of the cylinder is just intercepted, which means that $n_s S \ell \sigma_s = S$, i.e., (5.36). Equation (5.36) assumes that all scatterers have the same cross-section σ_s . If there are different types of scatterers, each one with concentration n_{sj} and cross-section σ_{sj} , then, (5.36) can be easily generalized to become

$$\ell \sum_j n_j \sigma_{sj} = 1, \quad (5.37)$$

or

$$\frac{1}{\ell} = \sum_j \frac{1}{\ell_j}, \quad \frac{1}{\ell_j} = n_{sj} \sigma_{sj}. \quad (5.38)$$

In particular, we have contributions to $1/\ell$ by the various types of defects (e.g., vacancies, interstitials, foreign atoms, etc.) and by the phonons. The additionality of the various contributions to $1/\ell$, which is valid under the same conditions guaranteeing the validity of (5.36), is known as the *Matthiessen rule*.

The transport scattering cross-section, σ_s , is connected to the differential scattering cross-section $d\sigma_s/d\Omega$ by the relation

$$\sigma_s = \int \frac{d\sigma_s}{d\Omega} (1 - \cos \theta) d\Omega, \quad (5.39)$$

where $d\Omega$ is the infinitesimal element of the solid angle Ω , θ is the angle between the direction of the unperturbed electronic flow and its direction after the scattering. The integration extends over all values of θ , ϕ ; the extra factor $(1 - \cos \theta)$ has been included to take into account that *for transport properties* the forward ($\theta = 0$) component of the scattering does not count as impediment to the flow. Finally, the differential cross-section is given in terms of scattering potential $\mathcal{V}_s(\mathbf{r})$ by the so-called *Born approximation* (see (B.62, B.63)):

$$\frac{d\sigma_s}{d\Omega} \simeq \frac{m^2}{4\pi^2 \hbar^4} \left| \tilde{\mathcal{V}}(\mathbf{k}) \right|^2. \quad (5.40)$$

where m is the mass of the electron and $\tilde{\mathcal{V}}(\mathbf{k})$ is the Fourier transform of $\mathcal{V}_s(\mathbf{r})$:

$$\tilde{\mathcal{V}}(\mathbf{k}) = \int d^3r e^{-i\mathbf{k}\cdot\mathbf{r}} \mathcal{V}_s(\mathbf{r}), \quad (5.41)$$

$\mathbf{k}$ is the difference between the electronic wavevector after and before the scattering

$$\mathbf{k} = \mathbf{k}_f - \mathbf{k}_i. \quad (5.42)$$

5.4 Phonon Contribution to Resistivity³

The defect scattering depends on each individual specimen and consequently no general theory can be developed. In contrast, the phonon scattering is amenable to a generic theoretical approach. Notice that the scattering of electrons by phonons is in general inelastic, since it involves mainly emission or absorption of a phonon; however, at higher temperatures, $k_B T > \hbar\omega$, where ω is the phonon frequency, this scattering can be treated as an elastic one with no appreciable error. Since the phonons extend over the whole volume of the solid, their scattering field, $\mathcal{V}_{\text{ph}}(\mathbf{r})$, also extends over the whole volume V , i.e., there is only one scattering potential and the corresponding concentration is $1/V$. The Fourier transform of $\mathcal{V}_{\text{ph}}(\mathbf{r})$ is

$$\tilde{\mathcal{V}}_{\text{ph}}(\mathbf{k}) = \frac{4\pi e^2 n_e}{4\pi\epsilon_0} \frac{\mathbf{i}\mathbf{k} \cdot \mathbf{u}(\mathbf{k})}{k^2 \epsilon(k)}, \quad (5.43)$$

where $\mathbf{u}(\mathbf{k})$ is the Fourier transform of the ionic displacement $\mathbf{u}(\mathbf{r})$, and $\epsilon(k) \equiv \epsilon(k, 0)$ is the static electronic dielectric function given either by (5.10) or by (D.26–D.28). For a proof of (5.43), see Problem 5.5t. Notice that (5.43) includes the contribution of only longitudinal phonons, since for transverse phonons the factor $\mathbf{k} \cdot \mathbf{u}(\mathbf{k})$ is zero by definition; however, in actual solids transverse phonons contribute to the scattering potential (see Sect. 12.7).

Problem 5.5t. Prove (5.43).

Hints: Show that the ionic displacement $\mathbf{u}(\mathbf{r})$ sets up a change, δn_a , in the ionic concentration, given by

$$\delta n_a = \delta \left(\frac{\Delta N_a}{\Delta V} \right) = -\frac{\Delta N_a}{\Delta V^2} \delta(\Delta V) = -\frac{\Delta N_a}{\Delta V} \frac{\delta(\Delta V)}{\Delta V} = -n_a \nabla \cdot \mathbf{u}(\mathbf{r}), \quad (5.44)$$

(see also (E.2)); the change δn_a creates an excess ionic charge $\delta \rho_i = \zeta e \delta n_a = -\zeta e n_a \nabla \cdot \mathbf{u}(\mathbf{r})$. The resulting Coulomb field, $\phi(\mathbf{r})$, satisfies Poisson's equation,

$$-4\pi\epsilon_0 \nabla (\hat{\epsilon} \nabla \phi) = 4\pi \delta \rho_i, \quad (5.45)$$

where $\epsilon_0 \hat{\epsilon}$ is the static permittivity (in SI) and $\hat{\epsilon}$ is the dielectric function due to the free electron screening. By taking the Fourier transforms of (5.45), we have

$$4\pi\epsilon_0 k^2 \epsilon(k) \phi(k) = 4\pi \delta \rho_i(k) = -4\pi i e n_e \mathbf{k} \cdot \mathbf{u}(\mathbf{k}). \quad (5.46)$$

³ This section can be omitted at this stage except for (5.55, 5.56) and (5.63).

Hence, the Fourier transform of the screened ionic potential felt by an electron of charge $-e$ is

$$\tilde{V}_{\text{ph}}(\mathbf{k}) = -e\phi(\mathbf{k}) = \frac{4\pi e^2 n_e}{4\pi\epsilon_0} \frac{i\mathbf{k} \cdot \mathbf{u}(\mathbf{k})}{k^2 \epsilon(k)}.$$

Problem 5.6t. Show that within the JM

$$(\mathbf{k} \cdot \mathbf{u}(\mathbf{k}))^2 = \frac{V}{B} \hbar\omega_k \langle n_k \rangle, \quad \langle n_k \rangle = \frac{1}{e^{\beta\hbar\omega_k} - 1}. \quad (5.47)$$

Hints: Within the JM, the average elastic deformation energy, $\int \Delta d^3r$, equals $\frac{1}{2} \int B (\nabla \cdot \mathbf{u}(\mathbf{r}))^2 d^3r$ (see (E.12) and (E.13)). The total ionic energy (elastic plus kinetic) is twice the average elastic, i.e.,

$$U_{\text{ph}}(T) = B \int (\nabla \cdot \mathbf{u}(\mathbf{r}))^2 d^3r = B \int \frac{d^3k}{(2\pi)^3} (\mathbf{k} \cdot \mathbf{u}(\mathbf{k}))^2 = \frac{B}{V} \sum_k (\mathbf{k} \cdot \mathbf{u}(\mathbf{k}))^2. \quad (5.48)$$

To obtain (5.48), we Fourier-transformed the first integral and then we used the basic relation (B.19). However, $U_{\text{ph}}(T) = \sum_k \hbar\omega_k \langle n_k \rangle$. Show also that at high temperatures, $T \gtrsim \Theta_D$, $\hbar\omega_k \langle n_k \rangle \rightarrow k_B T$.

Problem 5.7t. We define the quantity

$$E_s \equiv 4\pi e^2 n_e / 4\pi\epsilon_0 k_s^2, \quad (5.49)$$

which is called *deformation potential*. Using the relations $k_s^2 = \omega_{\text{pi}}^2 / c_0^2$ and $c_0^2 = B / \rho_M$, show that

$$E_s = B / n_e, \quad (5.50)$$

(in the simple JM with the potential energy omitted, $B = 2n_e E_F / 3$, and hence, $E_s = \frac{2}{3} E_F$). We define also the dimensionless quantities ξ_t and λ_0 ,

$$\xi_t \equiv \frac{1}{4\pi} \int d\Omega (1 - \cos\theta) \frac{k_s^4}{k^4 \epsilon^2(k)}, \quad (5.51)$$

$$\lambda_0 \equiv \frac{E_s^2}{B} \frac{\rho_F}{V} = \frac{3B}{4n_e E_F}. \quad (5.52)$$

The quantity λ_0 is a dimensionless measure of the strength of electron–phonon interaction. Show that, within the framework of the simple JM with the potential energy omitted,

$$\lambda_0 = 0.5 \quad (5.53)$$

while, within the framework of the RJM,

$$\lambda_0 = 0.091\alpha/\zeta^{5/3}, \quad (5.54)$$

where α is given by (4.41). Using these definitions and (5.30), (5.36) (i.e., $\rho = \sigma^{-1} = 4\pi v_F / 4\pi\epsilon_0\omega_p^2\ell$), $1/\ell = \sigma_s/V$ (for phonons), (5.39), (5.40), (5.43), and (5.47), we can easily show that at high temperatures (at which $\hbar\omega_k \langle n_k \rangle \rightarrow k_B T$) the phonon due electrical resistivity is given by

$$\rho_{\text{ph}} = \frac{8\pi^2}{4\pi\epsilon_0\hbar} \frac{\lambda_t}{\bar{\omega}_{\text{pf}}^2} k_B T = 1.6 \frac{\lambda_t}{\bar{\omega}_{\text{pf}}^2} \frac{T}{295} \mu\Omega \text{ cm}, \quad \text{SI}^4, \quad (5.55)$$

$$= 1.81 \times 10^{-3} \lambda_t \bar{r}_s^3 T \mu\Omega \text{ cm}, \quad \text{simple JM} \quad (5.56)$$

where, in (5.56) and the last relation of (5.55), T is in degrees Kelvin and

$$\lambda_t \equiv \lambda_0 \xi_t.$$

Notice that (5.56) is almost identical to (2.45), which was obtained with dimensional analysis and a “little thinking.” The quantity, ξ_t , depends on the value of $\bar{r}_s$ and the details of the dielectric function, $\epsilon(k)$, and it is expected to be in the range between 0.25 and 0.55 with a typical value around 0.35. Thus, the dimensionless transport-electron-phonon coupling $\lambda_t \equiv \lambda_0 \xi_t$, according to the JM, is expected to satisfy the rough inequalities

$$0.1 \lesssim \lambda_t \lesssim 0.3.$$

The regular dimensionless electron-phonon coupling λ , i.e., the one that appears in the $(1 + \lambda)$ factor in the electronic specific heat, is defined as

$$\lambda = \lambda_0 \xi, \quad (5.57)$$

where ξ is as ξ_t but without the factor $(1 - \cos\theta)$:

$$\xi \equiv \frac{1}{4\pi} \int d\Omega \frac{k_s^4}{k^4 \epsilon^2(k)}. \quad (5.58)$$

The value of ξ is in the range between 0.30 and 0.65 so that for the JM

$$0.15 \lesssim \lambda \lesssim 0.35.$$

We give the experimental values of λ_t and λ for several metals in the following section (Table 5.2).

We see that alkali and noble metals, the transport properties of which are free-like, have λ and λ_t in reasonable agreement with the JM result. On the contrary, for metals that are not free-like, such as transition metals, and for soft metals, such as Hg and Pb, λ and λ_t are considerably larger than that of the JM predictions.

The formalism we developed allows us to obtain an expression for the phonon contribution to the resistivity for all temperatures. Indeed, by combining (5.30), (5.31), (5.36), (5.39), (5.40, 5.42), (5.43), (5.57), $k^2 = 2k_F^2(1 - \cos\theta)$,

⁴ In G-CGS $4\pi\epsilon_0$ must be replaced by one (i.e., it must be omitted).

Table 5.2. Values of the dimensionless electron–phonon couplings λ and λ_t for various metals

	Al	Pb	In	Hg	Cu	Ag	Au	Nb
λ_t	0.36	1.5	0.72	2.3	0.12	0.12	0.15	1.0
λ	0.43 ± 0.05	1.55 ± 0.02	0.805 ± 0.01	1.60 ± 0.01	0.14 ± 0.03	0.10 ± 0.04	0.14 ± 0.05	0.90 ± 0.2
	Li	Na	K	Rb	Cs	Mg	Zn	Cd
λ_t	0.34	0.14	0.11	0.15	0.16	0.32	0.69	0.51
λ	0.41 ± 0.15	0.16 ± 0.04	0.13 ± 0.03	0.16 ± 0.04	0.16 ± 0.04	0.35 ± 0.04	0.42 ± 0.05	0.40 ± 0.05

and the definitions (5.51, 5.52) we end up, after some straightforward but lengthy algebra, with the following formula for the $\rho_{\text{ph}}(T)$:

$$\rho_{\text{ph}}(T) = \frac{8\pi^2}{4\pi\epsilon_0\hbar\omega_{\text{pf}}^2} \lambda_0 \frac{4k_{\text{B}}T}{y_0^4} \int_0^{y_0} \frac{dy y^4}{(1 + (2by^2/y_0^2))^2 (e^y - 1)}, \quad (5.59)$$

where

$$y_0 = \frac{2\hbar\tilde{c}k_{\text{F}}}{k_{\text{B}}T} = 2^{2/3}\zeta^{1/3} \frac{\Theta_{\text{D}}}{T}, \quad (5.60)$$

and

$$b = \frac{2k_{\text{F}}^2}{k_{\text{TF}}^2 f} \quad (5.61)$$

For high⁵ temperatures $y_0 \ll 1$, and $e^y - 1 \approx y$ and (5.59) reduces to (5.55) with ξ_t being equal to $4/y_0^4$ times the integral in (5.59). At very low temperatures $T \ll \Theta_{\text{D}}$, $y_0 \rightarrow \infty$, and the integral goes to a numerical constant (equal to 24.89). Hence,

$$\rho_{\text{ph}}(T) \sim T^5, \quad T \ll \Theta_{\text{D}}. \quad (5.62)$$

The T^5 dependence of the phonon contribution to ρ at very low temperatures is confirmed experimentally for most metals; however, the coefficient in front of T^5 , according to (5.59), is much smaller than the corresponding experimental values. The origin of this discrepancy can be traced to our treatment of the electron–phonon interaction as a static field, and consequently, of the electron scattering by phonons as an elastic one. This approximation is justified at high temperatures but not at low temperatures, where $k_{\text{B}}T \lesssim \hbar\omega_{\text{ph}}$.

If the scattering is treated correctly as an inelastic one, (5.59) will be modified by the inclusion within the integral of an extra factor $y/(1 - e^{-y})$, which

⁵ The function, $f(k/k_{\text{F}})$, given by (D.28), can be approximated by an appropriate constant to facilitate the calculation of the integral in (5.59).

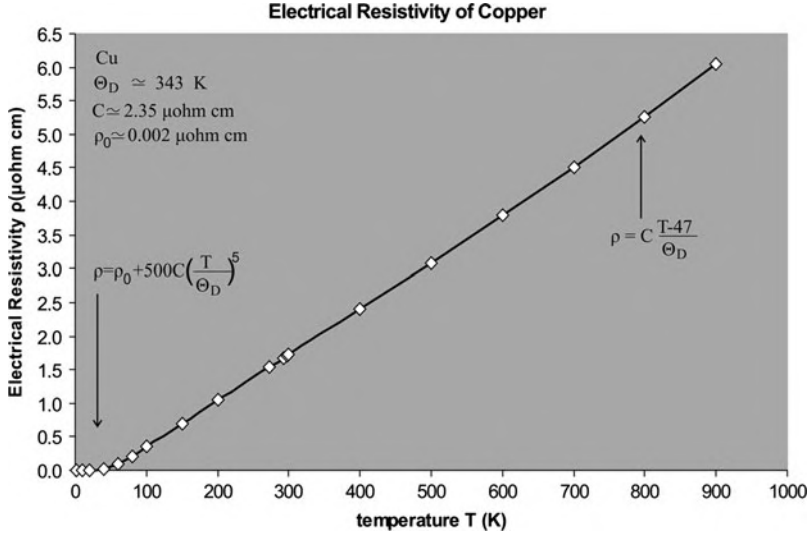


Fig. 5.3. The electrical resistivity of copper vs. temperature. The experimental data are in good agreement with the theoretical results presented in Sect. 5.4. The residual resistivity ρ_0 is due to defects

tends to one for high temperatures, as $y \leq y_0 \rightarrow 0$, but boosts significantly the value of the coefficient in front of the T^5 term at low temperatures:

$$\rho_{\text{ph}}(T) \simeq 498 C \left(\frac{T}{\Theta_D} \right)^5, \quad C \equiv \frac{1}{(4\zeta)^{4/3}} \frac{8\pi^2 \omega_D}{4\pi \varepsilon_0 \omega_p^2} \lambda_0, \quad T \ll \Theta_D. \quad (5.63)$$

For a detailed derivation of (5.55) to (5.63), see Problem 5.13s. In Fig. 5.3 we plot the resistivity of a typical metal, namely copper, vs. T .

5.5 Response in the Presence of a Static Uniform Magnetic Field

In this section, we give a brief presentation of how a solid responds to the presence of a preexisting static, uniform magnetic field, $\mathbf{B}_0$. We shall also consider the case where in addition to the field $\mathbf{B}_0$, a static electric field $\mathbf{E}$ is applied too. A third case of interest involves the field $\mathbf{B}_0$ as well as an additional EM wave of frequency ω , such that $\omega = \omega_{oi}$, where ω_{oi} are eigenfrequencies of the system, the existence and values of which depend on the presence and value of $\mathbf{B}_0$.

5.5.1 Magnetic Resonances

The presence of the magnetic field⁶ $\mathbf{B}$ creates certain eigenfrequencies that are absent, if $\mathbf{B} = 0$. These are due either to periodic electronic motions induced by the magnetic field or to the splitting of spin-dependent degenerate levels as a result of breaking the spherical symmetry by the presence of a special direction (that of $\mathbf{B}$). When the energy $\hbar\omega$, of an external electromagnetic field coincides with any of these eigenenergies, a resonance response is expected to take place appearing as a peak in the absorption coefficient.

Cyclotron Resonance Frequency

A free electron moving with a velocity $\mathbf{v}$ in the presence of $\mathbf{B}$ experiences the Lorentz force⁷

$$\mathbf{F} = -e(\mathbf{v}/c) \times \mathbf{B}, \quad \text{G-CGS.} \quad (5.64)$$

Such a force is zero along the direction of $\mathbf{B}$; thus the parallel to $\mathbf{B}$ component of $\mathbf{v}$, $v_{||}$, remains constant. The perpendicular component $v_{\perp}$ is subject to an acceleration $F/m_e = ev_{\perp}B/m_e c$ which, according to Newton's law of motion, is equal to $v_{\perp}^2/R$, where R is the radius of curvature of the electron trajectory. Thus,

$$\frac{v_{\perp}^2}{R} = \frac{ev_{\perp}B}{m_e c}, \quad (5.65)$$

or

$$\frac{v_{\perp}}{R} \equiv \omega = \frac{eB}{m_e c} \equiv \omega_c, \quad (5.66)$$

which means that the electron does a circular motion of radius $v_{\perp}m_e c/eB$ and of angular frequency $\omega = \omega_c$, which is independent of $\mathbf{v}$ and it is a linear function of the field B . The frequency ω_c is called *cyclotron frequency* ($\omega_c = eB/m_e c$ in G-CGS and $\omega_c = eB/m_e$ in SI).

The same problem treated quantum mechanically produces a spectrum of eigenenergies of the form

$$\varepsilon(k_{||}, n) = \frac{\hbar^2 k_{||}^2}{2m} + \hbar\omega_c \left(n + \frac{1}{2} \right), \quad n = 0, 1, 2, \dots \quad k_{||} = mv_{||}/\hbar. \quad (5.67)$$

Each of these eigenenergies is degenerate; the degeneracy, η , is obtained by the requirement that the average 2D DOS, $\eta/\hbar\omega_c$, (according to (5.67) and in the plane perpendicular to $\mathbf{B}$) is equal to the DOS of a 2D free electron:

⁶ The actual field $\mathbf{B}$ in the material is not exactly equal to $\mathbf{B}_0$; their difference is proportional to $\chi_m \mathbf{B}_0$, which is usually very small in comparison with $\mathbf{B}$ or $\mathbf{B}_0$, because the magnetic susceptibility, χ_m , of most materials is very small of the order of 10^{-6} – 10^{-4} . Therefore, in what follows we take $\mathbf{B} = \mathbf{B}_0$.

⁷ In SI, the velocity of light c (written in light letter) must be omitted so that $\mathbf{F} = -e\mathbf{v} \times \mathbf{B}$, $\omega_c \equiv eB/m_e$, and $R = v_{\perp}m_e/eB$.

$$\frac{\eta}{\hbar\omega_c} = \frac{mS}{2\pi\hbar^2}, \quad (5.68)$$

or

$$\eta = \frac{e}{\hbar c} BS = \frac{\Phi}{2\Phi_0}, \quad (5.69)$$

where $\Phi = BS$ is the magnetic flux through the specimen, and $\Phi_0 \equiv hc/2e$ is the flux quantum (see Chap. 23 and Table H.1). In real monocrystalline solids (as opposed to the JM), several cyclotron resonance frequencies appear as we shall see in a later chapter.

Electronic Paramagnetic Resonance (EPR) or Electronic Spin Resonance (ESR)

In the JM the ions left behind after the detachment of the valence electrons may possess a non-zero total angular momentum $\mathbf{J}$, or a non-zero orbital total angular momentum $\mathbf{L}$, or a non-zero total spin $\mathbf{S}$, where $\mathbf{J} = \mathbf{L} + \mathbf{S}$. Ions with only completed shells have $J = L = S = 0$. We shall consider here the splitting by the magnetic field of degenerate ionic levels in the case where the ground state of each ion is characterized by $J \neq 0$ and $J_z = -J, -(J-1) \dots J-1, J$, i.e., it is $2J+1$ degenerate and the excited electronic states of the ion are so high in energy that their thermal excitation under normal conditions is negligible.

The presence of the magnetic field $\mathbf{B}$ taken along the z -axis breaks the spherical symmetry and splits the $2J+1$ degenerate states through its interaction with the magnetic moment, $\mathbf{m}_i \equiv -\mu_B(\mathbf{L} + 2\mathbf{S})$, of the ion: $\varepsilon_i = -\langle \mathbf{m}_i \rangle \cdot \mathbf{B} = -\langle m_{iz} \rangle B$. The average magnetic moment is mainly due to the electrons attached to the ion and it is related to the total electronic angular momentum $\mathbf{J}$ as follows:

$$\langle \mathbf{m}_i \rangle = -g\mu_B \mathbf{J}, \quad (5.70)$$

where g is the so-called *Landé factor* and is given by⁸

$$g = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}, \quad (5.71)$$

and $\mu_B \equiv e\hbar/2m_e c$ is the so-called *Bohr magneton* (for $L = 0$, $g = 2$, while for $S = 0$, $g = 1$). In general, both the spin and the orbital degrees of freedom contribute to g . Taking into account (5.70) and the definitions presented earlier, we can write the interaction energy $-m_{iz}B$ as follows

$$\begin{aligned} \varepsilon_{J_z} &= g\mu_B B J_z, & J_z &= -J \dots, J \\ &= \hbar\omega_0 J_z, & J_z &= -J \dots, J \end{aligned} \quad (5.72)$$

⁸ For a proof of (5.70, 5.71), see Problem 5.12.

where the frequency of the paramagnetic resonance ω_0 is equal to

$$\omega_0 = \gamma B. \quad (5.73)$$

The quantity $\gamma \equiv g\mu_B/\hbar$ is called *gyromagnetic ratio*. For the pure-spin case $\omega_0 = eB/m_e c$, i.e., ω_0 incidentally coincides with the cyclotron frequency ω_c for free electrons. The EPR frequency for the purely electronic spin case is

$$f_0 = \frac{\omega_0}{2\pi} = 28B, \quad (5.74)$$

where f_0 in the last relation is in GHz and B in Tesla (1 Tesla = 10 kG). For the purely orbital case it is half this size: $f_0 = 14B$.

Nuclear Magnetic Resonance (NMR)

The nucleus of each atom may possess a total angular momentum $\mathbf{I}$ different from zero. In this case, the nucleus has an average magnetic moment $\langle \mathbf{m}_N \rangle$ related to $\mathbf{I}$ through the formula

$$\langle \mathbf{m}_N \rangle = g_N \mu_N \mathbf{I}, \quad (5.75)$$

where the *nuclear magneton*, μ_N , is by definition equal to $(m_e/m_p)\mu_B = \mu_B/1836$ and g_N is the Landé factor for the nucleus. (For the proton spin, $g_p = 2 \times 2.7928 = 5.5857$, while for the neutron spin, $g_n = -2 \times 1.9130 = -3.8261$). Thus, the lowest $2I + 1$ energy levels of the nucleus in the presence of B are given by

$$\varepsilon_{I_z} = -g_N \mu_N B I_z, \quad (5.76)$$

and the angular NMR frequency is $\omega_{0N} = |g_N \mu_N B/\hbar|$. In particular, for hydrogen, the frequency $f_0 = \omega_{0N}/2\pi$ is equal to $2.7928 eB/2\pi m_p c$, or numerically,

$$f_0 = 42.58B, \quad (5.77)$$

where f_0 is in MHz and B in Tesla. The NMR of hydrogen atoms is the principle on which the so-called magnetic resonance imaging (MRI) is based. The MRI tomography is one of the most important non-invasive diagnostic tools in today's medicine through which the anatomy and the function of various organs can be mapped. The NMR is also very useful in Chemistry and Biochemistry, because actually the energy levels ε_{I_z} depend also on the local environment of the ion; thus, NMR spectroscopy is an effective microscopic probe for exploring what is going on around an atom.

The nuclear magnetic moment, μ_N , interacts not only with the external magnetic field B but also with internal effective magnetic fields δB created by the orbital motion of electrons and by the electronic spins. In the absence of the external field B , δB in a nonmagnetic material is on average equal to zero; in the presence of B , δB is expected to be proportional to χB where χ is the magnetic susceptibility. For a diamagnetic solid, as we shall see in

Sect. 5.5.3, $\chi = \chi_L$ where χ_L is negative and very small. In contrast, for a metal, $\chi = \chi_L + \chi_c$ where χ_c is due to the conduction electrons and it is positive and larger than $|\chi_L|$; as we shall see, $\chi_c = (2/3)\chi_{m,P}$ (see (5.108) and (5.109)), where $\chi_{m,P}$ is the so-called Pauli susceptibility, which is proportional to the average concentration, $n_e = N_e/V$, of conduction electrons. However, what matters in the interaction of $\boldsymbol{\mu}_N$ with $\delta\mathbf{B}$ is the local value of the latter, which is proportional to the local value of χ , which in turn is proportional to the local concentration $|\psi(0)|^2$ of the conduction electrons at the site of the nucleus. Hence, $\chi_{c,local} = (|\psi(0)|^2/n)\chi_c$. Thus, the angular NMR frequency ω_{oN} will be shifted by $\delta\omega_{oN} = (g_N\mu_N/\hbar)\delta B$ where $\delta B = K \cdot B$ and

$$\begin{aligned} K &= \frac{2}{3} \frac{|\psi(0)|^2}{n} \chi_{m,P,SI}, & \text{SI.} \\ K &= \frac{8\pi}{3} \frac{|\psi(0)|^2}{n} \chi_{m,P,G-CGS}, & \text{G-CGS} \end{aligned} \quad (5.78)$$

K is known as the *Knight shift* or the *metallic shift*. Typical values of $\chi_{m,P,G-CGS}$ is of the order of 10^{-6} to 10^{-5} for free electron-like metals. Hence, K ought to be of the order of 10^{-5} to 10^{-4} for free electron-like metals, if $|\psi(0)|^2/n$ is of the order of one. Observed values of K in metallic elements are considerably higher (2.6×10^{-4} for Li^7 , 1.62×10^{-3} for Al^{27} , 2.65×10^{-3} for K^{39} , 6.53×10^{-3} for Rb^{87} , and -3.533×10^{-2} for Pt^{195}). According to (5.78), this strongly increased values of K (by almost three orders of magnitude) can be attributed partly to a much higher value of the DOS at E_F relative to that of the JM and partly to a ratio $|\psi(0)|^2/n$ much higher than one. Thus, measuring the Knight shift provides useful information regarding the DOS and the wavefunctions at E_F for metallic solids.

5.5.2 Hall Effect and Magnetoresistance

Within the framework of the JM, we shall examine in this subsection the electrical conductivity in the presence of a static magnetic field. The readers must be aware that in most cases the relevant JM results are not in agreement with the corresponding experimental data. Thus, we shall return to this subject in a later chapter. Moreover, the Hall effect exhibits impressive quantum behavior under certain conditions as we shall see in Sect. 18.9. For the time being, we shall follow the simple Newtonian approach for the equation of motion of the free electrons of charge $q = -|e| = -e$

$$m\dot{\mathbf{v}} = -(m\mathbf{v}/\tau) + q\mathbf{E} + q(\mathbf{v}/c) \times \mathbf{B}, \quad (5.79)$$

Taking the z -axis along the direction of $\mathbf{B}$ and assuming a time dependence of $\mathbf{v}$ and $\mathbf{E}$ of the form $\exp(-i\omega t)$, we can recast (5.79) in Cartesian coordinates

$$(1 - i\omega\tau) v_x + \omega_c \tau v_y = \frac{q\tau}{m} E_x, \quad (5.80)$$

$$-\omega_c \tau v_x + (1 - i\omega\tau) v_y = \frac{q\tau}{m} E_y, \quad (5.81)$$

$$(1 - i\omega\tau) v_z = \frac{q\tau}{m} E_z, \quad (5.82)$$

where we have set ω_c for $-qB/mc$. Taking into account that $\mathbf{j} = qn\mathbf{v}$ and solving the system (5.79, 5.81), we obtain

$$j_x = \frac{\sigma_0}{A} [(1 - i\omega\tau) E_x - \omega_c \tau E_y], \quad (5.83)$$

$$j_y = \frac{\sigma_0}{A} [\omega_c \tau E_x + (1 - i\omega\tau) E_y], \quad (5.84)$$

$$j_z = \frac{\sigma_0}{1 - i\omega\tau} E_z, \quad (5.85)$$

where $\sigma_0 = e^2 n \tau / m$ is the static conductivity in the absence of B and

$$A \equiv (1 - i\omega\tau)^2 + \omega_c^2 \tau^2, \quad (5.86)$$

By inspection of (5.83)–(5.85), we see that the components of the conductivity tensor are

$$\sigma_{xx} = \sigma_{yy} = \frac{\sigma_0 (1 - i\omega\tau)}{A}, \quad \sigma_{zz} = \frac{\sigma_0}{1 - i\omega\tau}, \quad (5.87)$$

$$\sigma_{xy} = -\sigma_{yx} = -\frac{\sigma_0 \omega_c \tau}{A} = \frac{\sigma_0 q B \tau}{A m c} = -\frac{\sigma_0 e B \tau}{A m c},$$

$$\sigma_{xz} = \sigma_{zx} = \sigma_{yz} = \sigma_{zy} = 0. \quad (5.88)$$

From (5.79)–(5.81), the electric field can be expressed in terms of the current density

$$E_i = \sum_{\ell} \rho_{i\ell} j_{\ell}, \quad i, \ell = x, y, z, \quad (5.89)$$

where the resistivity tensor at $\omega = 0$ is given by

$$\rho_{xx} = \rho_{yy} = \rho_{zz} = \frac{1}{\sigma_0}, \quad (5.90)$$

$$\rho_{xy} = -\rho_{yx} = \frac{\omega_c \tau}{\sigma_0} = -\frac{B}{qnc} = \frac{B}{enc}, \quad (5.91)$$

$$\rho_{iz} = \rho_{zi} = 0, \quad i = x, y. \quad (5.92)$$

The existence of a non-zero off-diagonal component in the conductivity or the resistivity tensors due to the presence of a magnetic field is called *Hall effect*. The resistivity ρ_{xy} is called *Hall resistivity* and the ratio $-\rho_{xy}/B$ is called *Hall constant* and is denoted by R ; thus, according to the JM, the Hall constant is equal to:

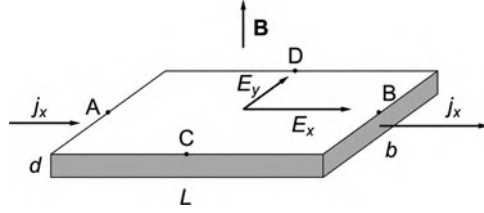


Fig. 5.4. Experimental setup (schematically) for measuring the Hall coefficient R and the reduced transverse magnetoresistance, $[\rho_{xx}(B) - \rho_{xx}(0)] / \rho_{xx}(0)$

$$R = \frac{1}{qnc} = -\frac{1}{enc}, \quad (5.93)$$

(in SI c must be set equal to one). Notice that both the transverse static relative magnetoresistance, $[\rho_{ii}(B) - \rho_{ii}(0)] / \rho_{ii}(0)$, $i = x, y$, and the longitudinal one, $[\rho_{zz}(B) - \rho_{zz}(0)] / \rho_{zz}(0)$, are, within the JM, zero, while in actual solids they are different from zero. Finally, from the conductivity tensor $\sigma_{ij}(\omega)$, we can obtain the dielectric function tensor $\varepsilon_{ij}(\omega) = \delta_{ij} + 4\pi i \sigma_{ij}(\omega) / 4\pi \varepsilon_0 \omega$; the latter, in the limit $\omega_c \tau \gg 1$, exhibits a sharp peak at $\omega = \omega_c$, demonstrating thus the resonance response of the system to an EM field the frequency of which coincides with the cyclotron frequency.

In Fig. 5.4 the experimental setup for Hall effect studies is shown. Since the current, j_y , in the y -direction is zero, it follows, from (5.81) and the relation $j_y = -env_y$, that E_y is non-zero and equal to

$$E_y = \frac{1}{qnc} B j_x = -\frac{1}{enc} B j_x = R B j_x. \quad (5.94)$$

To obtain the last relation, (5.93) was used. The electric field E_y gives rise to a voltage $U_{CD} = E_y b$ perpendicular to the flow of electric current $I = j_x b d$. The voltage $-U_{CD}$ is called *Hall voltage*. The importance of the Hall coefficient stems from the simple formula (5.93), which allows us to determine the concentration n and to verify the sign of the current carriers. Unfortunately, the simple, JM-based, result (5.93), although in fair agreement with the experimental data for alkali and noble metals, fails dismally for certain materials, e.g., for Al, (5.93) gives $R = -0.385$, while the experimental value is $R = +1.136$ in G-CGS units. To explain this discrepancy even in the sign, we need to take explicitly into account the non-zero periodic potential under the influence of which the electrons are moving within the solid (see Chaps. 10 and 13, Sects. 10.7 and 13.1.3).

5.5.3 Magnetic Susceptibility, χ_m

The magnetic susceptibility is a *dimensionless* quantity, defined in Appendix A, which connects the magnetic field-induced magnetization $\mathbf{M}$ to

the auxiliary magnetic field $\mathbf{H}$ according to the relation

$$\chi_m \equiv \left(\frac{\partial \mathbf{M}}{\partial \mathbf{H}} \right)_T, \quad (5.95)$$

usually, but not always, in the limit $\mathbf{H} \rightarrow 0$. In the linear regime (where χ_m is field-independent), the field $\mathbf{H}$ satisfies the relation $\mathbf{H} = \mathbf{B}/\mu$, where the permeability $\mu = \mu_0(1 + \chi_{m,\text{SI}})$ (or $\mu = 1 + 4\pi\chi_{m,\text{G-CGS}}$ in G-CGS; remember: $\chi_{m,\text{SI}} = 4\pi\chi_{m,\text{G-CGS}}$). It is worth to point out that in the framework of classical physics, χ_m is identically zero. The observed non-zero values of χ_m are due to the intrinsic magnetic moment of the particles (see (5.70) and (5.75)) and to the quantum nature of the particle motion. Within the JM, the contributions to χ_m are coming in general from both the free electrons and the electrons associated with the ions and from both the spin and the orbital electronic degrees of freedom.

Ionic Contribution to χ_m

For the *ionic contribution*, one must distinguish three cases:

- (a) Completely filled shells, where $L = S = J = 0$ (*Larmor diamagnetism*)
- (b) $J \neq 0$ (Curie paramagnetism)
- (c) $J = 0$, but $L = S \neq 0$ (*van Vleck paramagnetism*)

The starting point for the calculation of χ_m is the combination of the definition (5.95) and (A.63) of Appendix A, which give

$$\chi_m = -\frac{1}{V} \frac{\partial}{\partial \mathbf{H}} \left\langle \frac{\partial H_{\text{int}}}{\partial \mathbf{B}} \right\rangle = -\frac{1}{V} \frac{\partial^2 \tilde{F}'}{\partial \mathbf{H} \partial \mathbf{B}} \Big|_{T,V}. \quad (5.96)$$

The interaction Hamiltonian of the magnetic field with an electronic system $\hat{H}_{\text{int}}$ is given by (B.68) and (B.69) of Appendix B

$$\hat{H}_{\text{int}} = \sum_i \{ (e/m_e c) \mathbf{A}_i \cdot \mathbf{p}_i + (e^2 A_i^2 / 2m_e c^2) - \mathbf{m}_i \cdot \mathbf{B}_i \}, \quad (5.97)$$

where $\mathbf{B}_i = \mathbf{B}(\mathbf{r}_i) = \nabla \times \mathbf{A}(\mathbf{r})_{\mathbf{r}=\mathbf{r}_i}$ with $\nabla \cdot \mathbf{A} = 0$ and $|\mathbf{m}_i| = \mu_B$ for electrons (see (5.70) and set $|g \cdot \mathbf{s}| = 1$ for a single spin). As before, to obtain the formulae in SI, set $c = 1$, while in the G-CGS expression keep the velocity of light. For the electrons bound to an ion, it is more convenient to choose the following gauge for $\mathbf{A}$

$$\mathbf{A} = \frac{1}{2} (-By, Bx, 0),$$

which gives $\mathbf{B} = \nabla \times \mathbf{A} = (0, 0, B)$. With this choice, the interaction Hamiltonian between the electrons bound to a single ion, and $\mathbf{B}$, $\hat{H}_{\text{int},s}$, can be recast in the more convenient form,

$$\hat{H}_{\text{int},s} = \mu_B \mathbf{B} \cdot (\mathbf{L} + 2\mathbf{S}) + \frac{e^2 B^2}{8m_e c^2} \sum_{i=1}^{Z^*} (x_i^2 + y_i^2), \quad (5.98)$$

- (a) For an ion for which the total angular momenta L , S , and J are all zero, the first term in (5.98) is zero and

$$\left\langle \frac{\partial \hat{H}_{\text{int},s}}{\partial B} \right\rangle = \frac{e^2 B}{4m_e c^2} Z^* \frac{2}{3} \langle r^2 \rangle, \quad (5.99)$$

where

$$\langle r^2 \rangle \equiv \frac{1}{Z^*} \left\langle \sum_{i=1}^{Z^*} (x_i^2 + y_i^2 + z_i^2) \right\rangle = \frac{3}{2} \frac{1}{Z^*} \left\langle \sum_{i=1}^{Z^*} (x_i^2 + y_i^2) \right\rangle, \quad (5.100)$$

and Z^* is the number of electrons in the ion. Then the total contribution to the susceptibility from the N_i ions in the volume V is equal (assuming that $H \simeq B/\mu_0$ in SI and $H \simeq B$ in G-CGS)

$$\begin{aligned} \chi_{mi,\text{SI}} &= -\frac{N_i}{V} \frac{e^2 \mu_0}{6m_e} Z^* \langle r^2 \rangle, \quad \text{SI}, \\ \chi_{mi,\text{G-CGS}} &= -\frac{N_i}{V} \frac{e^2}{6m_e c^2} Z^* \langle r^2 \rangle, \quad \text{G-CGS}. \end{aligned} \quad (5.101)$$

Thus, the contribution, χ_{mi} , to χ_m from ions with only completed shells is negative (i.e., diamagnetic) and of the order of $10^{-6} Z^*$ within the SI system; (we made also the reasonable assumption that $\langle r^2 \rangle$ is of the order of a_B^2 ; see Table 5.3). Keep in mind that $\chi_{m,\text{SI}} = 4\pi \chi_{m,\text{CGS}}$.

- (b) For ions with $J \neq 0$, the ground state in the absence of magnetic field is characterized by J , L , S and J_z and it is $2J + 1$ degenerate. In the presence of a magnetic field, this degeneracy is lifted and the eigenvalues of $\mu_B \mathbf{B} \cdot (\mathbf{L} + 2\mathbf{S})$ are

$$E_i = g \mu_B B J_z, \quad (5.102)$$

where g is given by (5.71).⁹

The next step is to calculate $\tilde{F}'_s$ for a single ion following the general formulae (C.33, C.34) of Appendix C

$$\tilde{F}'_s = -k_B T \ln \sum_i e^{-\beta E_i}, \quad (5.103)$$

The summation in (5.103) is restricted to the lowest $2J + 1$ states; higher lying states have $\beta E_i \gg 1$ and thus can be neglected. We have also

⁹ This is so because the average value of the $\mathbf{L} + 2\mathbf{S}$ must be proportional to the only vector that is conserved, i.e., proportional to $\mathbf{J}$: $\langle \mathbf{L} + 2\mathbf{S} \rangle = g\mathbf{J}$. (See Problem 5.12).

Table 5.3. Experimental values for the Larmor magnetic susceptibility, $\chi_{mi,G-CGS}^{\text{mol}}$

Z^a	Ion or atom	$\chi_{mi,G-CGS}^{\text{mol}}$ ($10^{-6} \text{ cm}^3 \text{ mol}^{-1}$) ^a	$\langle r^2 \rangle / a_B^2 +$
2	Li ⁺	-0,7	0,44
2	He	-1,9	1,20
10	Na ⁺	-6,1	0,77
10	Ne	-7,2	0,91
10	F ⁻	-9,4	1,19
18	K ⁺	-14,6	1,03
18	Ar	-19,47	1,36
18	Cl ⁻	-24,2	1,70
36	Rb ⁺	-22,0	0,77
36	Kr	-28	0,98
36	Br ⁻	-34,5	1,21
54	Cs ⁺	-35,1	0,82
54	Xe	-43	1,00
54	I ⁻	-50,6	1,19

^a $\chi_{mi,G-CGS}^{\text{mol}} \equiv (V/N_i) N_A \chi_m$, where $(V/N_i) N_A$ is the volume per mol. Combining this definition with (5.101), we obtain:

$$\chi_{mi,G-CGS}^{\text{mol}} = - [0.79 Z^* \langle r^2 \rangle / a_B^2] \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1} (1) \\ + \langle r^2 \rangle / a_B^2, \text{ was calculated from the experimental value} \\ \text{of } \chi_m^{\text{mol}} \text{ and (1) above}$$

neglected the second term in (5.98), because it would give a very small diamagnetic contribution which has already been calculated. For very small field B , the eigenvalues $E_i = g\mu_B B J_z$ are very small; as a result, the $\exp(-\beta E_i)$ can be expanded

$$e^{-\beta E_i} \simeq 1 - \beta E_i + \frac{1}{2} \beta^2 E_i^2 + \dots,$$

and the sum in (5.103) becomes

$$\begin{aligned} \sum_i e^{-\beta E_i} &= 2J + 1 - \beta \sum_i E_i + \frac{1}{2} \beta^2 \sum_i E_i^2 + \dots \\ &= 2J + 1 + \frac{1}{2} (\beta g \mu_B B)^2 \sum_i J_z^2 \end{aligned} \quad (5.104)$$

The term $\sum_i E_i \sim \sum_i J_z$ is zero and the sum $\sum_i J_z^2 = \frac{1}{3} \sum_i \mathbf{J}^2$ is equal to $(2J+1)J(J+1)/3$.

The total free energy is $\tilde{F}' = N_i \tilde{F}'_s$, where N_i is the total number of ions. Hence, the ionic contribution to χ_m (for $B \rightarrow 0$) can be obtained by combining (5.104), (5.103), and (5.96):

$$\chi_{mi,SI} = \frac{1}{3} \frac{n_i p^2 \mu_0 \mu_{B,SI}^2}{k_B T}, \quad SI, \quad (5.105)$$

$$\chi_{mi,G-CGS} = \frac{1}{3} \frac{n_i p^2 \mu_{B,G-CGS}^2}{k_B T}, \quad G-CGS, \quad (5.106)$$

where $p \equiv g[J(J+1)]^{1/2}$ and $n_i = N_i/V$. The quantity p is called the *effective number of Bohr magnetons*. Thus, the ions with $J \neq 0$ give a paramagnetic contribution to the magnetic susceptibility (i.e., $\chi_{mi} > 0$); this contribution follows the so-called *Curie law* regarding its temperature dependence, $\chi_{mi} \simeq c_1/T$, where $c_1 = n_i \mu_B^2 p^2 / 3k_B$ for G-CGS. At room temperature, this paramagnetic contribution is about $500 p^2 / Z^*$ times larger than the diamagnetic contribution given in (5.101). It is worthwhile to point out that for the 3d elements the formula for p must be modified; it is more accurate to relate p to the total spin S rather than the total angular momentum:

$$p \simeq 2[S(S+1)]^{1/2}, \quad 3d \text{ elements}. \quad (5.107)$$

The reason is that the nearby atoms in the crystal break the spherical symmetry of the atom and thus $\mathbf{L}$ is not conserved (this phenomenon is called *quenching* of the orbital angular momentum: $\mathbf{J} \rightarrow \mathbf{S}$).

- (c) The third case of $J = 0$ with $L = S \neq 0$ is rare and more complicated. It is treated in the problem 5.8.

Electronic Contribution to χ_m

The *free electrons* give two types of contribution to χ_m . The first one is due to their spin and the second one to their quantized motion in the plane perpendicular to $\mathbf{B}$.

Spin Contribution of Free Electrons. Pauli Paramagnetism

The spin contribution to χ_m of an isolated electron confined in a volume V is according to (5.105)

$$\chi_{m,s} = \frac{\mu_B^2 \mu_0}{V k_B T}, \quad SI. \quad (5.108)$$

(In G-CGS set μ_0 equal to one, i.e., delete μ_0). For the spin contribution of N_i electrons in the volume V , one would naively expect it to be N_i times the value of (5.108). However, for $T \ll T_F$, most of the electrons, since they share the same volume, V , cannot change their spin orientation in spite of the presence of the field B , because, if they do so, they would occupy already filled states and thus they would violate Pauli's principle; Only those within a range of $k_B T$ just below E_F are allowed to respond to the magnetic field; their number is of the order of $2\rho_F k_B T$. Thus, the free electron spin contribution to χ_m is expected to be

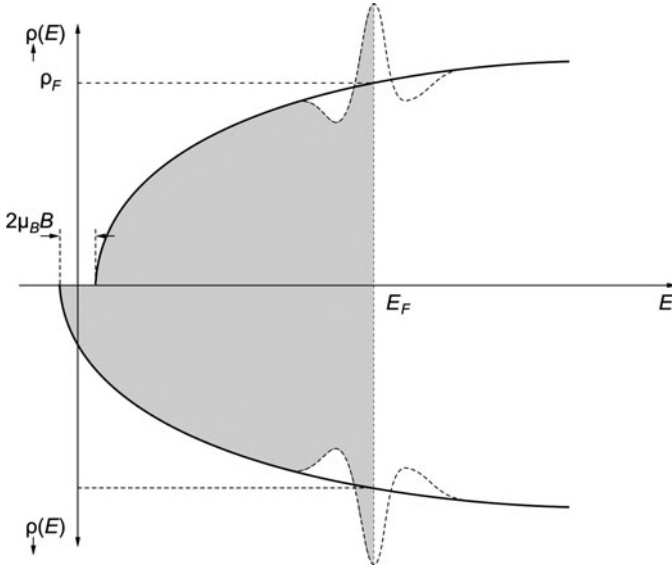


Fig. 5.5. Up-spin DOS, $\rho_{\uparrow}(E)$, for electrons with spin parallel (magnetic moment antiparallel) to the applied field $\mathbf{B}$; down-spin DOS, $\rho_{\downarrow}(E)$, for electrons with spin antiparallel (magnetic moment parallel) to $\mathbf{B}$. The quantization shown in (5.64) has been ignored. The dip/peak structure at E_F is due to the electron-phonon coupling and it is responsible for the enhancement by the factor $(1 + \lambda)$ of the electronic specific heat. This structure is canceled in the difference $\mu_B \int^{E_F} \rho_{\downarrow}(E) dE - \mu_B \int^{E_F} \rho_{\uparrow}(E) dE$ which is proportional the total magnetic moment; hence, the latter is equal to $2\mu_B^2 B \rho_F$ and the Pauli susceptibility is equal to $2\mu_B^2 \mu_0 \rho_F / V$; the enhancement factor, $(1 + \lambda)$, does not appear in the Pauli susceptibility

$$\chi_{m,p} = \frac{2\rho_F k_B T}{V} \frac{\mu_B^2 \mu_0}{k_B T} = 2 \frac{\rho_F}{V} \mu_B^2 \mu_0, \quad T \ll T_F, \quad (5.109)$$

and it is called *Pauli's paramagnetic contribution*. The result of (5.109) can be verified by simple inspection of Fig. 5.5. The number of uncompensated magnetic moments is equal to $2\mu_B B \rho_F$; hence, the total magnetic moment is μ_B times $2\mu_B B \rho_F$, i.e., equal to $2\mu_B^2 B \rho_F$; the magnetization is $2\mu_B^2 B \rho_F / V$ and the susceptibility is $2\mu_B^2 B \rho_F / H V = 2\mu_B^2 \mu_0 \rho_F / V$ (in G-CGS $\mu_0 = 1$).

Quantized Free Electron Motion Contribution. Landau Diamagnetism

It is clear from (5.67) that the motion of a free particle in the plane perpendicular to the applied magnetic field is quantized and that the corresponding DOS is a set of equidistant delta functions, as shown in Fig. 5.6a, each of weight η (see (5.69)). The 3-D DOS has a field induced saw-like shape (see Fig. 5.6b, which produces a non-zero diamagnetic contribution to $\chi_{m,L}$, called *Landau's diamagnetic contribution*; for free electrons and at $k_B T \gg \hbar \omega_c$, $\chi_{m,L}$ is equal to

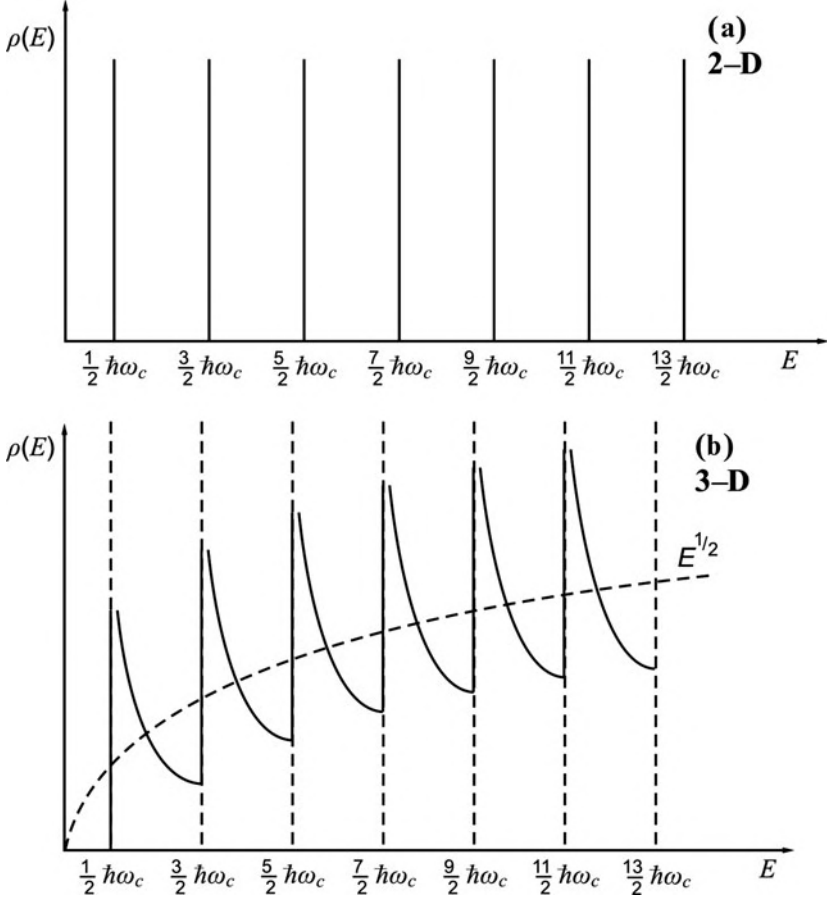


Fig. 5.6. (a) 2-D DOS of a free particle moving in a plane perpendicular to the uniform static applied magnetic field. The quantized levels, $E_n = \hbar \omega_c (n + \frac{1}{2})$, $n = 0, 1, 2, \dots$, $\omega_c = eB/m$ (or eB/mc in G-CGS) are called *Landau levels*. (b) 3-D DOS for a free particle in the presence of a uniform magnetic field; this saw-like DOS is created by combining the 2-D DOS with the $(E - E_n)^{-1/2}$ DOS associated with the 1-D free motion along the direction parallel to $\mathbf{B}$

$$\chi_{m,L} = -\frac{1}{3}\chi_{m,P}, \quad \text{JM.} \quad (5.110)$$

For a proof of this relation see Sect. 59 of the book by Landau and Lifshitz, *Statistical Physics*, [ST35]. The generalization of (5.110) to real solids will be given in Chap. 13.

Notice that, as B increases, the distance between consecutive peaks increases and the degeneracy η of each peak increases too. Hence, the value of ρ_F , and hence, χ_m , changes periodically as B varies. This is the *de Haas-van Alphen effect*. (See Problem 5.14). We shall return to this impressive phenomenon in Chaps. 10 and 13.

5.6 Thermoelectric Response

In the presence of a macroscopic electrical potential, $\phi(\mathbf{r})$, the electron chemical potential μ is equal to

$$\mu = \mu_0 - e\phi, \quad (5.111)$$

where μ_0 (not to be confused with the permeability of the vacuum) is the chemical potential in the absence of the field ϕ ; μ_0 is a function of the local values of the electron concentration and the temperature. It is convenient to introduce the so-called electrochemical potential $\tilde{\phi}$ defined by

$$\tilde{\phi} \equiv -\frac{\mu}{e} = \phi - \frac{\mu_0}{e}, \quad (5.112)$$

and the corresponding electrochemical field, $\mathcal{E}$,

$$\mathcal{E} = -\nabla\tilde{\phi} = -\nabla\phi + \frac{\nabla\mu_0}{e} = \mathbf{E} + \frac{\nabla\mu_0}{e}. \quad (5.113)$$

Thermodynamic equilibrium, which implies no electric current ($\mathbf{j} = 0$), requires that both temperature and chemical potential (or equivalently, $\tilde{\phi}$) are constant throughout the body. If there is a gradient of either $\tilde{\phi}$ or T or both, a current will be established tending to restore equilibrium; for small $\nabla\tilde{\phi}$ and ∇T , the electric current is expected to depend linearly on $-\nabla\tilde{\phi}$ and $-\nabla T$:

$$\mathbf{j} = \sigma\mathcal{E} - \sigma Q\nabla T, \quad (5.114)$$

where σ is the electrical conductivity (since for $\nabla\mu_0 = \nabla T = 0$, we must recover the relation $\mathbf{j} = \sigma\mathbf{E}$) and the linear coefficient of $-\nabla T$ has been written in the form σQ , where Q is called *thermopower*. The physical meaning of Q becomes clear if we consider a straight wire the two ends of which are kept at different temperatures T_1, T_2 ; then, if no current can flow, $\mathcal{E} = Q\nabla T$, or by integrating along the length of the wire, an electrochemical difference proportional to $T_1 - T_2$ will be established: $\tilde{\phi}_1 - \tilde{\phi}_2 = -Q \cdot (T_1 - T_2)$. (*the Seebeck effect*).

The departure from the thermodynamic equilibrium, besides setting up the electrical current, drives also an energy current, $\mathbf{j}_E$; $\mathbf{j}_E$ has a contribution $\tilde{\phi}\mathbf{j}$, which depends explicitly on the electrochemical potential, and the rest $\mathbf{j}_E - \tilde{\phi}\mathbf{j}$, which involves the gradients $-\nabla\tilde{\phi} \equiv \mathcal{E}$ and $-\nabla T$

$$\mathbf{j}_E - \tilde{\phi}\mathbf{j} = c_1\mathcal{E} - c_2\nabla T, \quad (5.115)$$

$$= \frac{c_1}{\sigma}\mathbf{j} - (c_2 - c_1Q)\nabla T, \quad (5.116)$$

$$= \Pi\mathbf{j} - K\nabla T, \quad (5.117)$$

To arrive at (5.116), we have replaced in (5.115) $\mathcal{E}$ in terms of $\mathbf{j}$ and ∇T using (5.114); in (5.117), we rewrote the ratio c_1/σ as Π , called the *Peltier coefficient*, and the coefficient of $-\nabla T$ as K , the *thermal conductivity*. The latter by definition is the ratio of the energy current to minus the temperature gradient *in the absence of electric current* $\mathbf{j}$. The Peltier coefficient is related to the thermopower by the *Kelvin relation*

$$\Pi = TQ, \quad (5.118)$$

which stems from the symmetry of the kinetic coefficients (see [ST35]).

The heat $\tilde{q}$ produced per unit time and volume in the presence of both gradients $\nabla\tilde{\phi}$ and ∇T is equal to $-\nabla \cdot \mathbf{j}_E$, which, in view of (5.116), (5.117), and (5.113) and taking into account that $\nabla \cdot \mathbf{j} = 0$ (because no charge accumulation is allowed), becomes

$$\begin{aligned} \tilde{q} &= \nabla \cdot (K\nabla T) + \mathcal{E} \cdot \mathbf{j} - \mathbf{j} \cdot \nabla (TQ) \\ &= \nabla \cdot (K\nabla T) + j^2/\sigma + Q\mathbf{j} \cdot \nabla T - \mathbf{j} \cdot \nabla (TQ). \\ &= \nabla \cdot (K\nabla T) + j^2/\sigma - T\mathbf{j} \cdot \nabla Q. \end{aligned} \quad (5.119)$$

The first term in the last line of (5.119) is associated with ordinary thermal conduction, the second is the Joule heat, and the third, which is proportional to the first power of the current, gives the thermoelectric effect (also called the *Thomson effect*). Notice that by changing the direction of current, this term changes sign and thus it can be separated experimentally from the rest. If the gradient of Q is due only to the temperature gradient, we have

$$-T\mathbf{j} \cdot \nabla Q = T_H \mathbf{j} \cdot \nabla T, \quad \text{where} \quad T_H \equiv -\left(\frac{\partial Q}{\partial T}\right)_P T. \quad (5.120)$$

T_H is called the *Thomson coefficient*.

An approximate expression for both Q and K can be obtained by employing simple kinetic theory arguments. Let us start with Q , which, according to (5.114), is given by the ratio $-j/\sigma|\nabla T|$ under the condition that $\mathcal{E} = 0$. We take the x -axis to coincide with the direction of the current, $\mathbf{j}$; the latter at the arbitrary point x, y, z is calculated as the difference of the flow from left to right, j_+ , minus the flow from right to left, j_- , where $j_+ = -e(n/2)v_{x+}$ and $j_- = -e(n/2)v_{x-}$. Since, during a length equal to the mean free path, ℓ , there is no collision $v_{x+} = v_x(x - \ell)$ and $v_{x-} = v_x(x + \ell)$ so that

$$v_{x+} - v_{x-} = -\frac{dv_x}{dx}2\ell = -\frac{dv_x}{dT}\frac{dT}{dx}2\ell. \quad (5.121)$$

Hence, the current $j = j_+ - j_-$ equals

$$j = en\ell \frac{dv_x}{dT} \frac{dT}{dx} = en\tau v_x \frac{dv_x}{dT} \frac{dT}{dx} = \frac{en\tau}{2} \frac{d}{dT} (v_x^2) \frac{dT}{dx}. \quad (5.122)$$

However, $v_x^2 = v_y^2 = v_z^2 = v^2/3$ and $v^2 = 2\tilde{\epsilon}/m$, where $\tilde{\epsilon}$ is the average energy per particle. Hence

$$j = \frac{en\tau}{3m} \frac{d\tilde{\varepsilon}}{dT} \frac{dT}{dx} = \frac{en\tau}{3m} c_V \frac{dT}{dx}, \quad (5.123)$$

where $c_V = d\tilde{\varepsilon}/dT$ is the electronic specific heat per electron. Dividing (5.123) by $-\sigma |dT/dx|$, we find:

$$Q = -\frac{en\tau}{3m\sigma} c_V = -\frac{en\tau m c_V}{3me^2 n \tau} = -\frac{c_V}{3|e|}, \quad (5.124)$$

$$Q = -\frac{c_V}{3|e|} = -\frac{\pi^2}{6} \frac{k_B^2 T}{|e| E_F}. \quad (5.125)$$

The first part of (5.125) is valid approximately for both metals and semiconductors, while the last relation in (5.125) is valid approximately only for metals. A more sophisticated approach for *metals*, which goes beyond the JM, gives the following result for Q (see [SS75], p. 257):

$$Q = -\frac{\pi^2}{3} \frac{k_B^2 T}{|e|} \frac{\sigma'}{\sigma}. \quad (5.126)$$

where $\sigma' \equiv (d\sigma/dE_F)_T$ is the derivative of the conductivity, σ , with respect to the Fermi energy.

The thermal conductivity, K , can be obtained by calculating the energy current, j_E , under conditions $j = 0$, and by dividing by $-|\nabla T|$. (See (5.117).) The energy current, j_E , can be obtained by following the same procedure as before:

$$j_E = j_{E+} - j_{E-}, \quad (5.127)$$

where

$$j_{E\pm} = \frac{n}{2} \tilde{\varepsilon}_{\pm} v_x, \quad (5.128)$$

$$\tilde{\varepsilon}_{\pm} = \tilde{\varepsilon}(x \pm \ell) = \tilde{\varepsilon}(x) + \frac{d\tilde{\varepsilon}}{dT} \frac{dT}{dx} (\pm \ell). \quad (5.129)$$

Notice that in (5.128) instead of $v_{x\pm}$ we have used the same velocity, v_x for both the left, v_+ , and the right coming v_- ; this is necessary in order to assure that the current $j = 0$, as required by the definition of K . From (5.127) to (5.129), we have

$$K = -\frac{j_E}{dT/dx} = nv_x \ell c_V = nv_x^2 \tau c_V = \frac{1}{3} nv^2 \tau c_V = \frac{1}{3} nv \ell c_V, \quad (5.130)$$

where $nc_V = Nc_V/V = C_V/V$ is the specific heat per unit volume. Notice that both mobile electrons and phonons can carry energy. Hence, there are in general two contributions to the thermal conductivity

$$K = K_e + K_{ph}. \quad (5.131)$$

Each one of them is given by a formula of the type (5.130). For the mobile electron contribution K_e to the thermal conductivity, v is, obviously, v_F , and

$$nc_V = \frac{2\pi^2}{3} k_B^2 \frac{\rho_F}{V} T. \quad (5.132)$$

Using (5.35) for the electrical conductivity, σ , and (5.130) and (5.132) for the electronic thermal conductivity, K_e , we find the so-called **Wiedemann-Franz** relation

$$\frac{K_e}{T\sigma} = \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2 = 2.44 \times 10^{-8} \text{ W} \cdot \text{ohm}/\text{K}^2. \quad (5.133)$$

This relation is in impressive agreement with experimental results for most metals.

The phonon contribution, K_{ph} , to the thermal conductivity is always present; according to (5.130), it is given by

$$K_{\text{ph}} = \frac{1}{3} \langle c \rangle \frac{C_{V\text{ph}}}{V} \ell_{\text{ph}}, \quad (5.134)$$

where $\langle c \rangle$ is an appropriate average of c_ℓ and c_t , $C_{V\text{ph}}$ is given by (4.94), and ℓ_{ph} is of the general form

$$\frac{1}{\ell_{\text{ph}}} = \frac{1}{\ell_{\text{phs}}} + \frac{1}{\ell_{\text{ph-ph}}}, \quad (5.135)$$

ℓ_{phs} is due to the scattering of phonons by defects and even the surface of the solid; and $\ell_{\text{ph-ph}}$ is due to the momentum not conserving phonon scattering by other phonons. In the JM, because of its assumed homogeneity, momentum is conserved in the collision among phonons; in actual solids, and especially at high temperatures, momentum not conserving phonon processes (called *Umklapp processes*) are very common leading to the inequality, $\ell_{\text{ph-ph}} \ll \ell_{\text{phs}}$. On the other hand, for very low temperatures, $\ell_{\text{phs}} \ll \ell_{\text{ph-ph}}$

Problem 5.8t. Plot schematically K_{ph} vs. T , taking into account that $\ell_{\text{ph-ph}} \sim T^{-\nu}$ ($1 < \nu < 2$) and that ℓ_{phs} is temperature independent (SS75). The same for K_ϵ . (Figs. 5.7 and 5.8)

5.7 Key Points

- The dielectric function is a complicated function of both ω and k . Within the JM, we have the following approximate relations:

$$\epsilon(k, \omega) \simeq 1 + \frac{k_s^2}{k^2}, \quad \omega \ll v_F k; k \ll 2k_F$$

$$\epsilon(k, \omega) \simeq 1 - \frac{\omega_{\text{pf}}^2}{\omega^2 + i\omega/\tau_f} - \sum_b \frac{\omega_{\text{pb}}^2}{\omega^2 - \omega_b^2 + i\omega/\tau_b} - \frac{\omega_{\text{pi}}^2}{\omega^2 - \omega_i^2 + i\omega/\tau_i}, \text{ when } \omega \gg v_F k,$$

where $k_s^2 = \omega_{\text{pi}}^2/c_0^2 \simeq 4k_F/\pi a_B \equiv k_{\text{TF}}^2$; and $\omega_{\text{pf}}^2 = 4\pi e^2 n_f / 4\pi \epsilon_0 m_e$ is the free-electron plasma oscillation frequency assuming that $\tilde{\chi}_b = 0$ (in G-CGS $4\pi\epsilon_0$ must be replaced by 1).

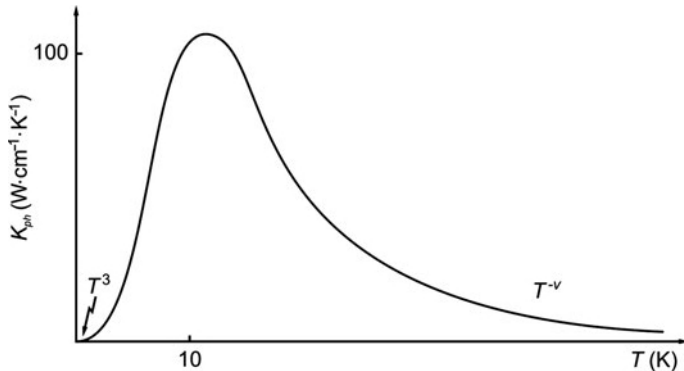


Fig. 5.7. Schematic plot of the phonon contribution, K_{ph} , to the thermal conductivity plotted against the Kelvin temperature T

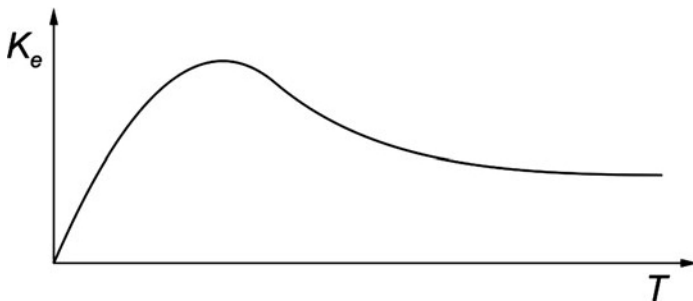


Fig. 5.8. Schematic plot of the electron contribution, K_e , to the thermal conductivity plotted against the Kelvin temperature T

- $\varepsilon(k, \omega) = 0$ gives the longitudinal collective oscillations (acoustic waves and plasma waves) of the system.
- $\varepsilon(\mathbf{k}, \omega) = \infty$ gives approximately the transverse oscillations of the system (assuming that $\omega/k \ll c$).
- The static electrical conductivity, σ , is given by

$$\sigma = \frac{1}{12\pi^3} \frac{e^2}{\hbar} S_F \ell = \frac{2}{3} e^2 \rho_{\text{FV}} v_F \ell,$$

where S_F is the area of the Fermi surface and ℓ is the mean free path given by

$$\frac{1}{\ell} \simeq n_s \sigma_s, \quad (5.136)$$

n_s is the concentration of randomly placed scatterers, and σ_s is the transport scattering cross-section by each scatterer.

- Lattice vibrations dominate the value of $1/\ell$ in metals, leading to a linear increase of the resistivity with increasing temperature, when $T \gtrsim \Theta_D/5$.

In the opposite limit, $T \lesssim \Theta_D/10$, the lattice vibrations contribution is proportional to T^5 and goes to zero as $T \rightarrow 0$ K.

- A static magnetic field B influences the free electronic motion (giving rise to cyclotron frequency, $\omega_c = eB/m_e c$ (in SI c must be set equal to one)), and tends to align the spin of free electrons, bound electrons, ions, and nuclei (giving rise to eigenfrequencies of the form, $\omega_0 = \gamma B$, where γ is the corresponding gyromagnetic ratio).
- A static uniform magnetic field influences the conductivity (or the resistivity) tensor by giving rise to magnetoresistance and to the Hall effect. The latter is the appearance of an off-diagonal term in the resistivity tensor proportional to the magnetic field, $\rho_{xy} = -\rho_{yx} = -RB$. Within the JM,

$$R = \frac{1}{qnc} = -\frac{1}{enc}.$$

- A static magnetic field B produces a magnetization that is usually related to B by $M = \chi B/\mu$. Both electrons bound to ions and free electrons contribute to the magnetic susceptibility, χ . There are three cases of ionic contributions (Larmor, Curie, and van Vleck) and two kinds of free-electron contributions (Pauli, due to spin, and Landau, due to the orbital motion).
- In the presence of both an external electric field, $\mathbf{E}$, and a temperature gradient, ∇T , the electric current density, $\mathbf{j}$, is given by

$$\mathbf{j} = \sigma \mathcal{E} - \sigma Q \nabla T,$$

and the energy current density, j_E , is given by

$$j_E - \tilde{\phi} \mathbf{j} = \Pi \mathbf{j} - K \nabla T, \quad (5.137)$$

where $\mathcal{E} = \mathbf{E} + \nabla \mu_0/e$, $\tilde{\phi} = \phi - \frac{\mu_0}{e}$, and $\mathbf{E} = -\nabla \phi$; the quantities K , the thermal conductivity, Q , the thermopower, and Π , the Peltier coefficient, are characteristic of each material; Π and Q are related by the Kelvin relation: $\Pi = TQ$.

- $Q \simeq -c_V/3|e|$, where c_V is the electronic-specific heat per electron.
- Both free electrons and ionic waves contribute to K : $K = K_e + K_{ph}$.
- For metals, $K_e/T\sigma = (\pi^2/3)(k_B/e)^2$, while for ionic waves, $K_{ph} = \langle c \rangle C_{Vph} \ell_{ph}/3V$, where $\langle c \rangle$ is an appropriate average of c_ℓ and c_t .

5.8 Problems

5.1 Taking into account (5.2) and (5.87) and (5.88) in the limit $\omega\tau \gg 1$, calculate the dielectric tensor $\varepsilon_{xx} = \varepsilon_{yy}$ and $\varepsilon_{xy} = \varepsilon_{yx}^*$.

5.2 Show that (5.101) for χ_{mi} (in SI) can be written as follows:

$$\chi_{mi,SI} = -\frac{E_0}{m_e c^2} \frac{Z^*}{2\bar{r}_a^3} \frac{\langle r^2 \rangle}{a_B^2},$$

where $E_0 = \hbar^2/m_e a_B^2 = 27.2 \text{ eV}$ and $m_e c^2 = 511000 \text{ eV}$.

The factor $E_0/m_e c^2$ accounts for the smallness of χ_{mi} and shows that the response to the magnetic field is a weak relativistic effect.

- 5.3 Find the expression $\chi_{mL,SI}^{\text{mol}}$ for the Larmor susceptibility in units of cm^3/mol .
- 5.4 Calculate the values of ω_{pf} (for Li, Na, K, Rb, Mg, Al, and Ag) using (5.27) and the theoretical values of $\bar{r}_s$ and compare them with the theoretical values of ω_{pf} as given in the book by Papaconstantopoulos. What is the value of $\tilde{\chi}_b$ (see (5.25))?
- 5.5 Calculate the resistivity of Al at $T = 295 \text{ K}$, using the RJM value of $\bar{r}_s$ or the calculated value of ω_{pf} (in the book by Papaconstantopoulos). Compare it with the corresponding experimental value.
- 5.6 What is the value of the ratio $\hbar\omega_c/k_B T$ for $B = 1 \text{ Tesla}$ and $T = 1 \text{ K}$?
- 5.7 What value of τ is needed in order to have $\omega_c \tau \geq 1$ if $B = 1 \text{ Tesla}$?
- 5.8 Consider an ion such that $\langle \Phi_0 | \mathbf{J} | \Phi_0 \rangle = 0$, where Φ_0 is the ground state in the absence of magnetic field; the corresponding ground state energy is E_0 . Let Φ_ν and E_ν ($\nu = 1, 2, \dots$) be its excited eigenstates and eigenenergies (in the absence of magnetic field). Show that the ground state energy, E_G , in the presence of a magnetic field B is given (to second order in B) by

$$E_G = E_0 - \sum_{\nu=1} |\langle \Phi_\nu | \mu_B \mathbf{B} \cdot (\mathbf{L} + 2\mathbf{S}) | \Phi_0 \rangle|^2 / (E_\nu - E_0) \\ + (\epsilon^2 B^2 / 8m_e c^2) \sum_{i=0}^{Z^*} \langle \Phi_0 | (x_i^2 + y_i^2) | \Phi_0 \rangle.$$

If $E_1 - E_0 \gg k_B T$, show that the magnetic susceptibility is given by

$$\chi = -\frac{e^2 n_i \mu_0 Z^*}{6m_e} \langle r^2 \rangle + 2n_i \mu_B^2 \sum_{\nu=1} |\langle \Phi_\nu | (L_Z + 2S_Z) | \Phi_0 \rangle|^2 / (E_\nu - \epsilon_0), \text{ SI}$$

The second term in the rhs of the last equation is known as the *van Vleck paramagnetism*. (In G-CGS set μ_0 equal to $1/c^2$).

- 5.9 Estimate the value of the thermal conductivity of Si at $T = 300 \text{ K}$; employ (5.134). Compare it with the corresponding experimental value. Take $l_{\text{ph}} \simeq 300 \text{ \AA}$.
- 5.10 Estimate the value of the thermal conductivity of Cu at $T = 300 \text{ K}$.
- 5.11 Show that the Fourier transform of (5.8) is given by (5.9).
- 5.12 Prove (5.71), taking into account that the average magnetic moment ought to satisfy (5.70), since $\mathbf{J}$ is the only vector that is conserved. Multiply (5.70) by $\mathbf{J}$ to obtain $gJ(J+1) = L(L+1) + 2S(S+1) + 3\mathbf{L} \cdot \mathbf{S}$. You can find $\mathbf{L} \cdot \mathbf{S}$ from $\mathbf{J}^2 = J(J+1) = (\mathbf{L} + \mathbf{S})^2 = L(L+1) + S(S+1) + 2\mathbf{L} \cdot \mathbf{S}$.
- 5.13s. Prove (5.55)–(5.63).

- 5.14 Figure 5.6b implies that the DOS at E_F, ρ_F , would exhibit a peak, whenever E_F satisfies the relation $E_F = \hbar \omega_c (n + \frac{1}{2})$ (assuming that the temperature T is low enough, $k_B T \ll \hbar \omega_c$, for not smoothing out these peaks). Show that this equation implies that a peak in ρ_F (as well as in physical quantities being proportional to ρ_F , such as the magnetic susceptibility, etc) would appear whenever

$$\frac{1}{B} = \frac{\hbar e}{cmE_F} \left(n + \frac{1}{2} \right) = \frac{2\pi e}{c\hbar A_F} \left(n + \frac{1}{2} \right),$$

where $A_F \equiv \pi k_F^2$ is the maximal cross-section of the Fermi sphere. Thus, the magnetic susceptibility and other similar quantities are expected to exhibit peaks as functions of $1/B$ with a period $\Delta(1/B) = 2\pi e / c\hbar A_F$.

- 5.15s. Consider the motion of an electron under the action of static electric and magnetic fields normal to each other. By multiplying (5.79) by $\mathbf{B} \times$, show that (assuming that $\tau \rightarrow \infty$)

$$\mathbf{v}_\perp = -\frac{cm}{eB} \mathbf{B}_0 \times \dot{\mathbf{v}}_\perp + \mathbf{v}_0, \quad \mathbf{v}_0 = \frac{c}{B} \mathbf{E} \times \mathbf{B}_0, \quad \mathbf{B}_0 \equiv \mathbf{B}/B. \quad (5.138)$$

Further Reading

1. For the symmetry of the kinetic coefficients see Landau & Lifshitz, *Statistical Physics* [ST35], §120, pp. 365–368.
2. Thermoelectric and thermogalvanometric phenomena are briefly presented in the book by Landau & Lifshitz, *Electrodynamics of Continuous Media* [E15], §26, 27, pp. 97–102.
3. See also the book by Ashcroft & Mermin, *Solid State Physics* [SS75], Chaps. 1, 2, and 3, pp. 2–62.
4. An advanced study of the dielectric function is given in Many-Body theory books; among them I mention the book by Nozieres [MB58], pp. 45–57, and the book by Fetter and Walecka [MB45], pp. 151–183, as well as the paper by H. Ehrenreich and M.H. Cohen [5.2].

Solids as Supergiant Molecules: LCAO

Summary. A one-dimensional periodic model of coupled pendulums is introduced, which, on the one hand, reduces to that of ionic coupled oscillations, and on the other, is mathematically equivalent to the electronic motion in the framework of the LCAO. The latter, depending on its parameters, can describe one-dimensional “metals,” “ionic solids,” “molecular solids,” “elemental semiconductors,” and “compound semiconductors.” Furthermore, important concepts, such as band and gaps, effective masses, valence and conduction bands, and gap size, E_g , are introduced.

6.1 Diversion: The Coupled Pendulums Model

The fact that periodicity of a crystal would be essential was somehow suggested to me by remembering a demonstration in elementary physics where *many equal and equally coupled pendulums* were hanging at constant spacing from a rod and the motion of one of them was seen to “migrate” along the rod from pendulum to pendulum.

Returning to my rented room one evening in early January, it was with such vague ideas in mind that I began to use pencil and paper and to treat the easiest case of a single electron in a one-dimensional periodic potential...

*F. Bloch*¹

Let us take a pencil and paper to study, following Bloch’s example, the motion of the coupled pendulums of Fig. 6.1 (in the harmonic approximation). The forces acting on any of these masses, e.g., the n th one, are (a) the one due to gravity and the string tension as in a single isolated pendulum: $F_0 = -(mg/\ell)u(n, t)$, where g is the acceleration due to gravity and $u(n, t)$ is the displacement from equilibrium of the n th pendulum; (b) the force,

¹ In proceedings of the Royal Society of London, series A, vol. 371 (no. 1741, pp. 1–177): “The Beginnings of Solid State Physics”. A symposium organized by Nevill Mott, held on April 30–May 2, 1971.

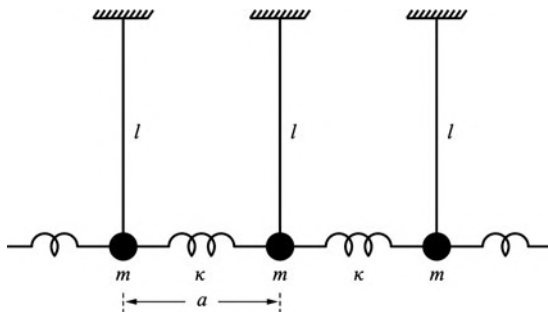


Fig. 6.1. The periodic one-dimensional system of coupled pendulums referred to by F. Bloch in the quote mentioned earlier. This system can serve as a simple model for ionic as well as electronic motion in crystalline solids

$F_{n-1} = -\kappa[u(n, t) - u(n-1, t)]$, by the spring to the left; and (c) the force, $F_{n+1} = -\kappa[u(n, t) - u(n+1, t)]$, by the spring to the right. Thus, the acceleration $\ddot{u}(n)$ is given by

$$m\ddot{u}(n) = -(mg/\ell + 2\kappa)u(n) + \kappa[u(n-1) + u(n+1)]. \quad (6.1)$$

Equation (6.1) is a typical coupled harmonic oscillation (in the present case any three consecutive pendulums are coupled). We shall try an eigensolution to (6.1) that would be as close as possible to a plane wave (see (4.55)).

$$u_q(n, t) = \text{Re} \left\{ A_q e^{i(q x_n - \omega_q t)} \right\}, \quad x_n = na \quad (6.2)$$

where q is the wavenumber characterizing the solution. Notice that this solution satisfies Bloch theorem, as it should (see Sect. 3.4.1). It is not difficult to show that (6.2) satisfies indeed (6.1) for every n with

$$\begin{aligned} \omega_q^2 &= \omega_0^2 + \frac{2\kappa}{m}(1 - \cos qa) \\ &= \omega_0^2 + 4\frac{\kappa}{m} \sin^2 \frac{qa}{2}, \end{aligned} \quad (6.3)$$

where $\omega_0 = (g/\ell)^{1/2}$ is the eigenfrequency of a single uncoupled pendulum. By imposing periodic boundary conditions, $u(N, t) = u(0, t)$, we find that

$$q = \frac{2\pi}{Na} \ell, \quad \ell = 0, \pm 1, \pm 2, \dots, \quad (6.4)$$

where N is the total number of coupled pendulums and $Na = L$ is the total length of the system ($N \rightarrow \infty$). Notice that two q 's differing by $G_p \equiv (2\pi/a)p$, where p is any integer, correspond to exactly the same solution, since $G_p x_n = 2\pi p n$. Thus, if we restrict q to the region from $-\pi/a$ to π/a , we obtain N nonequivalent values of q , which means N different eigenoscillations, i.e., all of them. The region $[-\pi/a, \pi/a]$ in q -space is the first *Brillouin Zone* (BZ, see Sect. 3.4.4); the one-dimensional vectors G_p are the vectors of the *reciprocal lattice* (see Sect. 3.4.2).

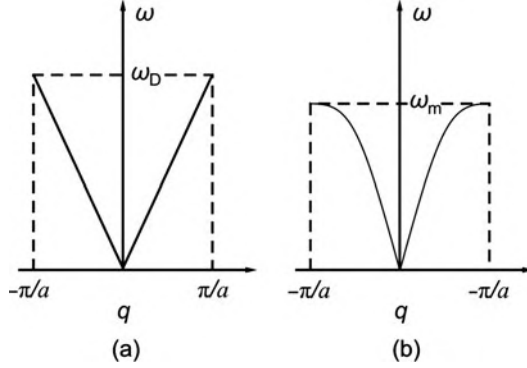


Fig. 6.2. The dispersion relation ω_q -vs.- q relation for the longitudinal acoustic waves in a one-dimensional system; in (a) the case of a continuum with an imposed cutoff $|k_D| = \pi/a$ is shown; in (b) the discrete periodic case is shown. Notice that $\omega_D = \pi c_s/a$, while $\omega_m = 2c_s/a$, where $c_s = a\sqrt{\kappa/m}$ is the phase velocity (for case (b), only for $qa \ll \pi$) for the acoustic wave; c_s is typically five orders of magnitude smaller than the velocity of light in vacuum

Problem 6.1t. Using the relation (6.4) and $x_n = na$, prove that $\frac{1}{N} \sum_{n=0}^{N-1} e^{-iq'x_n} e^{iqx_n} = \delta_{q', q+G_p}$, which shows the orthonormality of the eigensolutions $\exp(iqx_n)/\sqrt{N}$, for q in the 1st BZ.

Define

$$x_q(t) \equiv \frac{1}{\sqrt{N}} \sum_n u(n, t) e^{-iqx_n},$$

where $u(n, t)$ is any displacement of pendulum n and show that

$$u(n, t) \equiv \frac{1}{\sqrt{N}} \sum_q x_q(t) e^{+iqx_n},$$

and that

$$m\ddot{x}_q = -(m\omega_0^2 + 2\kappa - 2\kappa \cos qa) x_q.$$

Since the various $x_q(t)$'s are decoupled from each other, as shown by this equation, it follows that each $x_q(t)$ is the collective displacement corresponding indeed to each eigenoscillation q (see Sect. 2.3).

Notice that in the absence of gravity ($\omega_0 = 0$), the model shown in Fig. 6.1 describes the coupled ionic oscillations of a one-dimensional “solid,” which, according to (6.2), are plane-like propagating waves; their ω_q -vs.- q relation is

$$\omega_q = 2\sqrt{\frac{\kappa}{m}} \left| \sin \frac{qa}{2} \right| \xrightarrow{q \rightarrow 0} \sqrt{\frac{\kappa a}{m/a}} q. \quad (6.5)$$

The readers may convince themselves that κa is the one-dimensional analog of bulk modulus B , and m/a is the analog of ρ , so that, for $qa \ll \pi$, the formula $\sqrt{B/\rho}$ for the velocity of acoustic waves is recaptured. In Fig. 6.2b we

plot the ω_q -vs.- q relation for all nonequivalent values of q , i.e., for $-(\pi/a) < q \leq (\pi/a)$. It is worth to point out that the cut off $|q_{\max}| = \pi/a = q_D$ stems naturally out of the periodicity without any need to impose it a posteriori, as we did in Chap. 4. Furthermore, the so-called dispersion relation, ω_q vs. q , is linear only for $qa \ll \pi$ (i.e., $\lambda \gg 2a$); for larger values of q , the curve bends so that the group velocity, $v_g \equiv d\omega/dq = a\sqrt{\kappa/m} \cos(qa/2)$ becomes smaller and smaller as q increases and at the end of the BZ, $|qa| = \pi$ (or, equivalently, at $\lambda = 2a$), the group velocity vanishes.

6.2 Introductory Remarks Regarding the LCAO Method

As is pointed out in Appendix F, the method of the linear combination of atomic orbitals (LCAO) solves the time-independent Schrödinger equation, $\hat{H}\psi = E\psi$, by writing ψ as a weighted sum of atomic (or atomic-like) orbitals, ϕ_n

$$\psi = \sum_n c_n \phi_n, \quad (6.6)$$

where the known orbitals, ϕ_n , are assumed orthonormal. Then, Schrödinger's equation is transformed to a set of linear homogeneous equations²

$$\sum_n (H_{mn} - E\delta_{mn})c_n = 0, \quad m = 1, 2, 3, \dots, \quad (6.7)$$

for the unknown coefficient $\{c_n\}$. The matrix elements H_{mn} are given by

$$H_{mn} \equiv \int \phi_m^*(\mathbf{r}) \hat{H} \phi_n(\mathbf{r}) d^3r \equiv \langle m | \hat{H} | n \rangle. \quad (6.8)$$

In Appendix F the important advantages of the LCAO are presented; the main disadvantage of this method, namely the difficulty of calculating the matrix elements $\hat{H}_{mn}$, is overcome (with significant sacrifice in accuracy, of course) by employing the relations proposed by Harrison [SS76]

$$H_{mn} = \eta_{mn} \frac{\hbar^2}{m_e d^2}, \quad m \neq n, \quad (6.9)$$

for the off-diagonal matrix elements between s- and/or p-orbitals, belonging to nearest neighbor atoms; d is the distance between these nearest neighbor atoms and the numerical coefficients η_{mn} are given by (F.7)–(F.14). For the diagonal matrix elements

² Notice that (6.7) can be written also in the compact but familiar looking form, $Hc = Ec$, where H is a square matrix with matrix elements H_{mn} and c is a column matrix with matrix elements c_n .

$$H_{mm} = \varepsilon_m, \quad (6.10)$$

the values of Table B.3 are used. All other matrix elements of $\hat{H}$ are assumed to be zero.³ This simple version of the LCAO is usually called *Tight Binding* (TB).

In this chapter, we shall focus mainly on the study of some simple one-dimensional⁴ models of solids aiming to introduce with the minimum computational effort some basic concepts such as

- *Energy band(s) of finite width*
- *Relation between energy bands and atomic orbitals or molecular bonding and antibonding orbitals (made out of simple or hybridized atomic orbitals)*
- *Gaps in molecular, covalent, and ionic solids*
- *Conductors, vs. semimetals, vs. semiconductors, vs. insulators*

These concepts, which are missing completely from the jellium model (JM), are of fundamental importance for understanding and explaining the variety of behavior of solids.

It is worthwhile to point out that the model of coupled pendulums examined in Sect. 6.1 is *mathematically* equivalent to the LCAO method of studying the electronic motion. This mathematical equivalence, besides facilitating our computational effort, helps also readers not so familiar with the intricacies of Quantum Mechanics to develop a physical picture of the wavy nature of the electronic motion in solids.

Before continuing with the rest of this chapter the readers may find it profitable to familiarize themselves with the LCAO method by going over the material of Appendix F.

6.3 A Single Band One-Dimensional Elemental “Metal”

This is the simplest possible model of a “solid” within the framework of the LCAO. Identical atoms have been placed at the points $x_n = na$ of a one-dimensional Bravais lattice; each atom possesses only one atomic orbital, $\phi_n \equiv \phi(r - x_n i)$, the same for all atoms; these orbitals are assumed orthonormal, $\langle \phi_n | \phi_m \rangle = \delta_{nm}$; the only nonzero matrix elements of the Hamiltonian are the diagonal and the nearest neighbor off-diagonal ones

$$\langle \phi_n | \hat{H} | \phi_n \rangle = \varepsilon, \quad (6.11)$$

$$\langle \phi_n | \hat{H} | \phi_{n+1} \rangle = \langle \phi_{n+1} | \hat{H} | \phi_n \rangle = V_2. \quad (6.12)$$

³ For a modified and extended version of (6.9) and (6.10), see, e.g., the paper by Lei Shi and D.A. Papaconstantopoulos, Phys. Rev. B **70**, 205101 (2004).

⁴ In the next chapter 7 the corrections and extensions associated with the realistic 3-D systems will be presented.

The eigenfunctions ψ are of the form $\psi = \sum c_n \phi_n$, where, according to (6.7), the coefficients $\{c_n\}$ satisfy the following relations

$$Ec_n = \varepsilon c_n + V_2(c_{n-1} + c_{n+1}), \quad n = 0, 1, \dots, N-1. \quad (6.13)$$

Equation (6.13) is mathematically equivalent to (6.1) under the following correspondences:

$$\begin{array}{llll} \text{Pendulums motion :} & u(n) & m\omega^2 & m\omega^2 + 2\kappa \quad \kappa \\ \text{Electronic motion :} & c_n & E & \varepsilon \quad -V_2. \end{array} \quad (6.14)$$

Based on this equivalence and taking into account (6.2), (6.3), and (6.4), we have for the electronic problem

$$c_n = e^{ikan} / \sqrt{N}, \quad (6.15)$$

$$k = \frac{2\pi}{Na} \ell, \quad \ell = 0, \pm 1, \pm 2, \dots, N/2, \quad (6.16)$$

$$E(k) = \varepsilon + 2V_2 \cos ka, \quad (6.17)$$

where in the electronic case, we have used the symbol k (instead of q), for the wave number. Thus, the electron, according to Quantum Mechanics, “migrates” from atom to atom the same way that the motion in the model of Fig. 6.1 “migrates” from pendulum to pendulum, i.e., free-like without any back scattering. In Fig. 6.3 we plot $E(k)$ vs. k according to (6.17)

It is clear from (6.17) and from Fig. 6.3 that the only allowed eigenenergies (as $N \rightarrow \infty$) lie in a finite band of width $4|V_2|$ centered at the atomic level ε . Near the lower band edge the $E(k)$ can be approximated by

$$E(k) - \varepsilon - 2V_2 \simeq |V_2| a^2 k^2, \quad |k|a \ll \pi, \quad (6.18)$$

while near the upper band edge we have

$$E(k) - \varepsilon + 2V_2 \simeq -|V_2| a^2 \delta k^2, \quad 0 < a\delta k \ll \pi \quad (6.19)$$

where $\delta k = (\pi/a) - k$ or $\pi/a + k$.

This quadratic dependence on k or δk allows us to define an *effective mass* for the lower and the upper band edges, respectively,

$$m_e^* \equiv \frac{\hbar^2}{2|V_2|a^2}, \quad k \simeq 0, \quad (6.20)$$

$$m_e^* \equiv -\frac{\hbar^2}{2|V_2|a^2}, \quad k \simeq \pm\pi/a. \quad (6.21)$$

In the present simple model the two effective masses shown in (6.20) and (6.21) are equal; in general the lower and upper band effective masses are different. The concept of the effective mass near the lower or the upper band edge makes, as we shall see, the electronic motion in a periodic potential

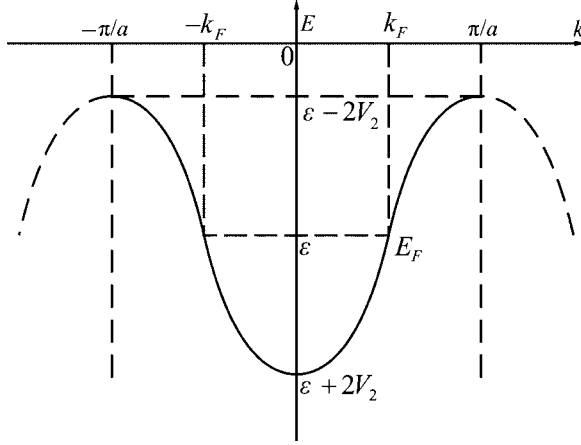


Fig. 6.3. The *band structure*, i.e., the $E(k)$ -vs.- k relation, for a one-dimensional solid, the Schrödinger equation of which for the electronic motion is (6.13) with $V_2 < 0$. For a k outside the first BZ, $[-\pi/a, \pi/a]$, the eigenfunction is the same as $k + G_p$, where G_p is a vector of the reciprocal lattice such that $k + G_p$ is in the first BZ. The Fermi energy E_F and the Fermi wavenumber k_F are also shown assuming one electron per atom

equivalent in many respects to free of force motion but with the mass being m_e^* instead of m_e .

More generally the effective mass is defined in terms of the band structure $E(k)$ as follows:

$$\frac{1}{m^*} \equiv \frac{\partial^2 E(k)}{\hbar^2 \partial k^2}. \quad (6.22)$$

Notice that near the upper band edge the effective electron mass is negative. To be on more familiar ground we shall introduce in the next chapter the concept of hole (i.e., of missing electron) with an effective hole mass m_h^* equal to minus the effective electronic mass, $m_h^* = -m_e^*$. Thus, m_h^* is a positive number.

The number of eigenstates, $R(E)$, with eigenenergies, $E(k)$, less than E is given by⁵

$$R(E) = \frac{L}{2\pi} 2|k(E)|, \quad L = Na. \quad (6.23)$$

Hence, the DOS per spin is

⁵ The basic formula $R(E) = \left(L^D / (2\pi)^D \right) c_D (k(E))^D$ is valid for D -dimensional systems both homogeneous and periodic, since in both cases the density of k points in any independent axis is $L/2\pi = Na/2\pi$ (see (6.16)). For 1-D systems, $c_D = 2$; in general $c_D k^D$ is the volume of a “sphere” of radius k in D -dimensional space.

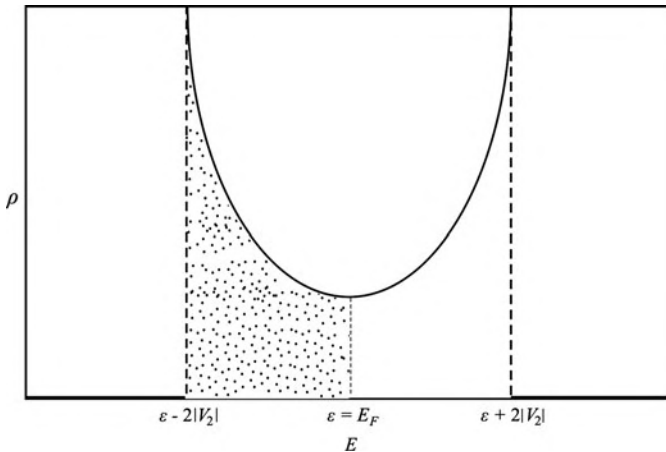


Fig. 6.4. DOS, ρ , vs. E for the one-dimensional model the dispersion relation of which is that of (6.17). For one electron per atom the Fermi energy coincides with the middle of the band implying a metallic behavior. Notice the characteristic 1-D singularities at the band edges, both at the lower one (as in Fig. 4.1) and the upper one (at which the effective electronic mass is negative)

$$\rho(E) = \frac{dR(E)}{dE} = \frac{L}{2\pi} \frac{2}{|dE/dk|} \quad (6.24)$$

$$= \frac{N}{\pi} \frac{1}{\sqrt{B^2 - (E - \varepsilon)^2}}, \quad B = 2|V_2|. \quad (6.25)$$

Note that (6.24) is of the form of (4.16) where the role of S is played by the number 2 (since there are only two k -points satisfying the equation $E(k) = E$) and $|dE/dk| = \hbar v$; of course, $V/(2\pi)^3$ is replaced by $L/2\pi$.

Problem 6.2t. Using (6.24) and (6.17) prove (6.25).

The DOS given by (6.25) is plotted in Fig. 6.4; in this figure the Fermi level, E_F , is also shown based upon the assumption that there is one electron per atom, which implies that the lowest $N/2$ eigenstates will be occupied each one with two electrons. Since the density of eigenstates in k -space is uniform (according to (6.16)), the Fermi wavenumber k_F must be such that the region from $-k_F$ to k_F , of total extent $2k_F$, to cover half the BZ, i.e., π/a (see Fig. 6.3); hence,

$$k_F = \pi/2a, \quad (6.26)$$

and consequently, $E_F = \varepsilon$. The DOS per spin at E_F , ρ_F , is equal to $N/2\pi |V_2|$.

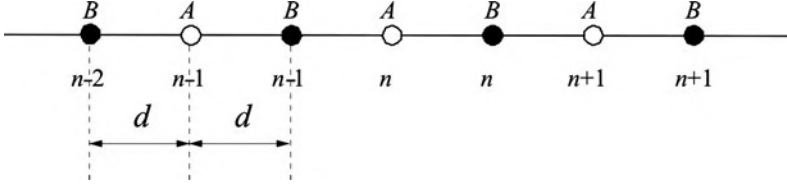


Fig. 6.5. A composite one-dimensional crystal structure of period $a = 2d$ consisting of two kinds of atoms A and B

6.4 One-Dimensional Ionic “Solid”

The periodic arrangement of the two kinds of atoms shown in Fig. 6.5 is the simplest one-dimensional model of an ionic solid with the atom A being the cation and B the anion ($\varepsilon_A > \varepsilon_B$).

Each atom of Fig. 6.5 is assumed to have only one atomic orbital $\phi_{A,n}$ or $\phi_{B,n}$, where each n is associated with a primitive cell of extent $a = 2d$. The nonzero matrix elements of the Hamiltonian are:

$$\langle \phi_A | \hat{H} | \phi_A \rangle = \varepsilon_A, \quad (6.27)$$

$$\langle \phi_B | \hat{H} | \phi_B \rangle = \varepsilon_B, \quad (6.28)$$

$$\langle \phi_{A,n} | \hat{H} | \phi_{B,n} \rangle = \langle \phi_{B,n} | \hat{H} | \phi_{A,n+1} \rangle = V_2. \quad (6.29)$$

Schrödinger’s equation (6.7) applied to the present case for the atom A, at primitive cell n , and B, at primitive cell n , gives respectively

$$(\varepsilon_A - E)c_{A,n} + V_2(c_{B,n-1} + c_{B,n}) = 0, \quad (6.30)$$

$$(\varepsilon_B - E)c_{B,n} + V_2(c_{A,n} + c_{A,n+1}) = 0. \quad (6.31)$$

To solve the system (6.30, 6.31), we shall try a generalization of (6.15)

$$c_{A,n} = c_A e^{ikan}, \quad (6.32)$$

$$c_{B,n} = c_B e^{ikan}, \quad (6.33)$$

which means that two equivalent orbitals displaced by any vector $x_\ell = \ell a$ of the Bravais lattice have coefficient differing by a factor of $\exp(ik\ell a)$ in accordance with Bloch’s theorem; thus, $c_{B,n-1} = c_{B,n} \exp(-ika)$ and $c_{A,n+1} = c_{A,n} \exp(+ika)$. Substituting these relations in (6.30, 6.31) and taking out the common factor $\exp(ikan)$, we find a system of two equations for the two unknowns c_A and c_B

$$(\varepsilon_A - E)c_A + V_2(e^{-ika} + 1)c_B = 0,$$

$$(\varepsilon_B - E)c_B + V_2(1 + e^{ika})c_A = 0.$$

To have a nonzero solution, the determinant of this system must be zero, i.e.,

$$(\varepsilon_A - E)(\varepsilon_B - E) - V_2^2(1 + e^{-ika})(1 + e^{ika}) = 0. \quad (6.34)$$

The solution to (6.34) is simplified by introducing the half sum, ε , and the half difference, V_3 , where

$$\varepsilon = \frac{\varepsilon_A + \varepsilon_B}{2}, \quad (6.35)$$

$$V_3 = \frac{\varepsilon_A - \varepsilon_B}{2} > 0. \quad (6.36)$$

Thus, $\varepsilon_A = \varepsilon + V_3$, $\varepsilon_B = \varepsilon - V_3$ and $(\varepsilon_A - E)(\varepsilon_B - E) = (\varepsilon - E)^2 - V_3^2$. Hence,

$$E_{\pm}(k) = \varepsilon \pm \sqrt{V_3^2 + 4V_2^2 \cos^2(ka/2)}. \quad (6.37)$$

It is clear from (6.37) that for each k there are two eigenfunctions corresponding to the two eigenenergies $E_{\pm}(k)$, which are plotted in Fig. 6.6. Obviously, there are two bands, the lower one extending from $\varepsilon - \sqrt{V_3^2 + 4V_2^2}$ to $\varepsilon - V_3 = \varepsilon_B$ and the upper one from $\varepsilon + V_3 = \varepsilon_A$ until $\varepsilon + \sqrt{V_3^2 + 4V_2^2}$. Notice that these bands are not centered around the atomic levels ε_B and ε_A ; their centers are closer to the bonding and antibonding molecular levels of (F.26), (F.27). There is a gap between the two bands of width E_g , where

$$E_g = 2V_3 = \varepsilon_A - \varepsilon_B. \quad (6.38)$$

In ionic solids the gap is of the order of 5–10 eV; e.g., for NaCl the actual gap is 8.5 eV, while (6.38) and Table B.3 gives $E_g = -4.95 + 13.78 = 8.83$ eV, surprisingly close to the experimental value.

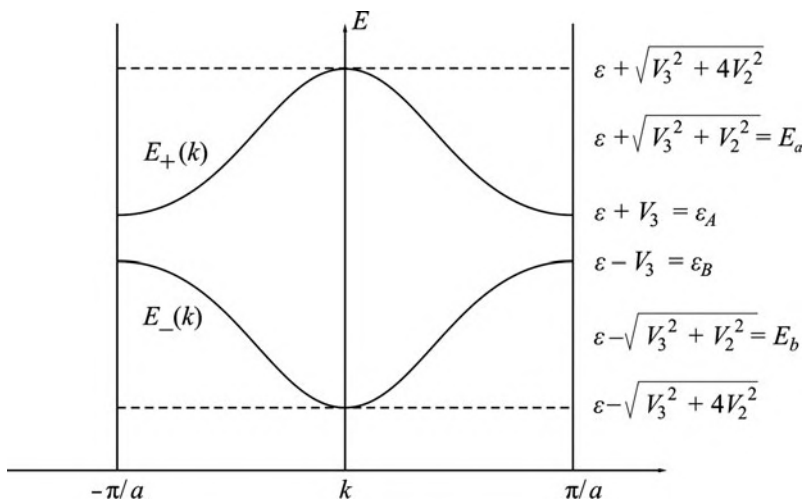


Fig. 6.6. The band structure $E_{\pm}(k)$ for the two bands of the model of Fig. 6.5. There is a gap between the two bands of width, $E_g = 2V_3 = \varepsilon_A - \varepsilon_B$. E_b, E_a are the bonding and antibonding molecular levels respectively (see. App. F)

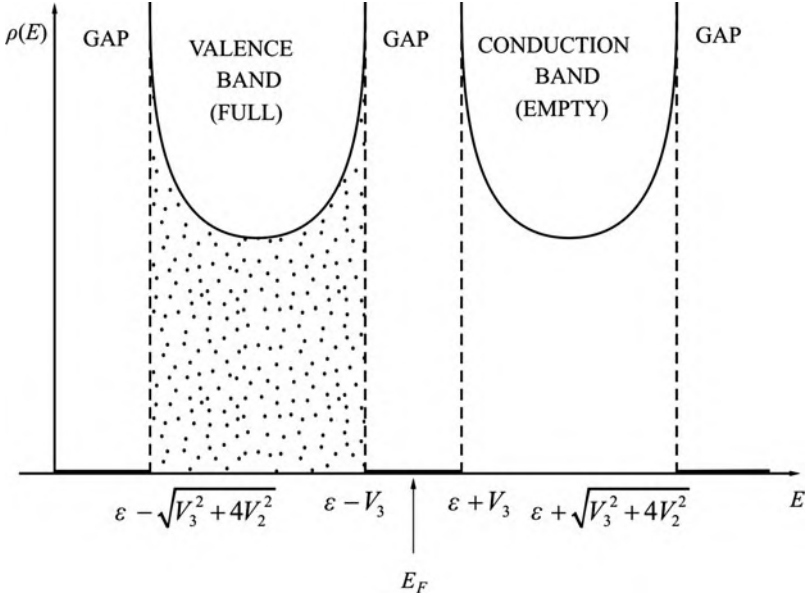


Fig. 6.7. Schematic plot of the electronic DOS vs. E for the one-dimensional model of Fig. 6.5 with only one orbital per atom and one electron per atom. The Fermi energy, E_F , is at the middle of the gap and the system exhibits insulating behavior

The number of states in each band is equal to $(L/2\pi)(2\pi/a) = L/a = N_c$, where N_c is the number of primitive cells in the system; the number of atoms, is equal to $2N_c$, since there are two atoms per primitive cell. If we assume that there is one electron per atom, i.e., a total of $2N_c$ electrons, then at $T = 0\text{K}$ these electrons would fill up completely the lower band (which is then called *valence band*) and leave the upper band empty (which is then called *conduction band*); the Fermi energy would be in the middle of the gap, as shown in Fig. 6.7 and the system would behave as an insulator. It is customary to call a material *insulator*, if the gap between the highest fully occupied band (the valence band) and the lowest completely empty band (the conduction band) is more than 3.5 eV. If this gap is less than 3.5 eV, we usually characterize the material as a *semiconductor*.

The band structure shown in Fig. 6.6 can be plotted in another equivalent way by transferring the upper branch from the first BZ to the second BZ which consists of two disjoint pieces $[-2\pi/a, -\pi/a]$ and $[\pi/a, 2\pi/a]$. This transfer is achieved by transporting horizontally half of the upper branch from $[0, \pi/a]$ to the $[-2\pi/a, -\pi/a]$ through the vector of the reciprocal lattice $-2\pi/a$; and the other half from $[-\pi/a, 0]$ to $[\pi/a, 2\pi/a]$ through the vector of the reciprocal lattice $2\pi/a$. The end result of these two operations is shown in Fig. 6.8.

Plotting all branches in the first BZ is called *reduced-zone scheme*; plotting the lowest branch in the first BZ, the second lowest to the second BZ, the third lowest (if any) to the third BZ, etc., is referred to as *extended-zone scheme*.

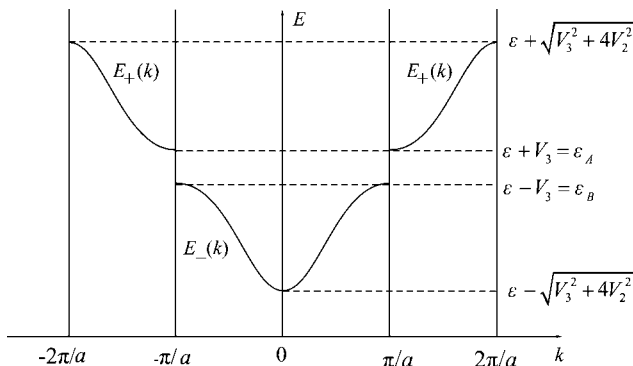


Fig. 6.8. Presented here is an equivalent way of plotting the band structure shown in Fig. 6.6. In Fig. 6.6 both the lower and the upper branch are plotted within the first BZ (a choice called *reduced-zone scheme*); in Fig. 6.8 the lowest branch is placed in the first BZ and the next one in the second BZ (this equivalent choice is called *extended-zone scheme*)

Notice that the present model ought to be reduced to that of Sect. 6.3, if $\varepsilon_A = \varepsilon_B$, i.e., when $V_3 = 0$; then the period is not $a = 2d$ but d , and the first BZ is twice as large and extends from $-\pi/d$ to π/d , i.e., equivalently, from $-\pi/a$ to $2\pi/a$, i.e., twice as large.

Using the extended-zone scheme makes it quite clear how Fig. 6.8 reduces to that of Fig. 6.3 when $\varepsilon_A = \varepsilon_B$.

6.5 One-Dimensional Molecular “Solid”

The simplest one-dimensional model resembling that of a molecular solid is shown in Fig. 6.9. The “molecule” at the cell m is weakly coupled with those at cells $m \pm 1$.

For the determination of the eigenfunctions and the eigenenergies of this model, we shall follow a procedure that is equivalent to what we did before but in a different order: Instead of writing Schrödinger’s equation in the basis $\{\phi_{1m}, \phi_{2m}\}$ and then using Bloch’s theorem stating that equivalent orbitals differing by a lattice vector, ma , are related by a factor $\exp(ikma)$ (see (6.32, 6.33)), we start first with the latter property by introducing the functions

$$g_{1,k} \equiv \frac{1}{\sqrt{N_c}} \sum_m e^{ikam} \phi_{1,m}, \quad (6.39)$$

$$g_{2,k'} \equiv \frac{1}{\sqrt{N_c}} \sum_m e^{ik'am} \phi_{2,m}, \quad (6.40)$$

with N_c being the total number of primitive cells and k and k' taking all allowed values in the first BZ. The functions $\{g_{i,k}\}$, $i = 1, 2$, form a complete

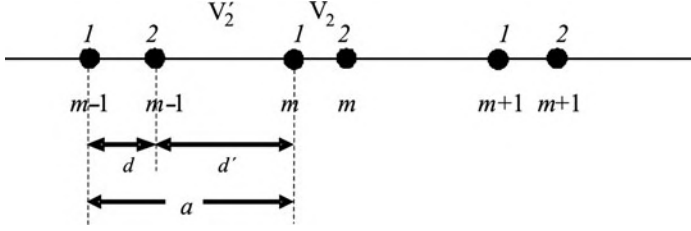


Fig. 6.9. Model of a one-dimensional molecular solid within the framework of LCAO. The primitive cell contains two identical atoms each one having an identical orbital; the period is $a = d + d'$, where $d' > d$; $|V'_2| \ll |V_2|$, where $V'_2 = \langle \phi_{2,m-1} | \hat{H} | \phi_{1m} \rangle$ and $V_2 = \langle \phi_{1m} | \hat{H} | \phi_{2m} \rangle$ and $\varepsilon = \langle \phi_{1m} | \hat{H} | \phi_{1m} \rangle = \langle \phi_{2m} | \hat{H} | \phi_{2m} \rangle$. This model can be thought of as a distorted version of the model of Sect. 6.3, where every second atom has been displaced to the left by the same distance

orthonormal set as k varies within the first BZ and $i = 1$ or 2 . Thus, they can be used as a basis instead of the set $\{\phi_{i,m}\}$. The big advantage of $\{g_{i,k}\}$ is that the matrix elements of the Hamiltonian between nonequivalent k 's are zero:

$$\langle g_{i,k} | \hat{H} | g_{j,k'} \rangle \equiv \int d^3r g_{i,k}^*(\mathbf{r}) \hat{H}(\mathbf{r}) g_{j,k'}(\mathbf{r}) = A_{ij} \delta_{k,k'+G_p}. \quad (6.41)$$

As a result of this property, the general equations (B.32–B.35) of Appendix B become in the framework of the $\{g_{i,k}\}$ basis

$$\psi_k = \sum_{i=1}^2 c_i g_{i,k}, \quad (6.42)$$

$$(A_{11} - E)c_1 + A_{12}c_2 = 0, \quad (6.43)$$

$$A_{21}c_1 + (A_{22} - E)c_2 = 0. \quad (6.44)$$

Problem 6.3t. Prove that the set $\{g_{i,k}\}$ is orthonormal, i.e.,

$$\langle g_{i,k} | g_{j,k'} \rangle = \delta_{ij} \delta_{k,k'+G_p}.$$

Prove also (6.41) and show that

$$A_{11} = A_{22} = \varepsilon, \quad (6.45)$$

$$A_{12} = A_{21}^* = V_2 + V'_2 e^{-ika}. \quad (6.46)$$

More generally, if within the primitive cell associated with the lattice vector $\mathbf{R}$, there are several atoms at the positions $\mathbf{R} + \mathbf{d}_i$ ($i = 1, 2, \dots$) each one of which has several atomic orbitals ϕ_{Ria} ($a = 1, 2, \dots$), we define the set $\{g_{iak}\}$ as follows

$$g_{iak} = \frac{1}{\sqrt{N_c}} \sum_{\mathbf{R}} e^{+i\mathbf{k} \cdot \mathbf{R}} \phi_{Ria}, \quad (6.47)$$

which, assuming orthonormality of the set $\{\phi_{Ria}\}$ and taking into account the periodicity, satisfies the following equations

$$\langle g_{ia\mathbf{k}} | g_{j\beta\mathbf{k}'} \rangle = \delta_{ij} \delta_{a\beta} \delta_{\mathbf{k}\mathbf{k}'}, \quad \mathbf{k}, \mathbf{k}', \text{ in the 1st BZ,} \quad (6.48)$$

$$\langle g_{ia\mathbf{k}} | \hat{H} | g_{j\beta\mathbf{k}'} \rangle = \delta_{\mathbf{k}\mathbf{k}'} \sum_{\mathbf{R}} e^{+i\mathbf{k}\cdot\mathbf{R}} \langle \phi_{0ia} | \hat{H} | \phi_{\mathbf{R}j\beta} \rangle, \quad \mathbf{k}, \mathbf{k}', \text{ in the 1st BZ.} \quad (6.49)$$

Obviously the summation in (6.49) is only over the lattice vectors for which the matrix element $\langle \phi_{0ia} | \hat{H} | \phi_{\mathbf{R}j\beta} \rangle$ is nonzero; taking into account that we have chosen the matrix elements of the Hamiltonian to be nonzero only for the diagonal and the nearest neighbor off diagonal, the summation over the lattice vectors includes the $\mathbf{R} = 0$ and the ones connecting the origin with the nearest neighboring Bravais lattice points; in any case, the number of terms in the summation is no more than the number of nearest neighbor atoms plus one. In problem 6.2, you are asked to prove (6.48) and (6.49), assuming periodic boundary conditions (PBC) for each of the Cartesian axis; PBC imply that

$$\sum_{\mathbf{R}} e^{i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{R}} = N_c \delta_{\mathbf{k}', \mathbf{k}}, \quad \mathbf{k}', \mathbf{k}, \text{ in the 1st BZ.}$$

For the system (6.43), (6.44) to have nonzero solutions its determinant $(A_{11} - E)(A_{22} - E) - A_{12}A_{21}$ must be equal to zero, which in view of (6.45), (6.46) leads to the following relation

$$\begin{aligned} E_{\pm} &= \varepsilon \pm \sqrt{V_2^2 + V'^2_2 + 2V_2V'_2 \cos ka} \\ &= \varepsilon \pm \sqrt{(V_2 - V'_2)^2 + 4V_2V'_2 \cos^2 \frac{ka}{2}}, \end{aligned} \quad (6.50)$$

which produces two bands. The lower one extends from $\varepsilon - |V_2 + V'_2|$ to $\varepsilon - |V_2 - V'_2|$ and the upper one from $\varepsilon + |V_2 - V'_2|$ to $\varepsilon + |V_2 + V'_2|$ assuming that $V_2V'_2 > 0$. The width of the gap between the two is

$$E_g = 2|V_2 - V'_2|. \quad (6.51)$$

Again if there is one electron per atom the lower band would be fully occupied, while the upper one would be completely empty and the model would exhibit insulating or semiconducting behaviour. The conclusion is that by dimerizing the model of Sect. 6.3 we open a gap at the Fermi level of Fig. 6.4 and we transform a metallic behaviour to an insulating one. Furthermore, the opening of the gap lowers the occupied energy levels and most probably lowers the total energy of the system. If this is the case, the model of Sect. 6.3 is unstable towards spontaneous dimerization. This is actually the case for one-dimensional systems and it is known as the *Peierls instability*. For three-dimensional systems, the occurrence or not of spontaneous

dimerization (or more generally, periodic distortions, which open up a gap at the Fermi energy) depends on the details of the system. For example, we can view the non-existence of metallic hydrogen under ordinary pressures as due to spontaneous dimerization, which leads to the formation of molecular solid hydrogen.

6.6 Diversion: Eigenoscillations in One-Dimensional “solid” with two Atoms Per Primitive Cell

The model of such a solid is shown in Fig. 6.10. The primitive cell of lattice constant a contains two atoms of mass m_A and m_B and spring constants κ_A and κ_B respectively.

In case of $m_A = m_B = m$ the problem is mathematically equivalent to that of the previous Sect. 6.5. Hence, using the analogies of (6.14), we have

$$\omega_{\pm}^2(q) = \frac{(\kappa_A + \kappa_B)}{m} \pm \frac{1}{m} \sqrt{(\kappa_A - \kappa_B)^2 + 4\kappa_A\kappa_B \cos^2 \frac{qa}{2}}, \quad m_A = m_B = m, \quad (6.52)$$

which is reduced to (6.5) if $\kappa_A = \kappa_B = \kappa$ and $a = 2d$. In the more general case of $m_A \neq m_B$ and $\kappa_A \neq \kappa_B$, one should write Newton’s equation of motion for the masses m_A and m_B in the n th primitive cell and then use the equations

$$u_A(n) = \text{Re}\{u_A e^{iqna}\}, \quad u_B(n) = \text{Re}\{u_B e^{iqna}\}, \quad (6.53)$$

(which satisfy Bloch’s theorem and are the analogs of (6.32), (6.33)) to obtain the following result:

$$\omega_{\pm}^2(q) = \Omega^2 \pm \sqrt{\Delta\omega^4 + \frac{1}{m_A m_B} (\kappa_A^2 + \kappa_B^2 + 2\kappa_A\kappa_B \cos qa)}, \quad (6.54)$$

where

$$\Omega^2 = \frac{\kappa_A + \kappa_B}{2m_r}, \quad m_r \equiv \frac{m_A m_B}{m_A + m_B}, \quad (6.55)$$

$$\Delta\omega^2 = \frac{\kappa_A + \kappa_B}{2} \left(\frac{1}{m_A} - \frac{1}{m_B} \right), \quad m_A < m_B. \quad (6.56)$$

In Fig. 6.11, we plot the two branches $\omega_{\pm}(q)$ vs. q for q in the first BZ.

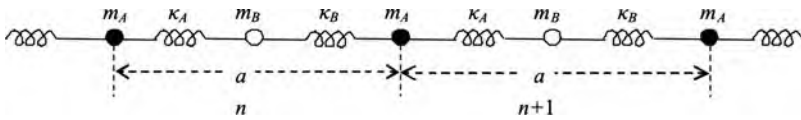


Fig. 6.10. One-dimensional model with two atoms per unit cell for studying the atomic vibrations

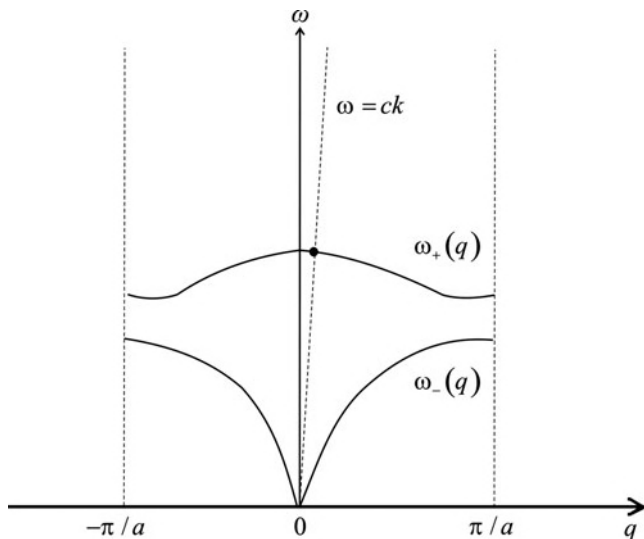


Fig. 6.11. Schematic plot of the two eigenfrequencies, $\omega_+(q)$ and $\omega_-(q)$ vs. the wavenumber q for the collective eigenoscillations of the model shown in Fig. 6.10. The lower curve, $\omega_-(q)$, is called *acoustic branch* because for $qa \ll \pi$ is behaving as an ordinary acoustic wave, i.e., $\omega_-(q) = c_a q$ where the sound velocity $c_a = \sqrt{\kappa_A \kappa_B a^2 / (\kappa_A + \kappa_B)(m_A + m_B)}$ (for $a = 2d$, $\kappa_A = \kappa_B = \kappa$ and $m_A = m_B = m$, $c_a = \sqrt{\kappa d^2 / m}$). The upper branch, $\omega_+(q)$ is called *optical branch*, because a photon of wavenumber k and frequency $\omega = ck$ could be absorbed giving rise to a trasverse optical phonon (at the point of intersection of the photon line $\omega = ck$ with the optical phonon curve $\omega_+ = \omega_+(q)$ both energy and momentum are conserved during the photon absorption/phonon creation process). The value $\omega_+(q)$ at $q = 0$ equals to $\sqrt{(\kappa_A + \kappa_B)/m_r}$, while at $q = \pm\pi/a$ and for $\kappa_A = \kappa_B = \kappa$, $\omega_+ = 2\kappa/m_A$ and $\omega_- = 2\kappa/m_B$ ($m_A < m_B$)

6.7 One-Dimensional Elemental sp^1 “Semiconductor”

Silicon and the other semiconductors, which are the foundation of the modern electronic and computer era, all involve in their bonding four atomic orbitals (s, p_x, p_y, p_z) of the same principal quantum number. The simplest one-dimensional analog of these materials is a periodic elemental “solid” the atoms of which have two atomic orbitals, one s -type and one p -type as shown in Fig. 6.12.

The only nonzero matrix elements of the Hamiltonian are the following:

$$\langle \phi_{np} | \hat{H} | \phi_{np} \rangle = \varepsilon_p, \quad (6.57)$$

$$\langle \phi_{ns} | \hat{H} | \phi_{ns} \rangle = \varepsilon_s, \quad (6.58)$$

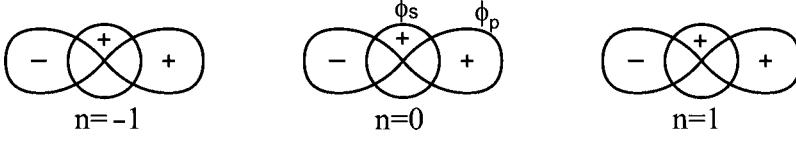


Fig. 6.12. Model of one-dimensional semiconductor with one atom per primitive cell, two atomic orbitals per atom, and two electrons per atom

$$\langle \phi_{np} | \hat{H} | \phi_{n\pm 1,p} \rangle = V_{pp\sigma} > 0, \quad (6.59)$$

$$\langle \phi_{ns} | \hat{H} | \phi_{n\pm 1,s} \rangle = V_{ss\sigma} < 0, \quad (6.60)$$

$$\langle \phi_{ns} | \hat{H} | \phi_{n+1,p} \rangle = -\langle \phi_{ns} | \hat{H} | \phi_{n-1,p} \rangle = V_{sp\sigma} > 0. \quad (6.61)$$

Then by applying in the present case the general formulae (6.47) and (6.49), we find the following system for the coefficient $c_{s,k}$ and $c_{p,k}$

$$(\varepsilon_p + 2V_{pp\sigma} \cos ka - E)c_{p,k} + (-2iV_{sp\sigma} \sin ka)c_{s,k} = 0, \quad (6.62)$$

$$(2iV_{sp\sigma} \sin ka)c_{p,k} + (\varepsilon_s + 2V_{ss\sigma} \cos ka - E)c_{s,k} = 0, \quad (6.63)$$

where $c_{s,k}$ and $c_{p,k}$ give the eigenfunctions, ψ_k , in terms of $g_{s,k}$ and $g_{p,k}$:

$$\psi_k = c_{s,k}g_{s,k} + c_{p,k}g_{p,k}. \quad (6.64)$$

By setting the determinant of the system (6.62, 6.63) equal to zero and solving the resulting equation with respect to E , we find two eigenenergies for each k :

$$E_{\pm}(k) = \varepsilon_h + \frac{(V_{pp\sigma} + V_{ss\sigma}) \cos ka}{\pm \sqrt{[V_1 + (V_{pp\sigma} - V_{ss\sigma}) \cos ka]^2 + 4V_{sp\sigma}^2 \sin^2 ka}}, \quad (6.65)$$

where $\varepsilon_h = (\varepsilon_p + \varepsilon_s)/2$ and $V_1 = (\varepsilon_p - \varepsilon_s)/2$. The plus sign corresponds to the upper branch, which gives rise to the upper band as k varies within the first BZ; the minus sign produces the lower band as k varies within the first BZ. In Fig. 6.13 we plot the dependence of the two branches on k for a particular (very small) value of $a = 2.2$ Å. Notice that, for such small values of a , the k at which the maximum of the VB occurs, $k_{\max}$, and the k at which the minimum of the CB occurs, $k_{\min}$, do not coincide with the boundaries or the center of the 1st BZ; furthermore, $k_{\max}$ is different from $k_{\min}$. Semiconductors for which $k_{\max} \neq k_{\min}$ are called *indirect gap* semiconductors; for such semiconductors, the optical gap (which is the minimum energy separation between CB and VB for the *same*⁶ $\mathbf{k}$) is larger than E_g .

⁶ Crystal momentum conservation for the excitation of an electron of wavevector $\mathbf{k}_i$ from the VB to the CB with the absorption of a photon of wave number $\mathbf{q}$ requires that $\mathbf{q} + \mathbf{k}_i = \mathbf{k}_f$, where $\mathbf{k}_f$ is the wavevector of the final state. However, $q = \omega/c$ is typically three orders of magnitude smaller than the linear size π/a of 1st BZ; hence, q is negligible and $\mathbf{k}_i \simeq \mathbf{k}_f$.

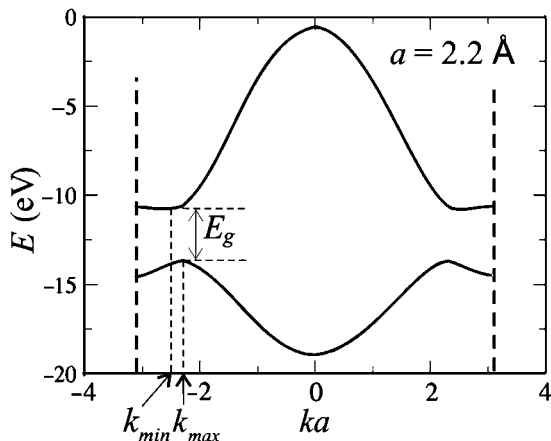


Fig. 6.13. The band structure $E_{\pm}(k)$ according to (6.65) describing qualitatively the behavior of an elemental semiconductor. Notice that the maximum of the VB occurs at $k_{\max}$ and the minimum of the CB at $k_{\min}$ with $k_{\max} \neq k_{\min} \neq \pm\pi/d$. Semiconductors for which $k_{\max} \neq k_{\min}$ are called *indirect gap* semiconductors, while *direct gap* are the semiconductors for which $k_{\max} = k_{\min}$

In Fig. 6.14, we plot the four edges of the two bands (and, hence, the size of E_g as well) vs. the lattice constant a (which in the present case coincides with the nearest neighbor separation d). In both Figs. 6.13 and 6.14 we have used the silicon values for ε_p , ε_s from Table B.3 and (F.11)–(F.13) (with $d = a$ in the present case) for the off-diagonal matrix elements $V_{pp\sigma}$, $V_{ss\sigma}$, and $V_{sp\sigma}$.

Figure 6.14 shows that the gap closes at a single value⁷ of a , which for the chosen matrix elements is $a_1 = 2.734$ Å. To the right of this value ($a > a_1$), the bands are formed approximately around ε_p and ε_s , with a total width equal to $4V_{pp\sigma}$ and $4|V_{ss\sigma}|$ respectively. Thus, for $a > a_1$ the gap is given approximately by $E_g = (\varepsilon_p - \varepsilon_s) - 2(|V_{pp\sigma}| + |V_{ss\sigma}|) = \varepsilon_p - \varepsilon_s - 7.08\hbar^2/ma^2$. On the left side of a_1 ($a < a_1$) the bands are formed approximately around the antibonding, ε_a and bonding, ε_b , molecular levels; the latter are antisymmetric and symmetric combinations respectively of neighboring sp^1 hybrids; the separation $\varepsilon_a - \varepsilon_b$ is equal to $2|V_{2h}| = 6.38\hbar^2/ma^2$ (see (F.77)).

Actually, the separation of the middles of the two bands is larger, i.e., $7.08\hbar^2/ma^2$, mainly because of level repulsion. The width of the two bands is approximately equal to $\varepsilon_p - \varepsilon_s + 1.8\hbar^2/ma^2$ and $\varepsilon_p - \varepsilon_s - 1.8\hbar^2/ma^2$ for the CB and the VB respectively. Thus, the gap for $a < a_1$ is

$$E_g \simeq 7.08\hbar^2/ma^2 - (\varepsilon_p - \varepsilon_s), \quad (6.66)$$

⁷ This is a peculiarity of the one-dimensional model. In 3-D models there is a region of values of a from a_1 to a_2 where there is no gap and the material behaves as a conductor.

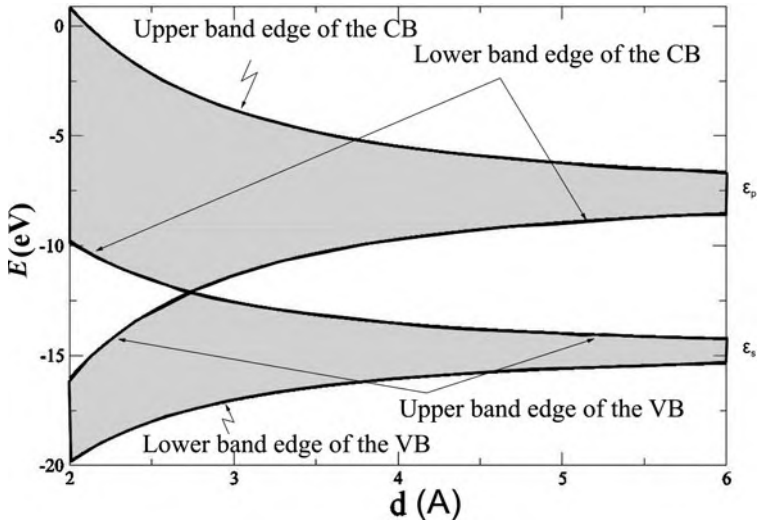


Fig. 6.14. Evolution of conduction and valence bands and the gap as the equilibrium lattice constant $a = d$ varies in a one-dimensional model of elemental semiconductor with two orbitals and two electrons per atom and one atom per primitive cell. Only at a single value of the lattice constant $a = a_1$ the gap closes. With the present choices of $\varepsilon_p, \varepsilon_s, V_{pp\sigma}, V_{ss\sigma}$, and $V_{sp\sigma}$, $a_1 = 2.734$ Å. The nearest neighbor separation for Si is $d = 2.35$ Å

or

$$E_g \simeq 2|V_{2h}| - (\varepsilon_p - \varepsilon_s), \quad (6.67)$$

where V_{2h} is given by (F.77). This simple formula allows us not only to roughly estimate the gap in real elemental tetrahedral semiconductors but it lets us understand why the gap diminishes and eventually disappears as we move down in the column of carbon of the periodic table of the elements, as shown in the following table:

	Diamond	Si	Ge	Sn	Pb
$\varepsilon_p - \varepsilon_s$ (eV) Table B.3	8.3	7.21	7.82	6.28	5.95
d (Å) Table H.7	1.54	2.35	2.45	2.81	3.50
$ V_{2h} $ (eV) (F.70)	10.33	4.44	4.12	3.13	2
E_g (eV) (6.67)	12.36	1.67	0.42	-0.02 ^a	-1.95 ^b
E_g (eV) exp.	5.5	1.17	0.744	0	Metal

^aNegative values of E_g close to zero imply semimetallic behavior

^bIf (6.67) produces appreciable negative values of E_g , a metallic behavior is implied

Equation (6.66) or (6.67) implies also that a smaller equilibrium a of a tetrahedral semiconductor will increase its gap,⁸ while larger a would give

⁸ Assuming that the tetrahedral structure is valid.

smaller gap. This behavior is expected to be reversed if the material happens to be to the right of the above-mentioned a_2 value (see footnote 7 of p. 166). Furthermore, in the regime $a < a_1$, the top of the valence band (which corresponds to $\sin ka \simeq 0$) consists of states of p -character in the sense that $|c_{p,k}/c_{s,k}| \gg 1$ (see (6.62, 6.63)), while the bottom of the conduction band is dominated by s -character states. More explicitly, for $k = \pm\pi/a$, (6.62) and (6.63) decouple giving (for $|V_{pp\sigma}| + |V_{ss\sigma}| > (\varepsilon_p - \varepsilon_s)/2$)

$$E_+(\pi/a) = \varepsilon_s + 2|V_{ss\sigma}|, \quad \psi_{\pi/a,+} = g_{s,\pi/a}, \quad (6.68)$$

$$E_-(\pi/a) = \varepsilon_p - 2|V_{pp\sigma}|, \quad \psi_{\pi/a,-} = g_{p,\pi/a}. \quad (6.69)$$

Similarly for $k = 0$, (6.62) and (6.63) decouple again giving

$$E_+(0) = \varepsilon_p + 2|V_{pp\sigma}|, \quad \psi_{0,+} = g_{p,0}, \quad (6.70)$$

$$E_-(0) = \varepsilon_s - 2|V_{ss\sigma}|, \quad \psi_{0,-} = g_{s,0}. \quad (6.71)$$

Thus, the tops of the VB and the CB are of pure p character, while the bottoms of both bands are of pure s character (assuming that both the tops and the bottoms appear either for $k = 0$ or for $k = \pi/a$). Hence, the band edges (for $a < a_1$, but not too small) can be found by inspection of the following figure

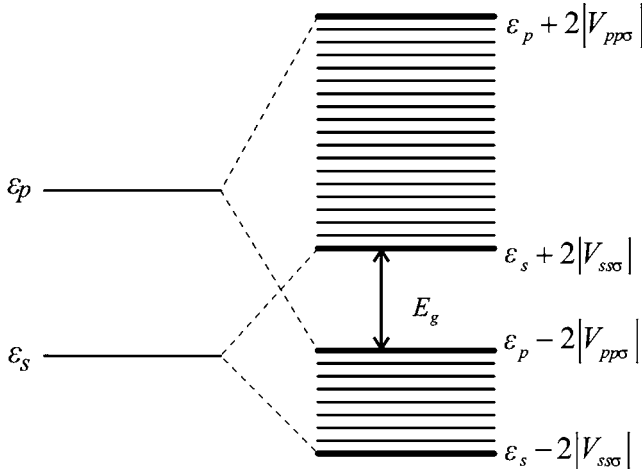


Fig. 6.15. Determination of the band edges from the splitting of the ε_p and ε_s atomic levels by $\pm 2|V_{pp\sigma}|$ and $\pm 2|V_{ss\sigma}|$ respectively. The size of the gap is given by $E_g = |2(|V_{ss\sigma}| + |V_{pp\sigma}|) - (\varepsilon_p - \varepsilon_s)| = |7.08\hbar^2/md^2 - (\varepsilon_p - \varepsilon_s)|$. The interior of the bands are of mixed s and p character, in contrast to the band edges, which are of pure either p or s character. For $|V_{ss\sigma}| + |V_{pp\sigma}| > (\varepsilon_p - \varepsilon_s)/2$, the tops of both bands are of p character, while the bottoms of both bands are of s character. For $|V_{ss\sigma}| + |V_{pp\sigma}| < (\varepsilon_p - \varepsilon_s)/2$, $\varepsilon_p - 2|V_{pp\sigma}|$ is higher than $\varepsilon_s + 2|V_{ss\sigma}|$

The behavior for $a < a_1$ can also be approximately obtained by a series of steps each one of which reduces the problem to a known one, i.e., to one already solved in Appendix F or in Sects. 6.3 and 6.4. The sequence is as follows:

Step 1: Do sp^1 hybridization (see Sect. F.3.1).

In the new basis, χ^1 , χ^2 , the matrix elements of the Hamiltonian are given by (F.35)–(F.39); In particular, the diagonal matrix element is $\varepsilon_h = (\varepsilon_s + \varepsilon_p)/2$.

Step 2: From the hybridized atomic orbitals, χ_1^1 , χ_2^2 (see Fig. F.4) go to the bonding, ψ_b , and antibonding, ψ_a , molecular orbitals associated with each bond (following the procedure of Sect. F.2.1) with diagonal matrix elements $\varepsilon_h \mp |V_{2h}|$ respectively (see also (F.39)).

Step 3: Find the matrix elements of the Hamiltonian in the new basis ψ_b and ψ_a , following the procedure of Sect. F.3.1. The results are

$$H_{n,n+1}^{bb} = \frac{1}{2} \left[0.9 \frac{\hbar^2}{md^2} - V_1 \right], \quad (6.72)$$

$$H_{n,n+1}^{aa} = \frac{1}{2} \left[0.9 \frac{\hbar^2}{md^2} + V_1 \right], \quad (6.73)$$

$$H_{n,n+1}^{ab} = -H_{n,n+1}^{ba} = \frac{1}{2} V_1, \quad (6.74)$$

$$H_{nn}^{ab} = 0, \quad (6.75)$$

where

$$V_1 \equiv \frac{\varepsilon_p - \varepsilon_s}{2}.$$

For a proof of (6.72–6.75) see Problem 6.5s.

Step 4: Omitting the matrix elements (6.74) as well as the nonzero matrix elements between second nearest neighbor bonding or antibonding molecular orbitals,⁹ the problem is reduced to that of Sect. 6.3. Hence, a VB is created around ε_b of width $4 |H_{n,n+1}^{bb}|$ and a CB around ε_a of width $4 |H_{n,n+1}^{aa}|$. The resulting gap E_g is approximately

$$E_g \simeq 2 |V_{2h}| - (\varepsilon_p - \varepsilon_s) = 6.44 \frac{\hbar^2}{md^2} - (\varepsilon_p - \varepsilon_s). \quad (6.76)$$

Step 5: (optional) Reintroduce the omitted matrix elements $H_{n,n+1}^{ab}$ and $H_{n,n+1}^{ba}$ and $H_{n,n+2}^{bb}$, $H_{n,n+2}^{aa}$; the first pair induces a level repulsion and an increase of the gap, while the second increases the bandwidths and tends to reduce the gap. The end result, for not so small a , is to increase the gap by changing the numerical factor from 6.44 to 7.08. However, given the approximate character of the LCAO method

⁹ The nonzero second nearest neighbor bonding and antibonding matrix element are responsible, when a is very small, for the maximum of the VB and the minimum of the CB to appear at $k_{\max}$, $k_{\min}$ such that $k_{\max} \neq k_{\min} \neq \pm\pi/a$ (see Fig. 6.13).

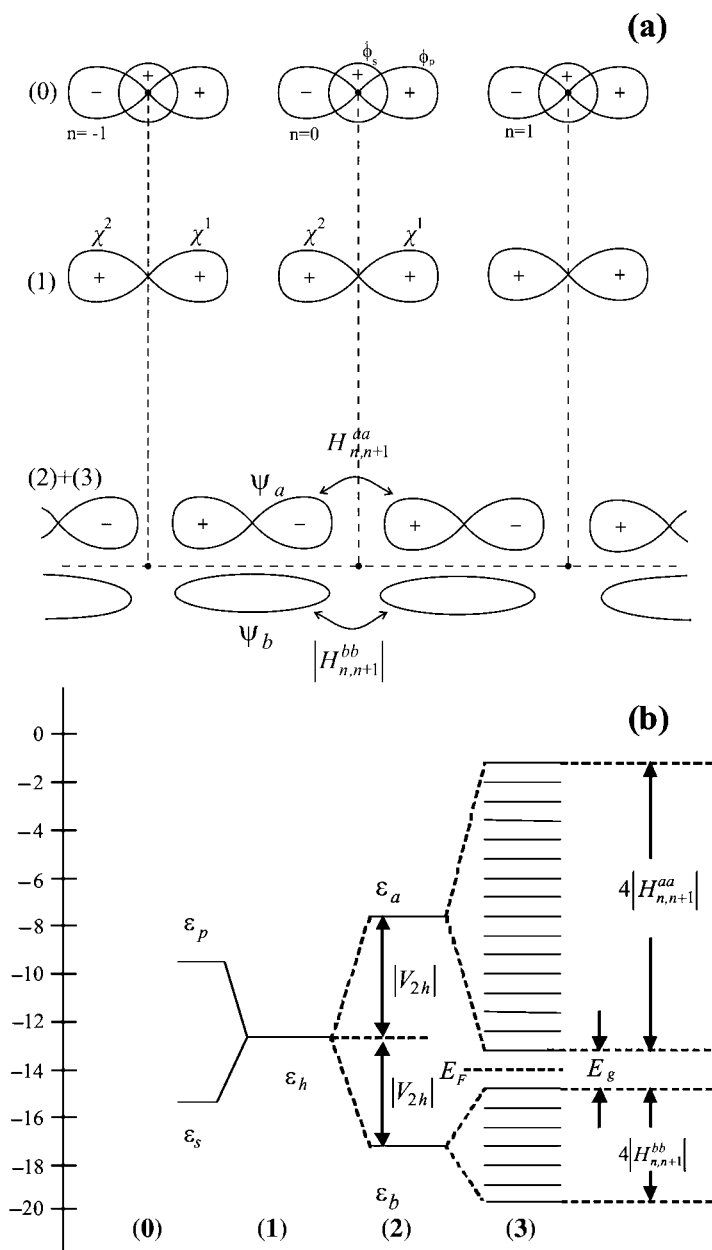


Fig. 6.16. Successive changes of the basis orbitals produced by step 1 [from ϕ_s, ϕ_p to χ^1, χ^2] and step 2 [from χ^1, χ^2 to ψ_b, ψ_a] (panel **a**) and the corresponding energy levels accompanying these changes (panel **b**) for the 1-D model shown in the top of the figure. The VB and the CB are formed around the bonding ϵ_b and the antibonding ϵ_a molecular levels respectively. Recall that the top of both bands is of pure p -character, while the bottom of both bands is of pure s -character. The band edges can be obtained by the simpler approach shown in Fig. 6.15

and the approximations involved in the expressions for the matrix elements of the Hamiltonian, it is doubtful whether step 5 would be beneficial or detrimental, as far as agreement with the experimental data is concerned. Usually (6.67) (or (6.76)) is closer to the experimental values than (6.66). In Fig. 6.16a we show the successive changes of basis from the initial atomic orbitals ϕ_s , ϕ_p to the atomic hybrids χ^1 , χ^2 and then to the molecular bonding, ψ_b , and antibonding, ψ_a ; the nearest neighbors off-diagonal matrix elements of the Hamiltonian in the basis ψ_b , ψ_a is also shown. In Fig. 6.16b the energy levels for each successive step are displayed.

6.8 One-Dimensional Compound sp^1 “Semiconductor”

In Fig. 6.17 (0) a 1-D model for a compound semiconductor (e.g., GaAs) is shown. In Fig. 6.18 the energy levels associated with the orbitals of Fig. 6.17 are also presented.

In these figures the approximate solution to the problem is shown by following the step-by-step approach from atomic orbitals to hybrid atomic orbitals, to bonding and antibonding molecular orbitals and finally to the bands. In analogy with Sect. F.2.2 ((F.26, F.27) and (F.28, F.29)), we have

$$\varepsilon_b = \varepsilon - \sqrt{V_{2h}^2 + V_{3h}^2}, \quad (6.77)$$

$$\varepsilon_a = \varepsilon + \sqrt{V_{2h}^2 + V_{3h}^2}, \quad (6.78)$$

$$\psi_b = \frac{1}{\sqrt{2}} [\sqrt{1 - a_p} \chi_c^1 + \sqrt{1 + a_p} \chi_a^2], \quad (6.79)$$

$$\psi_a = \frac{1}{\sqrt{2}} [\sqrt{1 + a_p} \chi_c^1 - \sqrt{1 - a_p} \chi_a^2], \quad (6.80)$$

$$\varepsilon_{hi} \equiv \frac{\varepsilon_{si} + \varepsilon_{pi}}{2}, \quad i = c, a, \quad (6.81)$$

$$\varepsilon \equiv \frac{\varepsilon_{hc} + \varepsilon_{ha}}{2}, \quad (6.82)$$

$$V_{3h} \equiv \frac{\varepsilon_{hc} - \varepsilon_{ha}}{2}, \quad (6.83)$$

$$V_{1i} \equiv \frac{\varepsilon_{pi} - \varepsilon_{si}}{2}, \quad i = c, a, \quad (6.84)$$

$$V_{2h} \equiv -3.19 \frac{\hbar^2}{m_e d^2}, \quad (6.85)$$

$$a_p \equiv \frac{V_{3h}}{\sqrt{V_{2h}^2 + V_{3h}^2}}. \quad (6.86)$$

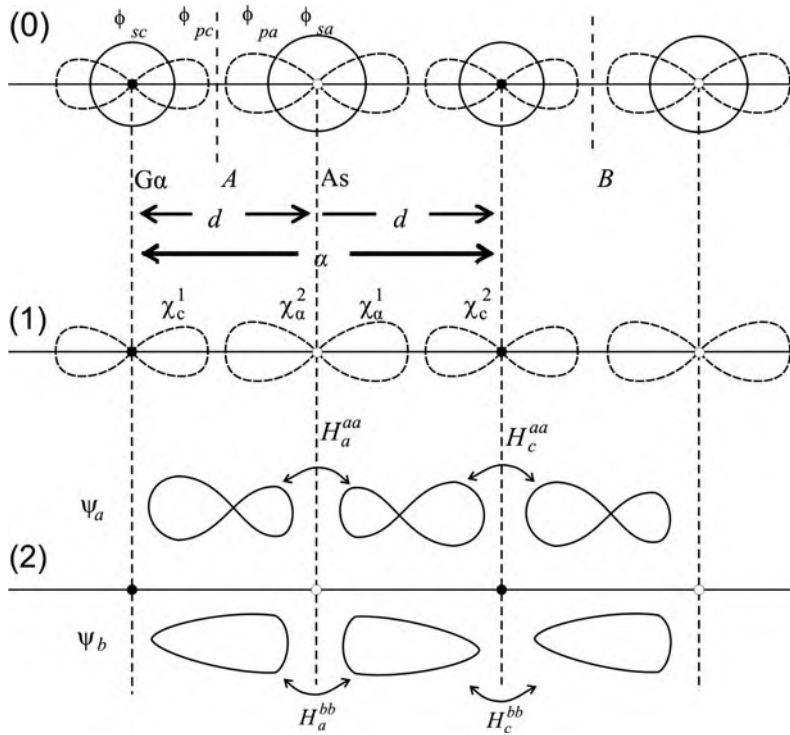


Fig. 6.17. (0) 1-D model of a compound semiconductor with two different atoms per primitive cell (AB) and two orbitals (ϕ_s and ϕ_p) per atom. The type c (cation) atom carries two electrons and the type a (anion) has also two electrons. In (1) the sp^1 hybridized atomic orbitals for each atom are shown and in (2) the bonding ψ_b and antibonding ψ_a orbitals, together with the corresponding off-diagonal nearest neighbor matrix elements H_i^{bb} and H_i^{aa} ($i = a$ or c) of the Hamiltonian are displayed

It requires some algebra (along the lines leading to the equation in the footnote 7 of p. 747) to obtain the matrix elements among nearest neighboring bonding and antibonding orbitals (as shown in Fig. 6.17 (2)). Here we quote the results (for a hint to the proof see Problem 6.7s)

$$H_a^{bb} = -\frac{1+a_p}{2} V_{1a} + \Lambda, \quad (6.87)$$

$$H_c^{bb} = -\frac{1-a_p}{2} V_{1c} + \Lambda, \quad (6.88)$$

$$H_a^{aa} = +\frac{1-a_p}{2} V_{1a} + \Lambda, \quad (6.89)$$

$$H_c^{aa} = +\frac{1+a_p}{2} V_{1c} + \Lambda, \quad (6.90)$$

where

$$\Lambda = 0.45 \sqrt{1 - a_p^2} \frac{\hbar^2}{md^2}. \quad (6.91)$$

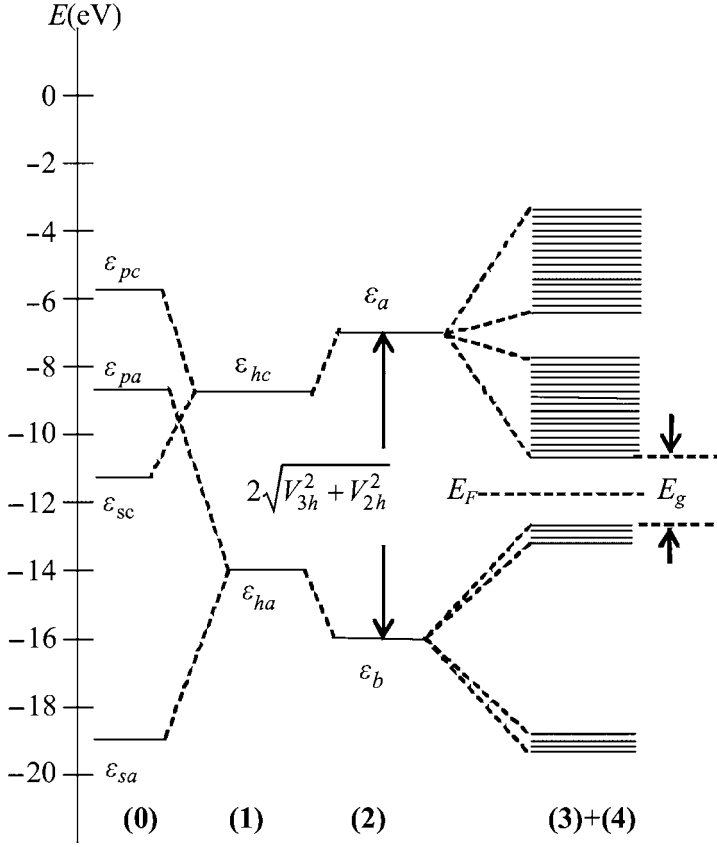


Fig. 6.18. The energy levels and the bands associated with the one-dimensional model of Fig. 6.17 (The numbers are appropriate for GaAs). The successive steps start from the atomic levels, to the atomic hybrid levels (step 1), to the bonding and antibonding levels (step 2), to the formation of the two valence subbands through the off-diagonal matrix elements H_a^{bb} and H_c^{bb} and the two conduction subbands through the matrix elements H_a^{aa} and H_c^{aa} (see Fig. 6.17 (2) and (3))

To obtain the two valence subbands we used the results of Sect. 6.5, (6.50), where the role of ε is played by ε_b and the roles of V_2 , V'_2 are played by H_a^{bb} and H_c^{bb} . Similarly, to obtain the two conduction subbands we follow (6.50) with the replacements: $\varepsilon \rightarrow \varepsilon_a$, $V_2 \rightarrow H_c^{aa}$, and $V'_2 \rightarrow H_a^{aa}$. The gap according to these equations is given approximately by

$$E_g = 2\sqrt{V_{2h}^2 + V_{3h}^2} - \frac{1}{2}(\varepsilon_{pc} + \varepsilon_{pa} - \varepsilon_{sc} - \varepsilon_{sa}). \quad (6.92)$$

For the results shown in Fig. 6.18 we used the *GaAs* values for ε_{pc} , ε_{sc} , ε_{pa} , ε_{sa} , and d . The readers must keep in mind that the results for a 3-D LCAO

model for semiconductors differs from the 1-D case in several significant points as we shall see in the next chapter.

6.9 Key Points

- The LCAO method expresses the unknown electronic eigenfunctions as a linear combination of selected known atomic orbitals of all the atoms participating in the formation of a solid; then Schrödinger's equation is reduced to a matrix equation of the form, $Hc = Ec$, where H is the square matrix of the Hamiltonian and c is the column matrix of the unknown coefficients. Against the many advantages of this method stands the difficulty of finding realistic values for the matrix elements H_{mn} of $\hat{H}$. To overcome this problem (at the expense of accuracy), Harrison [SS76] proposed simple expressions of the form

$$H_{mn} = \eta_{mn} \frac{\hbar^2}{m_e d^2}, \quad m \neq n,$$

and

$$H_{nn} = \varepsilon_n.$$

- Mathematically, the system $Hc = Ec$ is equivalent to that of harmonic oscillations in a set of coupled pendulums. The latter is easily reduced to that of coupled ionic oscillations as well.
- The LCAO method is capable of introducing the main conceptual tools of solid state physics such as bands, gaps, effective masses, reduced and extended-zone scheme, etc; furthermore, it is flexible enough to reproduce the main features of various kinds of solids such as metals, ionic solids, molecular solids, elemental semiconductors, and compound semiconductors.
- In this chapter the simple one-dimensional version of these types of solids was studied quantitatively by solving (repeatedly) no more than a homogeneous, linear system of two equations with two unknowns. Expressions for the gap size in semiconductors were obtained (see (6.76) and (6.92)) explaining, e.g., why as we go down the all important fourth column of the periodic table we start with an insulator (diamond), we pass through semiconductors (Si, Ge) to an “undecided” elemental solid (Sn) that switches between a metal and a semiconductor, and we end up with lead, a clear metal.
- In the next chapter, the results based on the 1-D models studied in this chapter will be generalized to 3-D realistic systems.

6.10 Problems

- 6.1 Show that (6.15) to (6.17) satisfy (6.13).
- 6.2 Prove (6.48) and (6.49).

- 6.3 Prove (6.54).
- 6.4 Calculate the group velocity $v_g = d\omega_+/dq$ for the optical phonon branch of the model of Sect. 6.6 for the case $\kappa_A = \kappa_B$.
- 6.5 Prove (6.72) to (6.75).
- 6.6s Prove (6.77) to (6.80).
- 6.7s Prove (6.87) to (6.91).
- 6.8s To obtain the matrix elements of the Hamiltonian in the g_{sck} , g_{sak} , g_{pck} , and g_{pak} basis, for the system shown in Fig. 6.17(0) use (6.49); c and a stand for the cation and anion respectively. Show that for $\sin kd = 0$ the 4×4 matrix of H decouples into two 2×2 matrices, one involving s-states only and the other p-states only. Assuming that the edges of the VB and the CB correspond to $\sin kd = 0$, calculate the energies of these edges and the size of the gap. Compare with the value of the gap given by (6.92).
- 6.9 Compare the band edges according to the scheme shown in Fig. 6.18 with those based on the approach of the previous (Problem 6.8s). Use the GaAs parameters.
- 6.10s Calculate the summation $2 \sum_{|k| \leq k_F} E(k)$ over the occupied states where $E(k)$ is given by (6.50). Compare with the corresponding result for the case, $V_2 = V'_2$.
- 6.11 For the model of Fig. 6.5 and (6.27)–(6.29) with one electron per atom show that the cation charge q_A (in units of $|e|$) is

$$q_A = \frac{2\sqrt{1-\lambda^2}}{\pi} \mathbb{K}(\lambda),$$

where $\lambda^2 \equiv 4V_2^2 / (V_3^2 + 4V_2^2)$ and $\mathbb{K}(\lambda)$ is the complete elliptic integral of first kind:

$$\mathbb{K}(\lambda) \equiv \int_0^{\pi/2} \frac{d\phi}{\sqrt{1-\lambda^2 \sin^2 \phi}}.$$

Show also that for $\lambda \ll 1$ (i.e., strongly ionic “solid”)

$$q_A \simeq 1 - \frac{V_2^2}{V_3^2}.$$

Further Reading

- Harrison in his book [SS76] fully explores the possibilities of the LCAO.
- The book by Papaconstantopoulos [SS81] provides more realistic values for the matrix elements employed by the LCAO method.

Semiconductors and Other Tetravalent Solids

Summary. The results of Chap. 6 are generalized to three-dimensional tetravalent real solids, which are characterized mainly by two dimensionless parameters: the polarity index, a_p , and the metallicity index, a_m . Depending on their values, we may have metallic or covalent or ionic behavior. The important concepts of holes, mass tensors, electronic and phononic DOS, impurity levels in the gap, and doping are introduced and/or examined. Tables of values of important quantities for various semiconductors are given.

7.1 Lattice Structures: A Reminder

In 3-D solids, as opposed to the 1-D models, the question of how the atoms are positioned in space is raised naturally and it is also of significant interest.

Metals tend to form dense-packed structures such as fcc and hcp, or bcc.

Elemental van der Waals and simple molecular solids form usually fcc structures. *Ionic solids* are commonly solidified in NaCl or CsCl structures, although other more complicated lattices do occur.

Elemental group IV *semiconductors* follow the *diamond* structure. Compound III–V (or II–VI) semiconductors crystallize usually in the *zincblende* (ZnSe) or the Wurtzite structure. Other lattice structures do appear (see Table 7.5). The diamond and zincblende structures consist of two interpenetrating fcc lattices displaced relative to each other by the vector $(a/4, a/4, a/4)$, where a is the fcc lattice constant; in elemental semiconductors, the points of both sublattices are occupied by the same type of atoms (e.g., Si), while in the perfect binary compounds, one sublattice has only one type of atoms (e.g., Ga) and the other only the other type (e.g., As). In these lattice structures, each atom is *tetrahedrally coordinated*; the same coordination appears also in the wurtzite structure (see Sect. 3.3.2). The physics behind these structural features is the sp^3 *hybridization* of the s , p_x , p_y , p_z atomic orbitals; this hybridization lowers the cohesive energy. Keep in mind that carbon solidifies not only in the diamond structure but also in the more common graphite structure which consists of 2-D sheets called *graphenes* (see

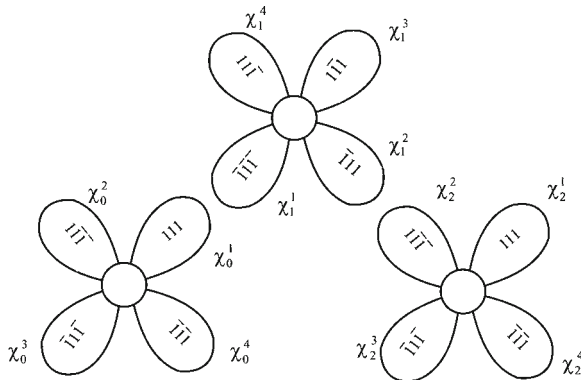


Fig. 7.1. 2-D drawing of the four 3-D sp^3 hybridized orbitals of atom (0) at the position $(0, 0, 0)$, of atom (1) at the position $(a/4, a/4, a/4)$, and of atom (2) at the position $(0, a/2, a/2)$ where a is the lattice constant of the fcc lattice. The direction for each hybrid is denoted by the three numbers, where $\bar{1} \equiv -1$. The lower index in each χ indicates the atom, and the upper one each of the four sp^3 hybrids

Sect. 13.8); the sp^2 hybridization of s, p_x, p_y atomic orbitals is responsible for the planar honeycomb structure of graphene.

In Fig. 7.1, we give a two-dimensional representation of the hybrid orbitals for three atoms in the lattice (see Fig. F.7 for the 3-D picture). The numbers inside each hybrid give its direction in space as well as the coefficients, λ_{xi} , λ_{yi} , λ_{zi} in (F.57), where $\bar{1} \equiv -1$.

7.2 Band Edges and Gap

In Fig. 7.2 we plot schematically the 3-D version of Fig. 6.14. We see first that there is a range of values of the equilibrium lattice constant a ($a_1 < a < a_2$) for which there is no gap, and hence, a metallic behavior is implied. For $a > a_2$ the lower band is of predominantly s -character, is centered approximately around the atomic level ε_s , and can accept up to two electrons per atom; the upper band is predominantly of p -character, is centered approximately around the atomic level ε_p , and can accept up to six electrons per atom. For $a < a_1$, the lower band is predominantly of molecular bonding character, is centered approximately around the bonding molecular level ε_b , and can accept up to four electrons per atom; the upper band is predominantly of molecular antibonding character; is centered approximately around the antibonding molecular level ε_a , and can accept up to four electrons per atom. Hence, for this type of elemental solids, we have the following cases:

If the number of electrons per atom is eight, the solid is always an insulator; if the number of electrons is four and a is to the left of a_1 , the material is either insulator or *semiconductor*; finally, if the number of electrons is two

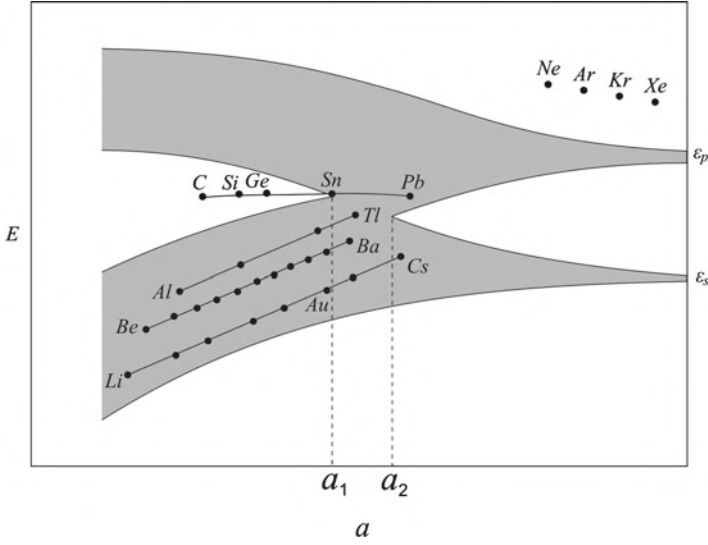


Fig. 7.2. Schematic plot of the bands of a genuinely 3-D elemental solid bonded through s , p_x , p_y , p_z atomic orbitals vs. the equilibrium lattice constant a . The number of electrons per atom is either one (as in Li, Au, Cs), or two (as in Be, Ba), or three (as in Al, Tl), or four (as in C, Si, Ge, Sn, Pb) or eight (as in Ne, Ar, Kr, Xe). The *dots* indicate the position of the Fermi level (in or out of the bands) for each of the elemental solid

and a is to the right of a_2 , the solid is a semiconductor.¹ In all other cases, the material is a metal.

The band edges of the sp^3 tetrahedrally bonded materials shown in Fig. 7.2 (for $a < a_1$) can be determined easily (but approximately) as in Fig. 6.19 (see p. 792 in the solutions section). The argument goes as follows: Since four atomic orbitals (one s and three p 's (p_x , p_y , p_z)) are associated with each atom and there are two atoms per primitive cell, we have in total eight orbitals per primitive cell. Hence, the matrix elements of the Hamiltonian in the $\{g_{iak}\}$ basis form for each $\mathbf{k}$ an 8×8 matrix (for the form of this matrix see the solution of Pr.7.1s). It turns out that for $\mathbf{k} = 0$, this 8×8 matrix reduces to four uncoupled 2×2 matrices. Out of the four 2×2 matrices, one involves only s orbitals and has the form.

$$\begin{pmatrix} \varepsilon_{sc} - E & 4V_{ss\sigma} \\ 4V_{ss\sigma} & \varepsilon_{sa} - E \end{pmatrix}, \quad k = 0, \quad (7.1)$$

¹ Only Ba and Hg could be candidates for such a behavior, since their valence is two and they have the largest equilibrium lattice constant a as a result of being at the bottom of their column in the periodic table. Nature kept them in the metallic regime, i.e., to the left of a_2 .

where ε_{sc} is the atomic level for the cation and ε_{sa} for the anion; for an elemental semiconductor, such as *Si*, $\varepsilon_{sc} = \varepsilon_{sa} = \varepsilon_s$. Following Harrison's choice, $V_{ss\sigma}$ is given by

$$V_{ss\sigma} = -1.32 \hbar^2 / md^2.$$

The other three 2×2 matrices are identical to each other, involve p levels only, and are of the common form

$$\begin{pmatrix} \varepsilon_{pc} - E & 4E_{xx} \\ 4E_{xx} & \varepsilon_{pa} - E \end{pmatrix}, \quad k = 0, \quad (7.2)$$

where ε_{pc} , ε_{pa} are the p atomic levels for the cation and anion respectively and E_{xx} is given by

$$E_{xx} = \frac{1}{3}V_{pp\sigma} + \frac{2}{3}V_{pp\pi} = 0.32\hbar^2/md^2. \quad (7.3)$$

Hence, if the band edges were associated with $k = 0$, they would be given by

$$E_{v\ell} \simeq +\bar{\varepsilon}_s - \sqrt{V_{3s}^2 + 16V_{ss\sigma}^2} = -22.8 \text{ eV}, \quad (7.4)$$

$$E_{vu} \simeq +\bar{\varepsilon}_p - \sqrt{V_{3p}^2 + 16E_{xx}^2} = -9.64 \text{ eV}, \quad (7.5)$$

$$E_{c\ell} = +\bar{\varepsilon}_s + \sqrt{V_{3s}^2 + 16V_{ss\sigma}^2} = -7.60 \text{ eV}, \quad (7.6)$$

$$E_{cu} = +\bar{\varepsilon}_p + \sqrt{V_{3p}^2 + 16E_{xx}^2} = -5.01 \text{ eV}, \text{ (WRONG)},^2 \quad (7.7)$$

$$E_{cu} = \bar{\varepsilon}_p + (V_{3p}^2 + 16E_{xy}^2)^{1/2} = -2.25 \text{ eV}, \quad (7.8)$$

where $E_{xy} = 0.95 \hbar^2 / md^2$ and numbers corresponding to GaAs have been used to arrive at the numerical values. The level E_{vu} (where the subscript v denotes the VB and the subscript u denotes the upper band edge) is threefold degenerate in correspondence to the three p -orbitals, whereas the lower edge of the CB, $E_{c\ell}$, is non-degenerate and of purely s -character. The gap is given by

$$\begin{aligned} E_g \simeq E_{c\ell} - E_{vu} &= \sqrt{V_{3s}^2 + 16V_{ss\sigma}^2} + \sqrt{V_{3p}^2 + 16E_{xx}^2} \\ &\quad - \frac{1}{2}(\varepsilon_{pc} + \varepsilon_{pa} - \varepsilon_{sc} - \varepsilon_{ca}) = 2.04 \text{ eV} \end{aligned} \quad (7.9)$$

vs. the experimental value for GaAs, of $E_g \simeq 1.52 \text{ eV}$ (for the value according to (6.92) see the following section). For *Si*, (7.9) gives $E_g \simeq 1.83 \text{ eV}$, while (6.67) leads to $E_g \simeq 1.66 \text{ eV}$. The experimental value is 1.17 eV .

² The upper CB edge does not correspond to $k = 0$. The values of $\mathbf{k} = ((\pm 2\pi/a), 0, 0)$ and the other four equivalent choices of $\mathbf{k}$ (as a result of cubic symmetry) reduce the 8×8 Hamiltonian matrix to four 2×2 uncoupled matrices. Two of those are identical to each other and of the form of (7.2) but with E_{xx} replaced by $E_{xy} = 0.95 \hbar^2 / md^2$. The resulting higher eigenvalue is equal to that of (7.8), where the numerical value corresponds to GaAs.

7.3 Differences in Formulas Between the 1-D and the 3-D Case and Energy Diagrams

For the sp^3 hybrids appropriate for the 3-D case, the quantities ε_h , V_1 , and V_{2h} are given by (see (F.73), (F.76), and (F.79))

$$\varepsilon_h = \frac{\varepsilon_s + 3\varepsilon_p}{4}, \quad (7.10)$$

$$V_1 = \frac{\varepsilon_p - \varepsilon_s}{4}, \quad (7.11)$$

$$V_{2h} = -3.22 \frac{\hbar^2}{md^2}, \quad (7.12)$$

instead of (6.81), (6.84), and (6.85) appropriate for 1-D.

The matrix elements of the Hamiltonian between neighboring bonding (or antibonding) orbitals (connected to the same atom, see Fig. 7.3a) in composite tetrahedral semiconductors are of the form

$$H_a^{bb} = -\frac{1 + a_p}{2} V_{1a} - \Lambda', \quad (7.13)$$

$$H_c^{bb} = -\frac{1 - a_p}{2} V_{1c} - \Lambda', \quad (7.14)$$

$$H_a^{aa} = -\frac{1 - a_p}{2} V_{1a} + \Lambda', \quad (7.15)$$

$$H_c^{aa} = -\frac{1 + a_p}{2} V_{1c} + \Lambda', \quad (7.16)$$

where

$$\Lambda' \equiv 0.185 \frac{\sqrt{1 - a_p^2} \hbar^2}{md^2}, \quad (7.17)$$

$$a_p \equiv \frac{V_{3h}}{\sqrt{V_{2h}^2 + V_{3h}^2}}, \quad (7.18)$$

$$V_{3h} \equiv \frac{\varepsilon_{hc} - \varepsilon_{ha}}{2}, \quad (7.19)$$

and $V_{1j} \equiv (\varepsilon_{pj} - \varepsilon_{sj})/4$, $j = c, a$ and V_{2h} is given by (7.12). Equations (7.10)–(7.19) are proved in the solved problem 7.4s.

The molecular levels and orbitals are given by (6.77) to (6.80) with V_{2h} , V_{3h} , and a_p defined by (7.12), (7.19), and (7.18), respectively. The quantity ε in (6.77) and (6.78) is

$$\varepsilon = \frac{\varepsilon_{hc} + \varepsilon_{ha}}{2}, \quad (7.20)$$

where ε_{hc} , ε_{ha} are defined according to (7.10).

Finally, the basic relation (6.92) giving an estimate of the gap is approximately valid for the 3-D case as well, provided that V_{2h} and V_{3h} are taken

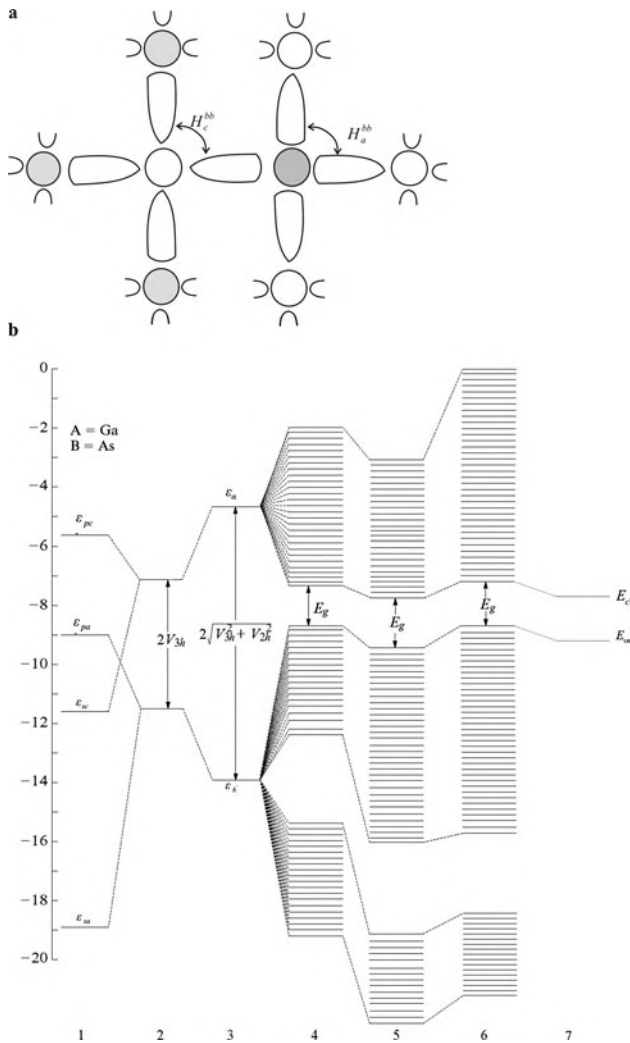


Fig. 7.3. (a) Schematic plot of the environment of a pair of nearest neighbor atoms in a compound tetrahedral semiconductor (c stands for cation and a for anion) together with the bonding molecular orbitals and their nearest neighbor matrix elements. (b) The energy levels and the bands for GaAs following the step by step approach within the LCAO (see step (4)). The outcome (5) is the result of the LCAO without the approximations involved in the step by step approach. The result (6) is the outcome of a sophisticated calculational technique which gives result in agreement with the experimental data. Result (7) is the result of (7.4)–(7.6) for the band edges, assuming that the latter correspond to $k = 0$

from (7.12) and (7.19) respectively (with $\varepsilon_{\text{ha}}, \varepsilon_{\text{hc}}$ defined according to (7.10)). Compare the value of E_{g} given by (6.92) with that of GaAs given by (7.9). Which one is closer to the experimental value of $E_{\text{g}} = 1.52 \text{ eV}$ ³?

In Fig. 7.3 we present a schematic plot of the bonding molecular orbitals and their nearest neighbors matrix elements of the Hamiltonian as well as the 3-D version of the energy levels and bands for GaAs. The readers are asked to compare Fig. 7.3b with Fig. 6.18 and to pinpoint the differences.

In this subsection, we summarize the formulas for a 3-D compound tetrahedral semiconductor within the framework of the LCAO method. It is obvious that these formulas can be used for elemental tetrahedral semiconductors by setting $a_{\text{p}} = V_{3h} = 0$ and $V_{1a} = V_{1c} = V_1$, $\varepsilon_{\text{ha}} = \varepsilon_{\text{hc}} = \varepsilon_{\text{h}}$.

7.4 Metals, Semiconductors, and Ionic Insulators

In this section, we summarize our previous study concerning solids (either elemental, or binary compounds) with an average valence equal to four, the bonding of which involves p and s atomic orbitals. There are four parameters characterizing such materials $V_{1a}, V_{1c}, V_{3h}, V_{2h}$ (for elemental solids $V_{3h} = 0$ and $V_{1a} = V_{1c} = V_1$; thus the parameters are only two). To keep the presentation as simple as possible, we shall group together V_{1a} and V_{1c} through $\bar{V}_1$

$$\bar{V}_1 \equiv \frac{V_{1a} + V_{1c}}{2}. \quad (7.21)$$

Out of the three parameters ($\bar{V}_1, V_{2h}, V_{3h}$), we can take ratios reducing thus the analysis in terms of two dimensionless parameters: the *polarity index*

$$a_{\text{p}} \equiv \frac{V_{3h}}{\sqrt{V_{2h}^2 + V_{3h}^2}}, \quad (7.22)$$

and the *metallicity index* (if V_{1a}, V_{1c} are retained, there are two metallicity indices)

$$a_{\text{m}} \equiv \frac{2\bar{V}_1}{\sqrt{V_{2h}^2 + V_{3h}^2}}. \quad (7.23)$$

In terms of a_{m} , the basic equation (6.92), giving an estimate of the gap E_{g} , becomes

$$E_{\text{g}} \simeq 2\sqrt{V_{2h}^2 + V_{3h}^2} (1 - a_{\text{m}}), \quad (7.24)$$

which shows that, if $a_{\text{m}} > 1$, E_{g} would be negative and the material would exhibit conducting behavior. Notice that a large value of a_{m} not only leads to the closing of the gap and to metallic conductivity but also changes the chemical character of the bond and the lattice structure. Indeed, a large value of a_{m} (which means a large value of $\bar{V}_1$ or $\bar{\varepsilon}_{\text{p}} - \bar{\varepsilon}_{\text{s}}$) implies a high energy cost for

³ The answer is (6.92), which gives 1.35 eV.

hybridization, measured by the promotion energy, which is equal to $\bar{\varepsilon}_p - \bar{\varepsilon}_s$ per atom (see (F.80)). Such a high energy cost will not be recovered through the expected stronger bonding of the hybrids (if a_m is large), and consequently, hybridization is energetically unfavorable. Under these circumstances, the s -orbitals would hardly participate in the bonding, which shall take place mainly through the p -orbitals. As a result of $a_m \gtrsim 1$, the chemical character of the bonding changes from mainly covalent to metallic and the lattice structure from a low coordination, open, tetrahedral one to a close-packed typical of metals.

Let us examine now what happens when the polarity index a_p increases. According to (7.13)–(7.16), the differences

$$|H_a^{bb} - H_c^{bb}| = a_p \bar{V}_1 + \frac{1}{2} (V_{1a} - V_{1c}), \quad (7.25)$$

$$|H_c^{aa} - H_a^{aa}| = a_p \bar{V}_1 - \frac{1}{2} (V_{1a} - V_{1c}), \quad (7.26)$$

between the two consecutive matrix elements (transferring electrons among bonding in case (7.25) (or antibonding in case (7.26)) molecular orbitals) increase as a_p increases. When $|H_c^{bb} - H_a^{bb}|$ exceeds a critical value, the valence band splits into two subbands (in analogy with the case in Sect. 6.5) with the lower one centered around ε_{sa} (see Fig. 7.3b). Similarly, when $|H_c^{aa} - H_a^{aa}|$ exceeds the same critical value, the conduction band also splits into two subbands (For the 1-D case, the critical value for splitting is zero and, as a result, any nonzero value of $|H_a^{bb} - H_c^{bb}|$ and $|H_c^{aa} - H_a^{aa}|$ splits both the valence and the conduction band into two subbands; see Fig. 6.18). Since $|H_a^{bb} - H_c^{bb}|$ is always larger than $|H_c^{aa} - H_a^{aa}|$ (compare (7.25) and (7.26)), the splitting of the VB into two subbands would occur first as a_p increases, while the splitting of the CB would come later (if at all). As a_p increases further, the four subbands become narrower and tend to be centered around the atomic levels ε_{sa} , ε_{pa} , ε_{sc} , and ε_{pc} , while the level ε_{pa} is moving below the level ε_{sc} (see Fig. 7.3b). Thus, the narrow bands around ε_{sa} and ε_{pa} become fully occupied, while the bands around ε_{sc} and ε_{pc} are empty. This means that the electrons have been transferred almost completely from the cation to the anion giving rise to an ionic insulator, which crystallizes in the NaCl or CsCl structures. Such a large a_p occurs usually in I–VII compounds such as NaCl or ClCl or LiF, etc. A diagram summarizes the discussion of this subsection (Fig. 7.4).

7.5 Holes

A fully occupied band is inert in the sense that its electronic contribution to the electrical current density, $\mathbf{j}$, and to the energy current density, $\mathbf{j}_E$, is zero. Indeed, for such a band, all $\mathbf{k}$ -points in the first BZ are occupied by two electrons; hence, the electronic concentration, f_k , in the combined $\mathbf{r}, \mathbf{k}$

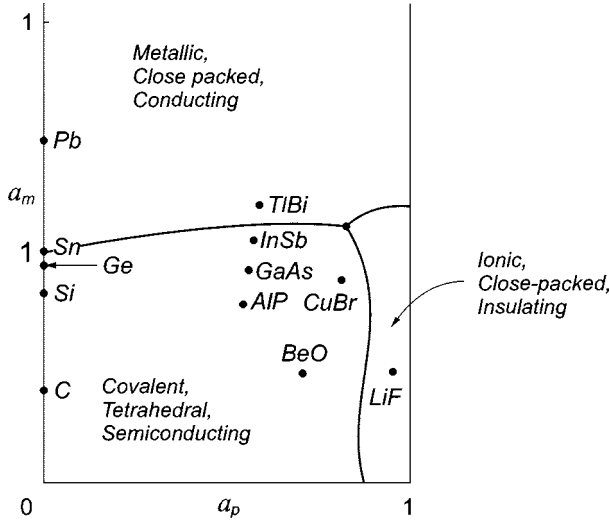


Fig. 7.4. Schematic “phase” diagram in the polarity, a_p , metallicity, a_m , plane showing the three different types of elemental solids or compounds produced by tetravalent (on the average) atoms (after Harrison, [SS76], p. 44)

space is necessarily $f_k = 2/V$ even in the presence of electrochemical and/or temperature gradients. As a result, we have for $\mathbf{j}$ and $\mathbf{j}_E$

$$\mathbf{j} = -|e| \sum_{\mathbf{k}} f_{\mathbf{k}} \mathbf{v}_{\mathbf{k}} = -2|e| \int_{BZ} \frac{d^3k}{(2\pi)^3} \mathbf{v}_{\mathbf{k}}, \quad (7.27)$$

$$\mathbf{j}_E = \sum_{\mathbf{k}} f_{\mathbf{k}} \varepsilon_{\mathbf{k}} \mathbf{v}_{\mathbf{k}} = 2 \int_{BZ} \frac{d^3k}{(2\pi)^3} \varepsilon_{\mathbf{k}} \mathbf{v}_{\mathbf{k}}. \quad (7.28)$$

In problem 7.6s, we show that these integrals are indeed zero. Hence, a fully occupied VB gives no contribution to the conductivity. It must be stressed that this zero contribution is not due to the electrons being trapped in the bond regions; on the contrary, the electrons in the VB of a semiconductor are as mobile as in the best of metals. What causes the zero conductivity is the inability of the electrons to readjust their state in response to the electric field; this is due to the absence of nearby empty states in combination with Pauli’s principle.

Let us now consider a band that is *almost* fully occupied. For such a band, the total electronic spin, $\mathbf{S}$, the total crystal momentum, $\mathbf{K}$, the electrical current-density, $\mathbf{j}$, and the electronic energy current-density, $\mathbf{j}_E$, are given by

$$\mathbf{S} = \sum_{\mathbf{k},s}^{(o)} \mathbf{s}_{\mathbf{k}} + \sum_{\mathbf{k},s}^{(e)} \mathbf{s}_{\mathbf{k}} - \sum_{\mathbf{k},s}^{(e)} \mathbf{s}_{\mathbf{k}} = - \sum_{\mathbf{k},s}^{(e)} \mathbf{s}_{\mathbf{k}}, \quad (7.29)$$

$$\mathbf{K} = \sum_{\mathbf{k},s}^{(o)} \mathbf{k} + \sum_{\mathbf{k},s}^{(e)} \mathbf{k} - \sum_{\mathbf{k},s}^{(e)} \mathbf{k} = - \sum_{\mathbf{k},s}^{(e)} \mathbf{k}, \quad (7.30)$$

$$\mathbf{j} = \frac{-|e|\hbar}{V} \sum_{\mathbf{k},s}^{(o)} \mathbf{v}_{\mathbf{k}} + \frac{-|e|\hbar}{V} \sum_{\mathbf{k},s}^{(e)} \mathbf{v}_{\mathbf{k}} - \frac{-|e|\hbar}{V} \sum_{\mathbf{k},s}^{(e)} \mathbf{v}_{\mathbf{k}} = \frac{|e|\hbar}{V} \sum_{\mathbf{k},s}^{(e)} \mathbf{v}_{\mathbf{k}}, \quad (7.31)$$

$$\mathbf{j}_E = \frac{1}{V} \sum_{\mathbf{k},s}^{(o)} \varepsilon_{\mathbf{k}} \mathbf{v}_{\mathbf{k}} + \frac{1}{V} \sum_{\mathbf{k},s}^{(e)} \varepsilon_{\mathbf{k}} \mathbf{v}_{\mathbf{k}} - \frac{1}{V} \sum_{\mathbf{k},s}^{(e)} \varepsilon_{\mathbf{k}} \mathbf{v}_{\mathbf{k}} = - \frac{1}{V} \sum_{\mathbf{k},s}^{(e)} \varepsilon_{\mathbf{k}} \mathbf{v}_{\mathbf{k}}. \quad (7.32)$$

In (7.29)–(7.32), the summation is not over all states $\mathbf{k}, s$, but only over the occupied states, a fact that is denoted by the symbol (o) over the summation sign. In these expressions, we have added and subtracted the summation over the empty states (denoted by the symbol (e) over the summation sign). Thus, we have the summation over all states (which gives zero) minus the summation over the empty states. Thus, we are left with the summations over the empty states of the quantities $-\mathbf{s}_{\mathbf{k}}, -\mathbf{k}, \mathbf{v}_{\mathbf{k}}, -\varepsilon_{\mathbf{k}} \mathbf{v}_{\mathbf{k}}$.

The final conclusion is that the quantities $\mathbf{S}, \mathbf{K}, \mathbf{j}$, and $\mathbf{j}_E$ can be obtained by introducing fictitious entities called *holes* (for obvious reasons, since the summation is over empty states) the properties of which are as follows:

$$e_h = |e|, \quad (7.33)$$

$$\mathbf{k}_h = -\mathbf{k}_e, \quad (7.34)$$

$$\mathbf{s}_h = -\mathbf{s}_e, \quad (7.35)$$

$$\mathbf{v}_h(\mathbf{k}_h) = \mathbf{v}_e(\mathbf{k}_e), \quad (7.36)$$

$$\varepsilon_h(\mathbf{k}_h) = -\varepsilon_e(\mathbf{k}_e). \quad (7.37)$$

In (7.33)–(7.37), the subscript h refers to holes and the subscript e refers to the missing electrons. Thus, the hole can be thought of as a particle of positive charge $|e|$, of velocity equal to the one that the missing electron would have, and of energy opposite to the one that the missing electron would have. In essence, the energy of the hole is the energy required for its creation, i.e., the energy needed to transfer an electron from the state $\mathbf{k}_e, s_e$ to the level chosen as the zero of energy.

7.6 Effective Masses and DOS

We have seen (in (6.22)) that in 1-D the effective mass is defined in terms of the second derivatives of the eigenenergy with respect to k . In 3-D, there is a direct generalization of this definition

$$(m^{-1})_{ij} \equiv \frac{\partial^2 E(\mathbf{k})}{\hbar^2 \partial k_i \partial k_j}, \quad (7.38)$$

Thus, the inverse of the effective mass is a symmetric tensor of rank two. With a proper orientation of the Cartesian axes at each point $\mathbf{k}$, the effective mass tensor at this point becomes diagonal

$$\frac{1}{m_i} = \frac{\partial^2 E(\mathbf{k})}{\hbar^2 \partial k_i^2}, \quad i, j, k \text{ along the principal axes} \quad (7.39)$$

Taking into account (7.34) and (7.37), we have for the effective mass of a hole

$$(m_h^{-1})_{ij} = \frac{\partial^2 \varepsilon_h(\mathbf{k}_h)}{\hbar^2 \partial k_{hj} \partial k_{hi}} = - \frac{\partial^2 \varepsilon_e(\mathbf{k}_e)}{\hbar^2 \partial k_{ej} \partial k_{ei}} = - (m_e^{-1})_{ij}, \quad (7.40)$$

$$\frac{1}{m_{hi}} = - \frac{1}{m_{ei}}, \quad i, j, k, \text{ along the principal axes} \quad (7.41)$$

Since the electronic effective mass at the top of the valence band (or at the top of any band) is negative, it follows that the hole effective mass at the top of the valence band is positive. This justifies the introduction of the hole concept as a convenient tool, since the almost-full valence band can then be described as being occupied by a few holes of positive effective mass at its top, instead of a huge number of electrons of negative effective mass.

Near the bottom of the conduction band (which we assume to be associated with a point $\mathbf{k}_o$ in the first BZ), we can expand the energy in a Taylor series:

$$\begin{aligned} \varepsilon(\mathbf{k}) &= \varepsilon(\mathbf{k}_o) + \frac{1}{2} \sum_{i=1}^3 \left(\frac{\partial^2 \varepsilon}{\partial k_i^2} \right)_{\mathbf{k}=\mathbf{k}_o} (k_i - k_{io})^2 + \\ &= \varepsilon_o + \sum_{i=1}^3 \frac{\hbar^2}{2m_i} (k_i - k_{io})^2, \quad \varepsilon_o \equiv \varepsilon(\mathbf{k}_o). \end{aligned} \quad (7.42)$$

In (7.42), there is no first-order term in $\mathbf{k} - \mathbf{k}_o$, since the expansion is around a minimum; the series was truncated after the second-order term; and (7.39) was used, assuming that the Cartesian axes at $\mathbf{k}_o$ were oriented along the principal axes at this point. If we set $\varepsilon(\mathbf{k})$, as given by (7.42), equal to E , we define a surface in 3-D $\mathbf{k}$ -space, the shape of which is an ellipsoid centered at $\mathbf{k}_o$, the main semiaxes being equal to $a_i = [2m_i(E - \varepsilon_o)/\hbar^2]^{1/2}$, $i=1, 2, 3$. The volume, V_k , enclosed by such an ellipsoid is equal to $V_k = (4\pi/3) a_1 a_2 a_3 = (8\sqrt{2}\pi/3\hbar^3) (m_1 m_2 m_3)^{1/2} (E - \varepsilon_o)^{3/2}$. Hence, according to the basic equation (4.11), the number of states (per spin) with $\varepsilon(\mathbf{k})$ less than E is given by

$$R(E) = \frac{V V_k}{(2\pi)^3} = \frac{\sqrt{2} V}{3\pi^2 \hbar^3} (m_1 m_2 m_3)^{1/2} (E - \varepsilon_o)^{3/2}, \quad E \rightarrow \varepsilon_o^+, \quad (7.43)$$

the DOS (per spin) is then

$$\rho(E) = \frac{dR}{dE} = \frac{\sqrt{2}V}{2\pi^2\hbar^3} (m_1 m_2 m_3)^{1/2} (E - \varepsilon_o)^{1/2}, \quad E \rightarrow \varepsilon_o^+. \quad (7.44)$$

If the minimum energy, ε_o , is g times degenerate, i.e., if there are g different points $\mathbf{k}_{oi}$ ($i = 1, 2, \dots, g$) satisfying (7.42), then both $R(E)$ and $\rho(E)$ must be multiplied by g (assuming that all g points have the same mass tensor). For example, for Si , $g = 6$ as we shall see later. Notice that the product $m_1 m_2 m_3$ equals the determinant of the tensor $M \equiv m_{ij}$ of the effective mass: $m_1 m_2 m_3 = \det(M)$. The latter expression remains invariant under rigid rotation of the Cartesian coordinate system.

Similar expression for the DOS are valid for the top, ε'_o , of the valence band:

$$\rho_v(E) = \frac{\sqrt{2}V}{2\pi^2\hbar^3} |m'_1 m'_2 m'_3|^{1/2} (\varepsilon'_o - E)^{1/2}, \quad (7.45)$$

or

$$\rho_h(E_h) = \frac{\sqrt{2}V}{2\pi^2\hbar^3} (m_{1h} m_{2h} m_{3h})^{1/2} (E_h - \varepsilon'_o)^{1/2}. \quad (7.46)$$

Actually, the DOS at the top of the valence band of a tetrahedral semiconductor consists of three terms like the ones shown in (7.46), since, as we have seen before, the top of the VB is threefold degenerate as a result of the decoupled p_x , p_y , p_z states which define the top of the VB (see (7.2)). If the top of the VB corresponds to $\mathbf{k} = 0$, as it is usually the case, cubic symmetry implies that the three masses along principal axes are equal, $m_{1h} = m_{2h} = m_{3h}$, for each one of the three degenerate branches at $\mathbf{k} = 0$. As we shall see in Sect. 11.8, the degeneracy is partly lifted, as a result of spin-orbit coupling giving rise to the so-called *split-off* branch with an effective hole mass denoted by m_{soh} . Among the other two branches, one has a small effective mass, called *light hole* mass, m_{lh} , and the other a larger effective mass, called *heavy hole* mass, m_{hh} . (See Fig. 7.7(c), p. 199; can you tell which is the split-off, the light hole, and the heavy hole branch along the line ΓK of this figure?)

7.7 Dielectric Function and Optical Absorption

In this section, we shall obtain a rough estimate of the static dielectric function $\varepsilon(0)$ for tetrahedral semiconductors by employing the Kramers–Kronig relation (A.53)

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\omega' \varepsilon_2(\omega') d\omega'}{\omega'^2 - \omega^2}. \quad (7.47)$$

We shall approximate the function $\varepsilon_2(\omega')$ by the simplest possible form

$$\varepsilon_2(\omega') = D\delta(\omega' - \omega_o). \quad (7.48)$$

The quantity $\hbar\omega_o$ can be estimated as the difference of the middle of the CB from the top of the VB:

$$\hbar\omega_o \simeq \frac{1}{2} \left(E'_g + \tilde{E}_{cu} \right), \quad (7.49)$$

where E'_g is the optical gap and $\tilde{E}_{cu} \equiv \tilde{E}'_{cu} - E_{vu}$ is the top of the CB measured from the top of the VB. For direct gap semiconductors $E'_g = E_g$, where, according to (7.9),

$$E_g = \sqrt{V_{3s}^2 + 16V_{ss\sigma}^2} + \sqrt{V_{3p}^2 + 16E_{xx}} - (\bar{\varepsilon}_p - \bar{\varepsilon}_s), \quad (7.50)$$

while for indirect gap semiconductors we take roughly $E'_g \simeq 2E_g$. The quantity $\tilde{E}_{cu}$ is given by combining (7.8) and (7.5)

$$\tilde{E}_{cu} = \sqrt{V_{3p}^2 + 16E_{xy}^2} + \sqrt{V_{3p}^2 + 16E_{xx}^2}, \quad (7.51)$$

The constant prefactor D in (7.48) can be obtained by considering the case of $\omega^2 \gg \omega_o^2$ in (7.47). For such high frequencies, all the four valence electrons behave as free, and hence, $\varepsilon_1(\omega)$ behaves as in the JM, i.e., $\varepsilon_1(\omega) = 1 - (\omega_p^2/\omega^2)$; on the other hand, in this limit, ω'^2 in (7.47) can be omitted in front of ω^2 . Hence, we have, taking into account (7.48), that

$$\varepsilon_1(\omega) \rightarrow 1 - \frac{2D\omega_o}{\pi\omega^2}, \text{ as } \omega \rightarrow \infty. \quad (7.52)$$

Comparing this with $\varepsilon_1(\omega) \rightarrow 1 - (\omega_p^2/\omega^2)$ for $\omega \rightarrow \infty$, we obtain

$$\frac{2D\omega_o}{\pi} = \omega_p^2. \quad (7.53)$$

Substituting (7.53) and (7.48) in (7.47), we obtain our final very approximate formula for $\varepsilon_1(0)$:

$$\varepsilon_1(0) \simeq 1 + \frac{\omega_p^2}{\omega_o^2}. \quad (7.54)$$

It must be stressed that the actual $\varepsilon_2(\omega)$ is different from the simple formula (7.48), which, however, allows easy integration and gives finite result even if $E'_g \rightarrow 0$.

In Fig. 7.5, we plot the actual imaginary part of the dielectric function, $\varepsilon_2(\omega)$, and the one based on (7.48), (7.53), and (7.49). In Table 7.1, we calculate $\varepsilon_1(0)$ according to these simplistic formulae for four semiconductors: Si, Ge, Sn, and GaAs. The quantity $\omega_p^2 = 4\pi e^2 n/m$ is given by (5.27), where $\bar{r}_s$ is related to $\bar{d}$ as follows: $\bar{r}_s = 0.4513\bar{d}$.

The quantities E'_g and $\tilde{E}_{cu}$ are obtained from (7.50), (7.51), and (7.4) to (7.8). The results are shown in Table 7.1.

7.8 Effective Hamiltonian

As we have seen in Sect. 7.6, the concept of the effective mass is very useful because it allows us to obtain the electronic DOS near the band edges simply by replacing the electronic mass by the effective mass.⁴ However, the effective

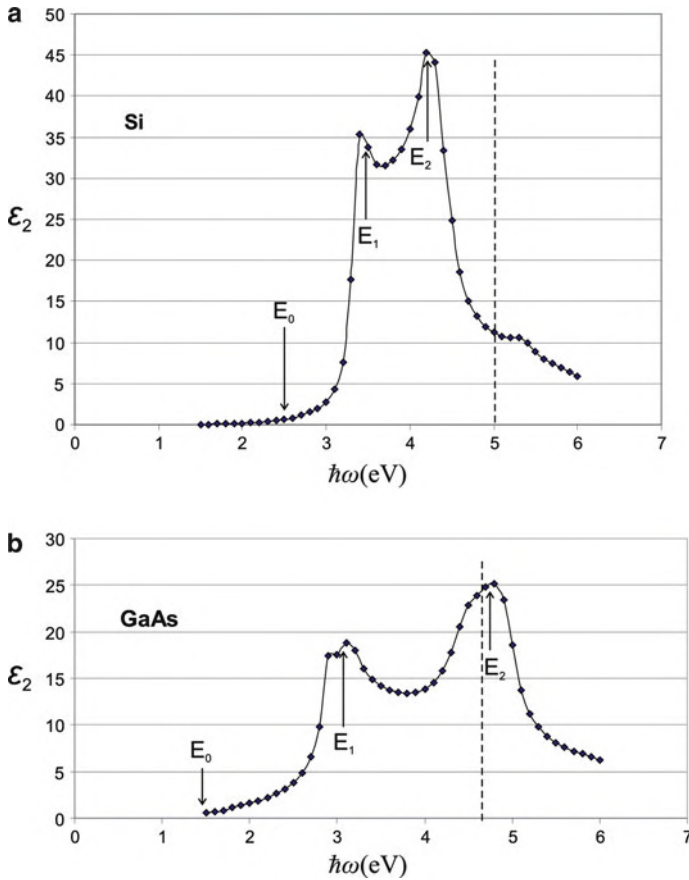


Fig. 7.5. Plot of the imaginary part ϵ_2 of the dielectric function vs. frequency for two semiconductors: (a) Si (see [D3], p. 21) and (b) GaAs (based on [D3], p. 108). *Solid lines* are experimental results. *Dash lines* are the simplistic formulae (7.48), (7.49). Remember that the absorption coefficient α' is equal to $\omega\epsilon_2/cn_1$ (in G-CGS), where n_1 is the real part of the index of refraction. Silicon is an indirect-gap semiconductor; thus $E'_g \simeq 2.5$ eV is larger than the indirect gap $E_g = 1.17$ eV. GaAs is a direct-gap semiconductor; thus $E'_g \simeq E_g = 1.52$ eV

mass concept shows its full power in the very common and important case where there are deviations from the periodic crystal potential due to unavoidable impurities and defects or to the presence of external electromagnetic fields. In those cases, the electronic Hamiltonian $\hat{H}$ has the form

$$\hat{H} = \hat{H}_0 + \hat{H}_1, \quad (7.55)$$

⁴ If the effective mass is anisotropic, m must be replaced by $m^* = (m_1, m_2, m_3)^{1/3}$.

Table 7.1. Bond length $\bar{d}$, plasma frequency ω_p , optical gap E'_g , CB top $\tilde{E}_{cu}$, “average” optical absorption frequency ω_o , and static dielectric constant $\varepsilon_1(0)$ for four semiconductors

	<i>Si</i>	<i>Ge</i>	<i>Sn</i>	<i>GaAs</i>
$\bar{d}$	4.44	4.63	5.31	4.36
$\hbar\omega_p$ (eV)	16.61	15.6	12.71	15.6
E'_g (eV)	$\simeq 3$	$\simeq 1$	$\simeq 0.1$	$\simeq 2$
$\tilde{E}_{cu}$ (eV)	7	6.46	4.9	7.4
$\hbar\omega_o$ (eV)	5	3.73	2.5	4.7
$\varepsilon_1(0)$, (7.54)	12	17.5	26.8	12
$\varepsilon_1(0)$, <i>exp.</i>	12.1	16.2	24	12.4

where $\hat{H}_o$ is the periodic crystal potential plus the kinetic energy $\hat{p}^2/2m$ of the electron, and $\hat{H}_1$ is the non-periodic perturbation due to impurities, defects, etc. If $\hat{H}_1$ is such that it produces negligible transitions from a given band to any other band, and if the band structure is of the form $\varepsilon(\mathbf{k}) = \varepsilon_o + \hbar^2 \mathbf{k}^2/2m^*$, then

$$\hat{H} \simeq \hat{H}_e, \quad (7.56)$$

where

$$\hat{H}_e = -\frac{\hbar^2}{2m^*} \nabla^2 + \hat{H}_1 + \varepsilon_o. \quad (7.57)$$

Equations (7.56) and (7.57) are valid only for those eigenfunctions of $\hat{H}_e$ for which their extent is much larger than the lattice constant; these equations mean that the periodic Hamiltonian $\hat{H}_o$ can be replaced, under the said conditions, by an almost-equivalent free electron Hamiltonian the mass of which is the effective mass,⁵ m^* . The analytical and calculational advantages of using (7.57) instead of (7.55) are quite obvious.

7.9 Impurity Levels

7.9.1 Impurity Levels: The General Picture

As we shall see in a later chapter, if the perturbing nonperiodic potential $\hat{H}_1$ is local and attractive, it deforms the local unperturbed DOS by increasing it near the lower edge of each band (and by decreasing it near the upper edge).

⁵ If the band structure is of the more general form $\varepsilon(\mathbf{k}) = \varepsilon_o + (\hbar^2 k_1^2/2m_1) + (\hbar^2 k_2^2/2m_2) + (\hbar^2 k_3^2/2m_3)$, then the effective hamiltonian is written as $\hat{H}_e = -\frac{\hbar^2}{2} \left(\frac{1}{m_1} \frac{\partial^2}{\partial x_1^2} + \frac{1}{m_2} \frac{\partial^2}{\partial x_2^2} + \frac{1}{m_3} \frac{\partial^2}{\partial x_3^2} \right) + \hat{H}_1 + \varepsilon_o$; in what follows, we shall assume for simplicity a form as in (7.57) with $m^* = (m_1 m_2 m_3)^{1/3}$.

As the strength of this local attractive potential exceeds a critical, band-dependent, value, a level is pulled down out of the band and into the gap below it; the corresponding eigenstate is bound in the vicinity of the local potential $\hat{H}_1$. As the strength of the local potential increases further, the bound level moves away from the band edge and the corresponding state becomes more localized. Impurity levels located well within the interior of the gap are called *deep levels*; they may be detrimental to the function of semiconducting devices, since they act as electron–hole recombination centers. If the local potential $\hat{H}_1$ is repulsive, the local DOS at each band is deformed so as to enhance its values near the upper band edge (at the expense of the values near the lower band edge); as the strength of this repulsive potential exceeds a critical, band-dependent, value, a level is pushed up out of the band and into the gap above it. Thus, in the presence of gaps, a repulsive potential may sustain bound eigenstates!

7.9.2 Impurity Levels: Doping

An important consequence of the preceding comments is the possibility of controlling the levels in the gap by introducing appropriate impurities. This is of crucial importance for semiconductor devices, such as diodes, solar cells, transistors, integrated circuits, etc., i.e., of crucial importance for our technological civilization. Of particular interest are substitutional impurities the valence ζ_i of which is equal to $\zeta_o \pm 1$, where ζ_o is the valence of the host atoms. If $\zeta_i = \zeta_o + 1$, the impurity is called *n-type* or *donor*, because out of its ζ_i electrons the ζ_o participate in the bonding, while the extra one is free to be donated to the CB by thermal excitation (see Sect. 7.10 below); thus, this substitution provides an extra electron to the CB (besides the ζ_o given for the bonding), i.e., an extra negative carrier; If $\zeta_i = \zeta_o - 1$ the impurity is called *p-type* or *acceptor*, because it accepts through thermal excitation an electron from the VB in order to complete the number required for the bonding. Thus, a hole is created, i.e., a positively charged particle, in the VB. In Table 7.2, we

Table 7.2. Host atoms and n-type (donor) and p-type (acceptor) substitutional impurities in various semiconductors

Impurities \ Host	Si	Ge	GaAs	
			Ga	As
n-type, donors	P, As, Sb, Bi	P, As, Sb, Bi	Si, Ge	S, Se
p-type, acceptors	B, Al, Ga, In, Tl	B, Al, Ga, In, Tl	Be, Mg, Zn, Cd, Mn ⁶	Si, Ge

⁶ Mn is important as a dopant in connection with the diluted magnetic semiconductors (DMS, see sect. 20.6)

give a list of n-type and p-type impurities in various host material. The process of introducing n-type (donors) or p-type (acceptors) impurities is called *doping* and the semiconductors with such dopants are called *doped* or *extrinsic* (see next section).

An n-type substitutional impurity attracts the extra electron (the one not tetrahedrally bonded) by a potential of the form

$$\hat{H}_1 = -\frac{e^2}{4\pi\epsilon_0\epsilon_1 r}, \quad (7.58)$$

where r is the distance between the impurity ion and the extra electron and ϵ_1 is the static dielectric function⁷ of the host material. Combining (7.57) and (7.58), we see that the problem has been reduced to that of the hydrogen atom with the replacements

$$m_e \rightarrow m_c^*, \quad e^2 \rightarrow e^2/\epsilon_1, \quad \epsilon_o = E_g, \quad (7.59)$$

where m_c^* is a properly averaged effective electronic mass at the bottom of the CB and E_g is the energy at the bottom of the CB (The top of the VB is chosen as the zero of energy). Hence,

$$a_B \rightarrow a_B^* = \frac{\hbar^2}{m_c^* (e^2/4\pi\epsilon_0\epsilon_1)} = a_B \frac{m_e}{m_c^*} \epsilon_1, \quad (7.60)$$

$$E_n \rightarrow E_n^* = E_g - \frac{1}{2n^2} \frac{e^2}{4\pi\epsilon_0\epsilon_1 a_B^*} = E_g - E_n \frac{m_c^*}{m_e \epsilon_1}, \quad (7.61)$$

Thus, the ground state binding energy $\epsilon_d \equiv E_g - E_1^* = 13.6 m_c^*/m_e \epsilon_1^2$ eV. For the results (7.60) and (7.61) to be even approximately valid, the effective Bohr radius a_B^* must be much larger than the lattice constant a : $a_B^* \gg a$. In Table 7.3, we compare the theoretical results (7.60) and (7.61) with experimental data and with theoretical results which are based on the full tensor expression of the effective mass (For *Si* $m_1 = m_2 = 0.1905 m_e$, $m_3 = 0.9163 m_e$, for *Ge* $m_1 = m_2 = 0.0807 m_e$, $m_3 = 1.57 m_e$, for *GaAs* $m_1 = m_2 = m_3 = 0.067 m_e$. See Table 7.5 at the end of this chapter).

We see from Table 7.3 that the best agreement with the experimental data was obtained for GaAs and the worst for Si. This is to be expected, since a_B^* for GaAs is 97.9 Å, indeed much larger than its lattice constant a , which is equal to 5.65 Å, while for Si a_B^* is only 19.9 Å not much larger than its lattice constant $a = 5.43$ Å. In all cases, the experimental values of ϵ_d is larger than the more accurate theoretical value (last column in Table 7.3); this too is to be expected, since in all cases the electron spends some time (which ranges from substantial in the case of Si to minute in the case of GaAs) very near the impurity where it feels almost the bare Coulomb potential $-e^2/4\pi\epsilon_0 r$ rather than the screened one $-e^2/4\pi\epsilon_0\epsilon_1 r$.

⁷ The employment of the static dielectric function is justified only if the average distance, r , is much larger than the interatomic distance, d , or the lattice constant, a .

Table 7.3. Experimental data and theoretical results for the ground state binding energy ε_d for n-type impurities in three commonly used semiconductors

Host		Exp. for various impurities				Theory (7.60, 7.61)	Theory, full tensor mass
		P	As	Sb	Bi		
Si	ε_d (meV)	45.58	47	42.77	71	29.9	29.8
	a_B^* (Å)	—	—	—	—	19.9	—
Ge	ε_d (meV)	12.89	14.17	10.29	12.81	11.25	9.81
	a_B^* (Å)	—	—	—	—	39.5	—
GaAs	ε_d (meV)	Si in Ga	Ge in Ga	S in As	Se in As	5.93	5.715
		5.839	5.882	6.87	5.789		
	a_B^* (Å)	—	—	—	—	97.9	—
Theoretical results for the effective Bohr radius a_B^* are also shown [$m_c^* = (m_1 m_2 m_3)^{1/3}$]							

For p-type impurities, which push up states out of the VB and into the gap, we can treat the problem either in terms of electrons, or equivalently, in terms of holes. Let us use the electron language. The impurity ion has now a proton less and thus it creates a minus e charge. Hence, an electron feels a potential $\hat{H}_1$ of the form

$$\hat{H}_1 = \frac{e^2}{4\pi\varepsilon_0\varepsilon_1 r} \quad (7.62)$$

and its effective Hamiltonian in its simplest version is as follows

$$\hat{H}_e = -\frac{\hbar^2}{2m_e^*} \nabla^2 + \frac{e^2}{4\pi\varepsilon_0\varepsilon_1 r},$$

where $m_e^* = -m_h$ is a negative number. Hence, Schrödinger's equation $\hat{H}_e\psi = E\psi$ multiplied by -1 , becomes

$$-\frac{\hbar^2}{2m_h} \nabla^2 \psi - \frac{e^2}{4\pi\varepsilon_0\varepsilon_1 r} \psi = -E\psi, \quad (7.63)$$

where m_h is the positive effective hole mass. Notice that if we had used the hole language, we would have obtained (7.63) with $-E$ replaced by E_h . Equation (7.63) becomes equivalent to the hydrogen atom case with the following replacements:

$$m_e \rightarrow m_h, \quad e^2 \rightarrow e^2/\varepsilon_1, \quad (7.64)$$

$$a_B \rightarrow a_B^* = \frac{m_e \varepsilon_1}{m_h} a_B, \quad (7.65)$$

$$E_n \rightarrow E_n^* = -\frac{m_h}{\varepsilon_1^2 m_e} E_n = |E_n| \frac{m_h}{m_e \varepsilon_1^2}, \quad (7.66)$$

The problem in applying the simple formulae (7.64)–(7.66) is that there are three different effective hole masses near the top of the VB, because there are

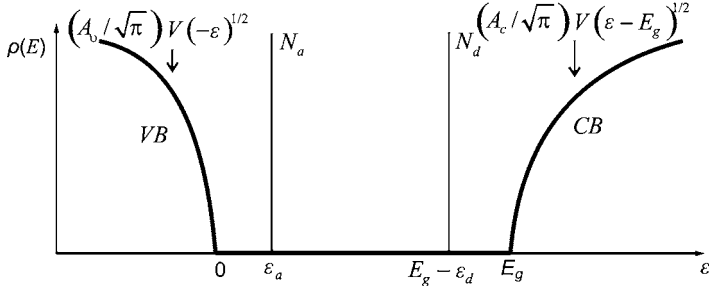


Fig. 7.6. DOS for a doped semiconductor with both acceptor and donor impurities, the levels of which are at ε_a and $E_g - \varepsilon_d$ respectively. N_a , N_d are their respective concentrations. The constants A_c and A_v for the CB and the VB DOS are: $A_j = (\sqrt{2}/2) (m_j/\pi\hbar^2)^{3/2}$, $j = c, v$, where $m_c^{3/2}$ is equal to $g_c (m_{c1}m_{c2}m_{c3})^{1/2}$ and g_c is the degeneracy for the CB, while $m_v^{3/2} \simeq m_{hh}^{3/2} + m_{soh}^{3/2} + m_{lh}^{3/2}$ for the VB

Table 7.4. Experimental data and theoretical results for the ground state binding energy, ε_a (in meV) for p-type impurities in three commonly used semiconductors (see [D3])

Host	B	Al	Exp. for various impurities	Ga	In	Tl	Theory, (7.66)	Theory, more accurate
Si	44.4	69		72.7	155.6	246	37.8	—
Ge	10.8	11.15		11.32	11.99	13.45	11.4	11.2
GaAs	Si in As	Ge in As	Sn in As	C in As	Mg in Ga	30.24	25.82	
	34.8	40.4	170.5	26.9	28.7			

three almost-degenerate branches at $\mathbf{k} = 0$ (see Sect. 7.11, and in particular, Fig. 7.7 later in this chapter): the heavy hole mass, m_{hh} , the light hole mass, m_{lh} , and the split-off hole mass, m_{soh} . The ground state is expected to be dominated by the heaviest mass; we have chosen for m_h in (7.64)–(7.66) the combination $m_h^{3/2} \simeq m_{hh}^{3/2} + m_{soh}^{3/2} + m_{lh}^{3/2}$. With this choice, we have the theoretical results shown in Table 7.4, which contains also the experimental data for $E_1^* \equiv \varepsilon_a$. The theoretical values of a_B^* according to (7.65) are 15.7 Å, 39 Å, 19.2 Å and for Si, Ge, and GaAs, respectively.

7.10 Concentration of Electrons and Holes at Temperature T

The great importance of the donor or acceptor impurities stems from their potential to control dramatically the concentration of carriers (of electrons in the CB and of holes in the VB), and consequently, the conductivity of the semiconductors. In this section, we shall demonstrate this point.

In Fig. 7.6, we plot schematically the DOS in and around the gap in a doped semiconductor with both p-type (or acceptor) and n-type (or donor) substitutional impurities.

Let us assume that the concentration of acceptor impurities N_a is larger than the concentration of donor atoms N_d . Then, at the absolute zero temperature, all electrons from the donor atoms would go to the lower acceptor level; as a result, the number of holes at ε_a (per unit volume) would be equal to $N_a - N_d$, the number of holes at the VB would be zero and the number of electrons at the level $E_g - \varepsilon_d$ and at the CB would be zero. At a nonzero temperature, let p , p_a be the number of holes per unit volume at the VB and the acceptor level respectively, and n_d and n be the number of electrons per unit volume at the donor level and the CB respectively. Obviously, the number of electrons is equal to the number of additional holes (beyond those, $N_a - N_d$, already existing at $T = 0$ K).

Hence

$$n + n_d = p + p_a - (N_a - N_d). \quad (7.67)$$

The readers may convince themselves that (7.67) remains valid in the opposite case where N_d is larger than N_a .

The concentration of electrons in the CB $n = N/V$ is given by (C.45)

$$n = \frac{2}{V} \int_{E_g}^{\infty} \frac{d\varepsilon \rho_c(\varepsilon)}{e^{\beta(\varepsilon - \mu)} + 1}. \quad (7.68)$$

The concentration of holes in the VB is, taking into account (C.45),

$$p = \frac{2}{V} \int_{-\infty}^0 d\varepsilon \rho_v(\varepsilon) \left[1 - \frac{1}{e^{\beta(\varepsilon - \mu)} + 1} \right] = \frac{2}{V} \int_{-\infty}^0 d\varepsilon \rho_v(\varepsilon) \frac{1}{e^{-\beta(\varepsilon - \mu)} + 1}. \quad (7.69)$$

Usually, but not always,⁸ $\beta(E_g - \mu) \gg 1$ and $\beta\mu \gg 1$, where $\beta = 1/k_B T$. Under these circumstances, the Fermi distributions are reduced to the Boltzmann's distributions by omitting the 1 in the denominators. Then, given the DOS shown in Fig. 7.6, the integrals in (7.68) and (7.69) can be performed analytically with the following results:

$$n = A_c (k_B T)^{3/2} e^{-\beta(E_g - \mu)}, \quad (7.70)$$

$$p = A_v (k_B T)^{3/2} e^{-\beta\mu}, \quad (7.71)$$

where $A_c = (\sqrt{2}/2)(m_c/\pi\hbar^2)^{3/2}$ and $A_v = (\sqrt{2}/2)(m_v/\pi\hbar^2)^{3/2}$. The product np is independent of μ and is given by

$$np = A_c A_v (k_B T)^3 e^{-\beta E_g}. \quad (7.72)$$

⁸ If these inequalities are violated, the semiconductor is called *degenerate*.

7.10.1 Intrinsic case

This is the case where the concentrations N_d and N_a of both donor and acceptor impurities are negligible (which means that $N_d \ll \sqrt{np}$ and $N_a \ll \sqrt{np}$). Then, (7.67) implies that $n = p$, which in combination with (7.72) gives the *intrinsic concentration*, n_i and p_i of electrons in the CB and holes in the VB

$$n_i = p_i = (A_c A_v)^{1/2} (k_B T)^{3/2} e^{-\beta E_g/2}. \quad (7.73)$$

Notice that the exponent in (7.73) is $E_g/2k_B T$ and not $E_g/k_B T$. If we choose the product $(m_c m_v / m_e^2)^{3/4}$ to be equal to one, we have for the intrinsic concentrations

$$n_i = p_i = 4.84 \times 10^{15} T^{3/2} \exp[-5802 E_g/T] \text{ cm}^{-3}, \quad (7.74)$$

where T is in degrees Kelvin and E_g in eV. The chemical potential μ_i for the intrinsic case is obtained by equating (7.71) with (7.73)

$$\mu_i = \frac{E_g}{2} + \frac{3k_B T}{4} \ln \frac{m_v}{m_c} \rightarrow \frac{E_g}{2}, T \rightarrow 0 \text{ K}. \quad (7.75)$$

7.10.2 Extrinsic case

This is the case where the concentration N_d or N_a of either donor or acceptor impurities or both is much larger than the intrinsic concentration. If $N_d = N_a$, the doped semiconductor is called *compensated*. If the chemical potential happens to be in between the acceptor and the donor levels but several times $k_B T$ away from both, then $n_d \ll N_d$ and $p_a \ll N_a$ so that, for uncompensated samples, $|n_d - p_a| \ll |N_d - N_a|$. In this case, (7.67) becomes

$$n - p \simeq N_d - N_a \equiv \delta N. \quad (7.76)$$

Knowing both the difference $n - p = \delta N$ and the product np (see (7.72)), we obtain both n and p

$$n \simeq \frac{1}{2} \left[(\delta N^2 + 4n_i^2)^{1/2} + \delta N \right], \quad (7.77)$$

$$p \simeq \frac{1}{2} \left[(\delta N^2 + 4n_i^2)^{1/2} - \delta N \right]. \quad (7.78)$$

As it was mentioned before, for (7.77) and (7.78) to be valid, we must have $E_g - \varepsilon_d - \mu \gg k_B T$ and $\mu - \varepsilon_a \gg k_B T$; thus, we have to calculate μ to see whether these inequalities are indeed satisfied. If in (7.70) and (7.71) we replace μ by μ_i , we shall obtain n_i and p_i respectively. Hence,

$$\frac{n}{n_i} = e^{\beta(\mu - \mu_i)} \text{ and } \frac{p}{p_i} = e^{-\beta(\mu - \mu_i)},$$

or

$$e^{\beta(\mu-\mu_i)} - e^{-\beta(\mu-\mu_i)} = 2 \sinh \beta(\mu - \mu_i) = \frac{n-p}{n_i} \simeq \frac{\delta N}{n_i},$$

or

$$\mu = \mu_i + k_B T \sinh^{-1} \frac{\delta N}{2n_i}. \quad (7.79)$$

If μ , as calculated by (7.79), does not satisfy the inequalities $\mu - \varepsilon_a \gg k_B T$ and $E_g - \varepsilon_d - \mu \gg k_B T$, use this μ in (7.70) and (7.71) to obtain approximately n and p .

Problem 7.11 For Si and for $T = 295$ K calculate:

- The intrinsic concentration n_i .
- The chemical potential, μ_i , for the intrinsic case.
- The *mobility*, μ_c , for electrons in the CB. (The mobility, μ_c , is by definition equal to $e\tau/m^*$, where $\tau = \ell/v_{th}$, $v_{th} \simeq (3k_B T/m^*)^{1/2}$ and $\ell \simeq 530$ Å (for Si at $T = 295$ K)).
- The resistivity, ρ , in the intrinsic case ($\rho_e = \sigma^{-1}$, $\sigma = en\mu_e + ep\mu_h$) (the hole mobility in Si is $\mu_h \simeq 0.36 \mu_e$)
- The resistivity of Si doped with P atoms of concentration $n_P = 10^{-6} n_{Si}$, where n_{Si} is the concentration of Si atoms (*Hint*: Use the approximate formula (7.77), but check whether the inequality $E_g - \varepsilon_d - \mu \gg k_B T$ is valid or not).

7.11 Band Structure and Electronic DOS

Following the approach of Sect. 6.5 (see in particular (6.47)–(6.49)), one could determine the electronic eigenfunctions and eigenenergies of tetrahedral semiconductors. Since there are two atoms in the primitive cell and four orbitals per atom, we have eight orbitals per primitive cell. Hence, one must diagonalize an 8×8 matrix, the elements of which are given by (6.49); each such matrix element is a sum of four terms associated with the four nearest neighbors of each atom. We shall not attempt such a calculation at this stage (see problem (7.1s) at the end of this chapter). We only point out that the end result for the band structure, $E_i(\mathbf{k})$ ($i = 1, 2, 3, \dots, 8$) will be eight branches, four in the VB and four in the CB.

The usual way to present graphically the band structure is to plot all the branches as $\mathbf{k}$ changes along some high symmetry straight segments of the first Brillouin zone. In Fig. 7.7, we show such a plot obtained through a sophisticated and accurate calculational method (see [7.1]). There are a few points in the plots of Fig. 7.7 worth drawing attention to:

The top of the VB is, to a very good approximation, at the Γ point (i.e., at $\mathbf{k} = 0$), where three p -type branches become almost degenerate. This generalizes in 3-D the result of Sect. 6.7 according to which the top of the VB is predominantly p -type, whereas the bottom of the CB is predominantly

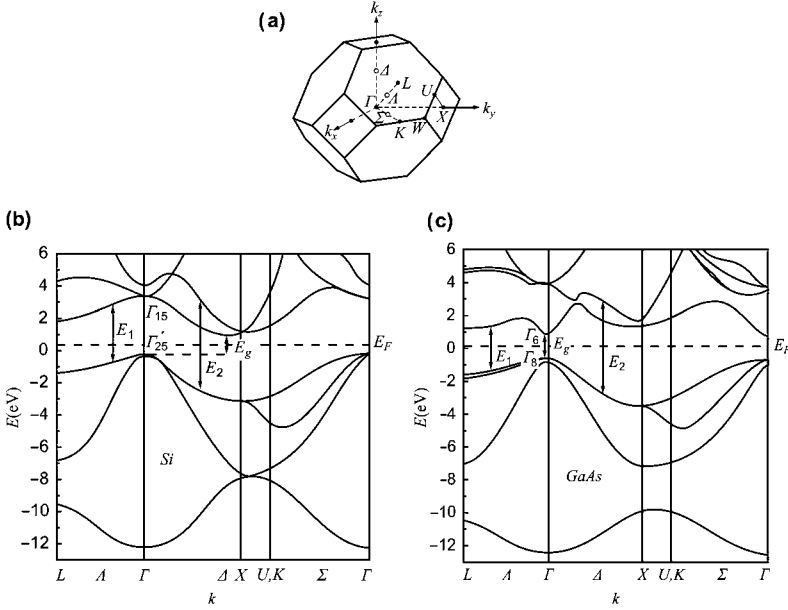


Fig. 7.7. Plot of the eight branches of the band structure, $E_i(\mathbf{k})$, ($i = 1, 2, \dots, 8$), as $\mathbf{k}$ is varied along specific straight segments of the first BZ shown in (a) above (The Bravais lattice for Si(b) and GaAs (c), as for most semiconductors, is fcc). For high symmetry direction (e.g., ΓL and ΓX for Si and ΓX for GaAs) two branches are degenerate. The optical transitions between the almost parallel branches in the VB and the CB are responsible for the peaks E_1 , E_2 shown in Fig. 7.5

s -type, and hence, nondegenerate. This is more pronounced in GaAs, where the bottom of the CB occurs at the Γ point ($\mathbf{k} = 0$) so that GaAs is a direct gap semiconductor. For Si the lowest energy of the CB occurs not at the point $\mathbf{k} = 0$, but at the two points $(0, 0, \pm 0.8(\Gamma X))$ as well as at four other equivalent points along the axes k_x and k_y . Thus, Si is an indirect gap semiconductor. Notice that:

- Almost-parallel branches between the VB and the CB lead to many photon-induced transitions of almost-equal frequencies and hence to peaks in the absorption coefficient (compare the peaks in Fig. 7.5 with the vertical transitions in Fig. 7.7)
- In (4.16), we have expressed the electronic DOS of the JM in terms of the area of the surface $S(E)$ of constant energy E and the velocity at E . This formula,

$$\rho(E) = \frac{V}{(2\pi)^3} \frac{S(E)}{\hbar v(E)} \quad (7.80)$$

has been extended to each branch n of the general band structure case in (4.17):

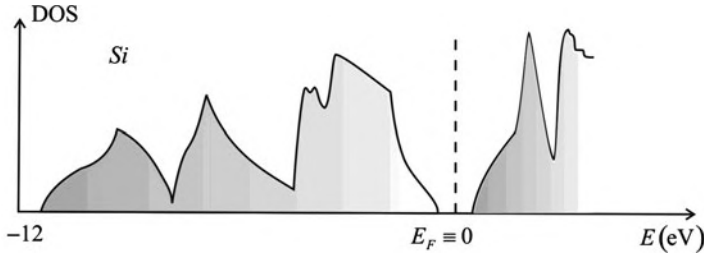


Fig. 7.8. Schematic plot of the electronic DOS vs. energy for Si

$$\rho_n(E) = \frac{V}{(2\pi)^3} \int \frac{dS_{\mathbf{k},n}}{\hbar v_n(\mathbf{k})}, \quad \rho(E) = \sum_n \rho_n(E), \quad (7.81)$$

where the integration is over the $\mathbf{k}$ -space surface $E_n(\mathbf{k}) = E$, $dS_{\mathbf{k},n}$ is the infinitesimal area of this surface, and $\hbar v_n = |\nabla E_n(\mathbf{k})|$. Relatively flat branches, for which $\hbar v_n$ is very small, produce large values in the DOS. Thus, it is not unusual to obtain a rough sketch of the DOS by simple inspection of the band structure plots. For example, the gross features of the *Si* electronic DOS shown in Fig. 7.8 could have been guessed from Fig. 7.7b.

7.12 Eigenfrequencies, Phononic DOS, and Dielectric Function at the Infrared

We have seen in Chap. 6 that the 1-D model with one atom per primitive cell produced one branch of acoustic collective atomic vibrations; in the case of two atoms per primitive cell besides the acoustic collective atomic vibrations, an optical branch appeared (see Fig. 6.11). In the three-dimensional case with one atom per primitive cell, we expect to have three acoustic branches, one, which in the long wavelength limit is expected to approach the longitudinal mode of the continuum and two others, which in the same limit would approach the two transverse acoustic waves of the continuum. The first branch is called longitudinal acoustic (LA) and the other two transverse acoustic (TA). If there are two atoms per primitive cell, we expect to have in addition to the three acoustic branches another three optical branches, one predominantly longitudinal called longitudinal optical (LO) and two predominantly transverse called transverse optical (TO) modes. In the long-wavelength limit, the optical modes correspond to the two sublattices moving as rigid bodies against each other, producing thus the highest eigenfrequencies. These expectations are supported by detailed theoretical results and experimental data shown in Figs. 7.9 and 7.10 for Si and GaAs respectively.

Notice a significant difference between Si and GaAs: For Si, all the three optic branches are degenerate at the Γ point ($\mathbf{q} = 0$); this feature stems from the fully homopolar nature of the bond. For GaAs, as a result of the partly

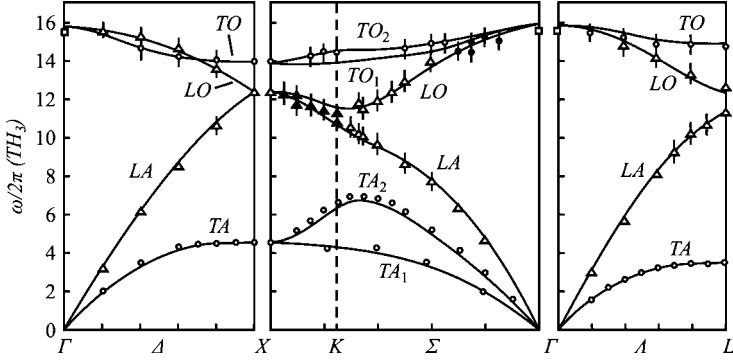


Fig. 7.9. Phonon dispersion relations, $\nu \equiv \omega/2\pi$ vs. the wavevector q for Si. Experimental points from neutron inelastic scattering. [D3], p. 16

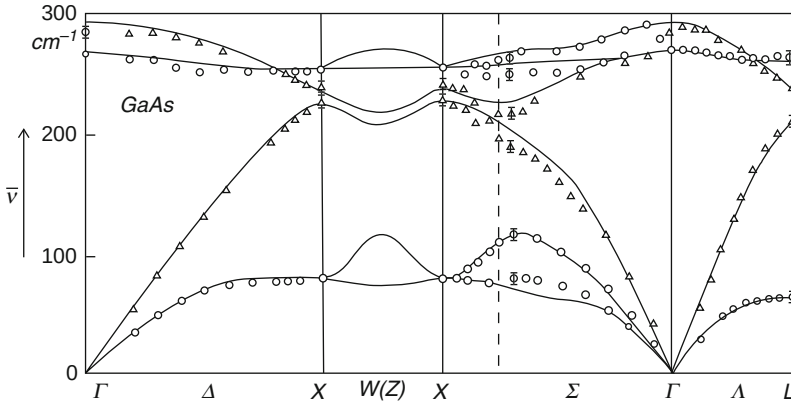


Fig. 7.10. Phonon dispersion relations $\bar{\nu} \equiv \omega/2\pi c$ vs. the wavevector q for GaAs (where c is the velocity of light in vacuum). Experimental points from neutron inelastic scattering. ([D3], p. 104)

ionic character of the bond, the LO mode sets up long-range charge oscillations, which increase the restoring force; thus, the LO mode has a higher frequency than the TO modes at the Γ point ($\mathbf{q} = 0$).

The phononic DOS is given by a similar analytical expression as the electronic DOS (see (7.81)), since the number of states in a volume element d^3k (or d^3q) is $Vd^3k/(2\pi)^3$ (or $Vd^3q/(2\pi)^3$) for both:

$$\tilde{\phi}_s(\omega) = \frac{V}{(2\pi)^3} \int \frac{dS_{\mathbf{q},s}}{v_s(\mathbf{q})}, \quad \tilde{\phi}(\omega) = \sum_s \tilde{\phi}_s(\omega), \quad (7.82)$$

where the integration is over the $\mathbf{q}$ -space surface $\omega_s(\mathbf{q}) = \omega$, $dS_{\mathbf{q},s}$ is the infinitesimal area of this surface, and $\mathbf{v}_s(\mathbf{q}) = \partial\omega_s/\partial\mathbf{q}$ is the group velocity.

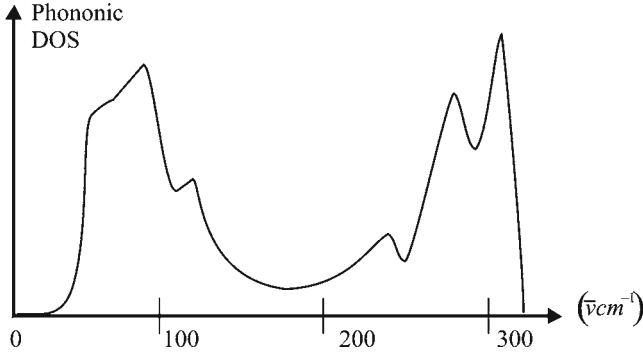


Fig. 7.11. Rough schematic plot of the total phononic DOS $\tilde{\phi}(\bar{\nu})$, vs. $\bar{\nu} = \omega/2\pi c$ for GaAs

Following the same argument that explained the shape of the electronic DOS for Si, we give a rough schematic guess for the phononic DOS in GaAs, taking into account Fig. 7.10.

For semiconductors or insulators *with a nonzero ionic component* in their bonding, there are transverse optic modes that can absorb a photon, and consequently, can produce a sharp peak in the absorption coefficient. This peak appears at a frequency $\omega_{\text{TO}}(q)$, where $q = \omega_{\text{TO}}/c$ and c is the velocity of light (see Fig. 6.11). Typical value of this q is about five to six orders of magnitude smaller than the linear extent of the first BZ; thus, for all practical purposes the peak would appear at the value of ω_{TO} corresponding to Γ point (Fig. 7.10).

Hence, near the frequency ω_{TO} , we expect the dielectric function of ionic semiconductors or insulators to have the form

$$\varepsilon(\omega) = A - \frac{B}{\omega^2 - \omega_{\text{TO}}^2 + i\omega/\tau_{\text{TO}}}, \quad (7.83)$$

since at a transverse collective eigenfrequency ω_{TO} , the dielectric function must blow up (at the limit of $\tau_{\text{TO}} \rightarrow \infty$). On the other hand, at a longitudinal collective eigenfrequency, such as ω_{LO} , the dielectric function must be zero (for $\tau_{\text{TO}} \rightarrow \infty$):

$$A = \frac{B}{\omega_{\text{LO}}^2 - \omega_{\text{TO}}^2}. \quad (7.84)$$

Furthermore, Eq. (7.83) for $\omega = 0$ gives

$$\varepsilon(0) = A + \frac{B}{\omega_{\text{TO}}^2}, \quad (7.85)$$

Expressing A and B in terms of ω_{LO} , $\varepsilon(0)$, and ω_{TO} and setting $\tau_{\text{TO}} = \infty$, we obtain

$$\varepsilon(\omega) = \varepsilon(0) \frac{\omega_{\text{TO}}^2}{\omega_{\text{LO}}^2} \frac{\omega^2 - \omega_{\text{LO}}^2}{\omega^2 - \omega_{\text{TO}}^2}. \quad (7.86)$$

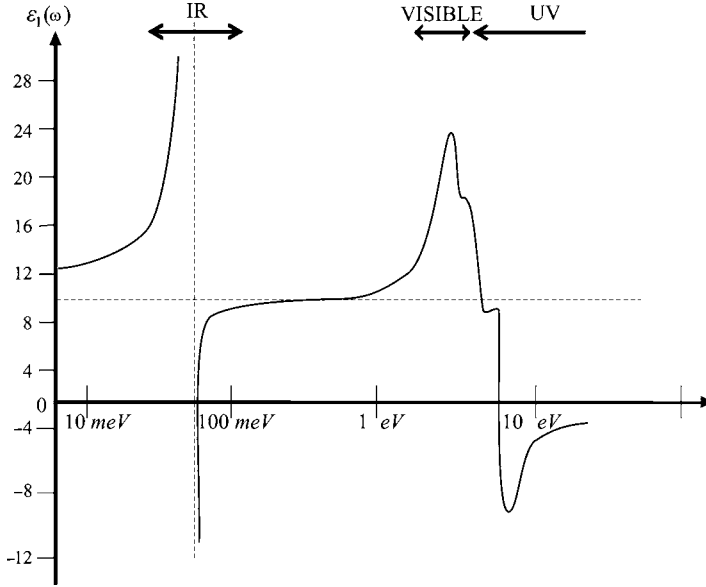


Fig. 7.12. Schematic plot of the real part of the dielectric function of GaAs, showing its value at $\omega = 0$ ($\epsilon(0) = 12.40$) and at the range $\omega_{LO} \ll \omega \ll E_g/\hbar$, ($\epsilon_\infty = 10.6$). The sharp structure at $\hbar\omega \simeq 33$ meV is due to photon absorption by TO phonon; the structure in the range above 1.5 eV is due to electronic transitions from the VB to the CB

In the literature, the value of $\epsilon(\omega)$ for ω in the range $\omega_{LO} \ll \omega \ll E_g/\hbar$ is denoted by the symbol ϵ_∞ . Substituting in (7.86) values of ω in this range, we have, since both ω_{LO}^2 and ω_{TO}^2 are negligible in comparison with ω^2 ,

$$\epsilon_\infty = \epsilon(0) \frac{\omega_{TO}^2}{\omega_{LO}^2}, \quad (7.87)$$

and

$$\epsilon(\omega) = \epsilon_\infty \frac{\omega^2 - \omega_{LO}^2}{\omega^2 - \omega_{TO}^2}. \quad (7.88)$$

Equation (7.87) is known as the Lyddane–Sachs–Teller (*LST*) relation. Equation (7.88) accounts for the absence of absorption at ω_{TO} when the bond is 100% homopolar (Because for a 100% homopolar bonding $\omega_{LO} = \omega_{TO}$ at $q = 0$).

Further examination of semiconductors is presented in Chap. 13.

It Table 7.5 values of the gap and the effective masses of various semiconductors are given, while in Table 7.6 values of ω_{TO} , ω_{LO} , $\epsilon(\infty)$, and $\epsilon(0)$ are presented.

Table 7.5. Data for various semiconductors

Semiconductor	E_g , d or i	m_{hh}/m	$m_{\ell h}/m$	m_{soh}/m	Δ	$m_{\ell c}/m$	$m_{\ell e1}/m$	$m_{\ell e2}/m$
<i>C (Diamond)</i>	5.5 ^a i	1.08	0.36	0.15	6	1.4	0.36	0.36
BN (<i>fcc</i>) ^b	6.4 ^a i	0.375	0.150	—	—	0.752	—	—
		0.926	0.108					
BN (H) ^c	5.2 ^a i	—	—	—	—	—	—	—
Si	1.17i	0.537	0.153	0.234	44	0.9163	0.1905	0.1905
AlP	2.505i	0.513	0.211	—	—	3.67	0.212	0.212
		1.372	0.145					
Ge	0.744i	0.284	0.0438	0.095	290	1.57	0.0807	0.0807
		0.376	0.0426					
		0.352	0.0430					
GaAs	1.519d	0.51	0.082	0.154	341	0.067	0.067	0.067
ZnSe	2.82d	0.75	0.57	—	400	0.13...0.17	0.13...0.17	0.13...0.17
CuBr	3.077d	1.5	1.1	—	154	>0.21	>0.21	>0.21
Sn(a)	0d	0.195	0.195	0.058	800	0.023	0.023	0.023
InSb	0.2368d	0.45	0.0158	0.11	850	0.01359	0.01359	0.01359
		0.42						
CdTe	1.606d	0.72	0.12	—	800	0.09	0.09	0.09
		0.84						
AgI	2.91d	—	—	—	840	—	—	—
SiC(fcc)	2.416i	—	—	—	—	0.677	0.247	0.247
SiC(6H)	3.023i	—	—	—	—	1.5	0.25	0.25
		1						

BP	2.4 ^a _i	—	—	—	—	—	—	—	—
AlN (W) ^c	6.25d	—	—	—	—	—	—	—	—
BeS	4.17 _i	—	—	—	—	—	—	—	—
AlAs	2.229 _i	1.022	0.153	—	—	1.1	0.19	0.19	0.19
		0.409	0.109	—	—	—	—	—	—
GaP	2.35 _i	0.67	0.17	0.4649	80	4.8	0.254	0.254	0.254
GaSb	0.822d	0.0412	0.0412	0.0412	760	1.2	0.25	0.25	0.25
InAs	0.418d	0.43	0.026	—	380	0.0239	0.0239	0.0239	0.0239
		0.35	—	—	—	—	—	—	—
ZnS	3.78d	1.76	0.23	—	—	0.34	0.184	0.184	0.184
ZnTe	2.3941d	0.6	—	—	910	0.13	—	—	—
GdSe (H) ^c	1.829d	>1	0.9	—	416	0.45	0.12	0.12	0.12
GaN	3.503d	0.8	—	—	11	0.27	0.2	0.2	0.2
AlSb	1.686 _i	0.336	0.123	—	673	1.8	0.259	0.259	0.259
		0.872	0.091	—	—	—	—	—	—
InP	1.4236d	0.60	0.12	0.121	108	0.0765	0.0765	0.0765	0.0765
		0.56	—	—	—	—	—	—	—
ZnO (W) ^c	3.4376d	0.59	0.31	0.55	—	0.24	0.28	0.28	0.28
CdS (H) ^c	2.573d	5	0.7	—	62	0.20	0.25	0.25	0.25

The quantity Δ (in meV) is the energy difference at $k = 0$ between the split off branch and the other two which determine the top of the VB (see Fig. 7.7c); d or i means direct or indirect gap

^aValues marked by a superscript a correspond to $T = 300$ K

^bDifferent values of m_{hh}/m , etc. correspond to different directions; this imply breakdown of cubic symmetry.

^c (W) Wurtzite structure; (H) hexagonal structure

Table 7.6. Experimental values of ω_{TO} , ω_{LO} (at $q = 0$); also of ϵ_∞ and $\epsilon(0)$ at $T = 300$ K

Semiconductor	ω_{TO} (10^{13}rad/s)	ω_{LO} (10^{13}rad/s)	$\epsilon(\infty)$	$\epsilon(0)$
C	25.07	25.07	5.7	5.7
BN	19.87	24.58	4.5	7.1
Si	9.758	9.758	11.9	11.9
			12.1	12.1
			(in 4.2 K)	(in 4.2 K)
AlP	8.277	9.437	7.54	9.8
Ge	5.667	5.667	16.2	16.2
			16.5	16.5
			(in 4.2 K)	(in 4.2 K)
GaAs	5.035	5.368	10.88	12.85
ZnSe	4.01	4.77	5.4	7.6
CuBr	2.34	3.07	4.062	7.9
Sn(a)	3.77	3.77	24	24
InSb	3.48	3.71	15.68	16.8
				17.3–18
CdTe	2.64	3.19	7.1	10.2
AgI(W)	2.04	2.34	4.1–4.9	7.0
SiC(fcc)	15.00	18.31	6.52	9.72
SiC(6H)	14.52	15.83	6.52 $\perp$	9.66 $\perp$
		16.26	6.70 $\parallel$	10.03 $\parallel$
BP	15.05	15.61	—	11
AlN(W)	12.65	16.86	4.84	9.14
	12.42	16.73		
AlAs	6.81	7.60	8.16	10.06
GaP	7	7.70	9.11	11.11
GaSb	4.21	4.38	14.44	15.69
InAs	4.09	4.49	12.25	15.15
ZnS	5.22	6.56	5.1–5.7	8.0–8.9
ZnTe	3.33	3.90	7.28	9.67
GdSe(H)	0.64 $\perp$	3.98 $\perp$	6.3 $\perp$	9.29 $\perp$
	3.11 $\parallel$	3.94 $\parallel$	6.2 $\parallel$	10.16 $\parallel$
GaN	10.53 $\perp$	14.05 $\perp$	5.35 $\perp$	9.5 $\perp$
	10.04 $\parallel$	14.01 $\parallel$	5.8	10.4 $\parallel$
AlSb	6.00	6.40	10.24	12.04
InP	5.78	6.47	9.61	12.5–12.61
ZnO(W)	7.72 $\perp$	11.08 $\perp$	3.70 $\perp$	7.8 $\perp$
	7.13 $\parallel$	10.86 $\parallel$	3.75 $\parallel$	8.75 $\parallel$
Cds(H)	4.56 $\perp$	5.73 $\perp$	5.32 $\perp$	8.45 $\perp$
	4.49 $\parallel$	5.67 $\parallel$	5.32 $\parallel$	9.12 $\parallel$

$10^{13} \text{ rad s}^{-1}$ corresponds to 6.582 meV or to 53.088 cm^{-1} .

(W) = wurtzite structure; (H) = hexagonal structure

7.13 Key Points

- The modifications of the results of Chap. 6, as we go from the simplistic 1-D models to the realistic 3-D solids, are presented (see Fig. 7.2).
- Figure 7.3 shows how bands and gaps are formed through a sequence of simple steps involving the bond length, d , and the energies of the relevant atomic orbitals.
- Three parameters are the most important for semiconductors: $V_1 \equiv (\varepsilon_p - \varepsilon_s)/4$ (if two different atoms are involved, we use $\bar{V}_1 = (V_{1a} + V_{1c})/2$); $V_{2h} = -3.22 \hbar^2/md^2$, the electron transfer matrix element; and $V_{3h} \equiv (\varepsilon_{hc} - \varepsilon_{ha})/2$, where $\varepsilon_{hi} = (\varepsilon_{si} + 3\varepsilon_{pi})/4$ ($i = c, a$). Two dimensionless parameters, the polarity index, a_p , and the metallicity index, a_m are defined as follows:

$$a_p \equiv \frac{V_{2h}}{\sqrt{V_{2h}^2 + V_{3h}^2}},$$

$$a_m \equiv \frac{2\bar{V}_1}{\sqrt{V_{2h}^2 + V_{3h}^2}}.$$

- In terms of these parameters, the gap is given approximately by

$$E_g \simeq 2\sqrt{V_{2h}^2 + V_{3h}^2} (1 - a_m).$$

The closing of the gap, which means $a_m \geq 1$, implies not only the metallic behavior but also the abandoning of the sp^3 hybridization and the changing of the lattice structure from that of diamond to a close-packed fcc. The results are summarized in Fig. 7.4 where the a_p , a_m plane is divided into three areas.

- The concept of hole at the top of the valence band is introduced as a particle of positive charge $|e|$, and effective mass of minus the corresponding electronic effective mass.
- The concept of effective mass becomes a tensor for the 3-D solids.
- The static dielectric constant of a semiconductor can be estimated by the formula

$$\varepsilon(0) \simeq 1 + \frac{\omega_p^2}{\omega_o^2}.$$

- In the presence of perturbations, the periodic part of the Hamiltonian for energy near the band edges can be replaced (under certain conditions) by a free Hamiltonian involving the effective mass: $-\hbar^2 \nabla^2 / 2m^*$.
- A point defect (e.g., a foreign atom) creates a local perturbation potential that besides scattering might trap an electron or a hole around it, giving rise to a so-called impurity level in the gap.

- If the perturbation potential is hydrogenic, a bound state is always formed, creating a level near the top of the gap (for attractive potential) or near the bottom of the gap (for repulsive potential). These levels are of crucial importance in the semiconductor technology, because they change dramatically the electron or hole concentration in the CB or the VB respectively, and consequently, they increase the conductivity by many orders of magnitude.
- For elemental and III–V semiconductors, there are six phononic branches (three acoustic and three optic). For ionic compound semiconductors or ionic insulators, the LO phonon frequency, ω_{LO} , at $q = 0$ is larger than the corresponding TO frequency, ω_{TO} . As a result, the dielectric function for ω less than the optical gap is given by

$$\varepsilon(\omega) = \varepsilon_{\infty} \frac{\omega^2 - \omega_{\text{LO}}^2}{\omega^2 - \omega_{\text{TO}}^2},$$

which implies that the value of $\varepsilon(\omega)$ in the range $\omega_{\text{LO}} \ll \omega \ll E_g/\hbar$, denoted by ε_{∞} , is related to the static value by the so-called LST relation:

$$\varepsilon_{\infty} = \varepsilon(0) \frac{\omega_{\text{TO}}^2}{\omega_{\text{LO}}^2}.$$

7.14 Problems

- 7.1s Write down the 8×8 matrix of the Hamiltonian for a compound semiconductor in the $\{g_{iak}\}$ basis.
- 7.2 Calculate the band edges and the gap E_g of InSb following the approaches based on (7.4)–(7.9) and on Fig. 7.3; plot and compare the two sets of results; $d = 2.8056 \text{ \AA}$.
- 7.3 For ZnSe, give the level- and band-diagram as in Fig. 7.3(b).
- 7.4s Prove (7.4) until (7.19).
Hint: To prove (7.4)–(7.7), you must find first the matrix element of the Hamiltonian in the hybridized basis χ_j^i , where the index j refers to the atom j and the index $i = 1, 2, 3, 4$ to the four sp^3 orbitals of atom j .
- 7.5 Calculate the matrix elements of the 8×8 matrix of problem 7.1s for $k = (2\pi/a)(1, 0, 0)$ and show that the initial 8×8 matrix reduces to four uncoupled 2×2 matrices; diagonalize them to obtain their eigenvalues.
- 7.6s Prove that $\mathbf{j}$ and $\mathbf{j}_E$ given by (7.27) and (7.28) are equal to zero.
- 7.7 Find the equilibrium distribution (Fermi distribution) of holes at temperature T and chemical potential μ .
- 7.8 Consider n -silicon with $N_d = 10^{17} \text{ cm}^{-3}$. Plot the concentration of electrons in the CB n vs. $1/T$ and μ vs. T .
Hint: See [SS75], Fig. 28.13, p. 584 and Problem 6 in p. 586.
- 7.9 Plot the resistivity vs. T for intrinsic Si.

Further Reading

- For the concentrations of electrons and holes, the concept of hole, and the concept of effective mass and effective Hamiltonian, see any book on solid state physics, e.g., Ashcroft and Mermin [SS75], pp. 221–229.
- The metallicity, polarity and related concepts, and their relations are treated in the book by Harrison [SS76], pp. 38–46 and 552–553.
- Semiconductor data can be found in the book by Madelung [D3].

Beyond the Jellium and the LCAO: An Outline

Summary. A systematic theoretical and computational approach to obtaining properties of solids starts with four approximations (Born–Oppenheimer, one-electron, harmonic, and periodicity). The most justified and effective approach to the one-electron approximation is based on the so-called density functional theory. However, there are phenomena, outlined in this chapter and examined later on, the very existence of which is related to the violation of one or more of these four approximations (broken periodicity, e.g., at interfaces, anharmonic interactions leading e.g., to melting, special el–el correlation producing, e.g., magnetic phases and superconductivity, and electron–phonon interactions giving rise, e.g., to attractive indirect el–el forces). Perturbation theory and other more advanced formalisms have been developed to face these challenges.

8.1 Introductory Remarks

There are two paths for approaching the quantitative theoretical explanation of the various properties of solids. The first one – which we followed up to now in this second part – starts from the simplest possible models (the jellium model (JM) and the LCAO together with the simplistic equations (6.9) and (6.10)) and gradually incorporates some of the features left out initially. For example, in Chap. 4, we improved the simple JM by reintroducing some aspects of the discrete character of the ions.

The second approach – which we outline in this chapter – starts from the most general formulation of the problem, capable in principle of providing all answers, but intractable in practice; then, one introduces a minimum number of appropriate simplifying approximations, which make possible the explicit calculations of various quantities. However, these approximations are not panacea; in some cases, they lead to quantitative and even qualitative failures. One is forced then either to modify these failed approximations by introducing some aspects left out before, or to fully abandon one or more of them and try to develop more sophisticated and subtle approaches.

8.2 The Four Basic Approximations

The general formulation of the study of solids starts with the many-body Schrödinger equation

$$\hat{H}\Psi = E\Psi, \quad (8.1)$$

for all the ions and electrons that through their mutual binding make up the condensed matter. The Hamiltonian $\hat{H}$ is of the form

$$\hat{H} = \hat{H}_e + \hat{H}_{ei} + \hat{H}_i, \quad (8.2)$$

where $\hat{H}_e$ is the electronic part, $\hat{H}_i$ is the ionic part, and $\hat{H}_{ei}$ is the electron-ion interaction. Since a typical number of particles in a solid is of the order of the Avogadro number, i.e., about 10^{24} , the explicit solution to (8.1) is out of the question. Some drastic approximations have to be introduced. For a whole group of topics, and at a first level of accuracy, the following four approximations are widely used, because, in combination, they make (8.1) and (8.2) tractable, without missing – in most cases – much of the physics:

A1: Born–Oppenheimer or adiabatic approximation

For the purpose of studying the motion of electrons, the ions are considered as immobile.

This approximation is justified physically because of the huge difference in mass between ions and electrons. Indeed the ratio m_a/m_e is typically of the order of 10,000 or larger. As a result, the motion of ions is very slow in comparison with that of the electrons. Thus, during the characteristic electronic time, the ions hardly have time to move.

A1 is important, because it allows us to study the combined motion of ions and electrons in two stages: first, to examine the motion of electrons, the ions are considered as immobile (at this first stage only); second, to examine the motion of ions, the electrons are assumed to adjust instantaneously to each temporary configuration of the ions.

A2: One-electron approximation

The electronic properties can be obtained from the solutions to the one-electron Schrödinger equation in the presence of a self-consistent effective potential.

This is indeed a very drastic approximation. It took several decades of research to provide a partial justification for **A2** and to obtain a reasonable form for the self-consistent potential $\mathcal{V}(\mathbf{r})$. Anyway, in view of **A2**, the electronic properties are determined by the solutions to the one-electron Schrödinger equation

$$\left[-\frac{\hbar^2}{2m_e} \nabla^2 + \mathcal{V}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}), \quad (8.3)$$

$$\mathcal{V}(\mathbf{r}) = f(\{\psi_i(\mathbf{r})\}), \quad (8.4)$$

where (8.4) is essentially an algorithm for obtaining the effective potential $\mathcal{V}(\mathbf{r})$ in terms of the solutions $\psi_i(\mathbf{r})$ to (8.3). To this algorithm we shall return in the next section.

A3: Harmonic approximation for ions in solids

Ions in solids undergo small coupled harmonic oscillations around their equilibrium positions.

Because of the very definition of a solid, ions have fixed equilibrium positions in space and undergo oscillations around these positions. Since the amplitude, Δx , of these oscillations is typically very small in comparison with the nearest neighbor ionic separation, d ($\Delta x/d$ is no more than a few percent), their nature to a very good approximation is harmonic, which means that the force $\mathbf{F}_\ell$ on the ℓ th ion is proportional to a linear combination of the ionic displacements, $\{\mathbf{u}_n\}$, from the equilibrium positions

$$F_{\ell,i} = \sum_n \sum_{j=1}^3 \kappa_{\ell n,ij} (u_{nj} - u_{\ell j}), \quad (8.5)$$

where $\{\kappa_{\ell n,ij}\}$ are the effective “spring constants” connecting ion ℓ to ion n ; i, j denote the Cartesian components of the vector $\mathbf{u}$ and the tensor $\boldsymbol{\kappa}$. Taking into account that (a) in the eigenoscillations, by definition, all ions move with the same angular frequency, so that their time dependence is of the form $\exp(-i\omega t)$; and (b) that $F_{\ell,i} = m_\ell \ddot{u}_{\ell i} = -\omega^2 m_\ell u_{\ell i}$, we have

$$\sum_n \sum_{j=1}^3 A_{\ell n,ij} u_{n,j} = 0, \quad (8.6)$$

where $A_{\ell\ell,ij} = \omega^2 m_\ell \delta_{ij} + \kappa_{\ell\ell,ij} - \sum_{n=1}^{N_a} \kappa_{\ell n,ij}$ and $A_{\ell n,ij} = \kappa_{\ell n,ij}$ for $\ell \neq n$; $\{A_{\ell n,ij}\}$ is a $3N_a \times 3N_a$ matrix multiplying the $3N_a$ component column matrix $\{u_{n,j}\}$, $\ell, n = 1, \dots, N_a$; $i, j = 1, 2, 3$. N_a is the number of ions (or atoms) in the solid. If we manage to diagonalize the matrix $\{A_{\ell n,ij}\}$, the problem has been reduced to that of $3N_a - 6$ one-dimensional independent harmonic oscillator (the remaining six degrees of freedom are associated with the rigid translation and the rigid rotation of the solid as a whole).

It must be stressed that the exact diagonalization of such a huge matrix as the $\{A_{\ell n,ij}\}$, as well as the exact solution of (8.3) over the *whole extent of the solid*, is still an impossible task. It is the fourth approximation that overcomes these huge obstacles to a solution.

A4: Periodicity

Crystalline solids are structurally and electronically periodic.

If solids were *perfect* crystals without defects, or foreign atoms, or phononic displacements, then **A4** would be an exact statement that, in combination with **A1**, would imply that $\mathcal{V}(\mathbf{r})$ in (8.3) and $A_{\ell n, ij}$ in (8.6) are periodic. However, even the best and purest monocrystals have some point defects and contain some traces of foreign atoms; furthermore, they are not free of some line defects called dislocations; and of course, phononic displacements are always present. Nevertheless, **A4** is a very good approximation not only for monocrystals but also for polycrystalline solids (because, usually, the size of each crystallite is much larger than the lattice constant). However, for some transport quantities, such as the electrical conductivity in metals at very low temperatures or in semiconductors, structural and chemical defects are the main factors determining the values of these quantities.

Finally, one should not forget that a large number of materials are not crystalline; several of them solidify in a glassy state; thin films may be amorphous possessing only very short-range imperfect order; solid soft matter under normal conditions does not form crystals. Since non-crystalline solids do not possess periodic order even approximately, the great simplification provided by this symmetry is absent. Thus, their study requires additional drastic approximations.

Returning to crystalline solids, we stress the fact that **A4** implies the validity of Bloch's theorem according to which the following relations hold:

$$\psi(\mathbf{r} + \mathbf{R}_n) = e^{i\mathbf{k} \cdot \mathbf{R}_n} \psi(\mathbf{r}), \quad (8.7)$$

$$\mathbf{u}_{\ell+\mathbf{n}} = e^{i\mathbf{q} \cdot \mathbf{R}_n} \mathbf{u}_{\ell}, \quad (8.8)$$

where $\hbar\mathbf{k}$ and $\hbar\mathbf{q}$ are the crystal momenta for electrons and phonons respectively and $\mathbf{R}_n$ is any *lattice* vector. Equation (8.7) means that there is no need to solve (8.3) over the whole volume of the solid; it is enough to solve it in a single primitive cell and use (8.7) to extend it over the whole volume. Similarly, (8.8) implies that all the $\mathbf{u}_{\ell+\mathbf{n}s}$, $\mathbf{n} \neq 0$, can be expressed in terms of the $\mathbf{u}_{\ell}s$ of the atom(s) in a single primitive cell; thus, the size of the linear homogeneous system is dramatically reduced from $3N_a$ equation to $3N_{a,pc}$, where $N_{a,pc}$ is the number of ions (or atoms) in a single primitive cell; $N_{a,pc}$ can be as low as one. This is indeed a tremendous simplification, which was used repeatedly in the LCAO electronic case in Chap. 6.

The combination of (8.3) and (8.7), through a procedure to be outlined later in Sect. 8.4, allows the determination of the electronic band structure, $E_n(\mathbf{k})$, and the corresponding eigenfunctions, which are of the form $\psi_{\mathbf{k},n}(\mathbf{r}) = w_{\mathbf{k},n}(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r})$ (see Chap. 3, Sect. 3.4.1, (3.8)). In Table 3.3 of Chap. 3, we compared the electronic Bloch waves with plane waves and we stressed both the similarities and the differences. Similarly the combination of (8.6) and (8.8) allows the determination of the relation between crystal wavevector $\mathbf{q}$ and the ionic eigenfrequencies, $\omega_s = \omega_s(\mathbf{q})$, where $s = 1, \dots, 3N_{a,pc}$.

We point out that the theory that has been developed in the framework of the four approximations, **A1**–**A4**, has been successful in obtaining both qualitatively and quantitatively many properties of crystalline solids:

- (a) It explains the fact that solids may be conductors, semimetals, semiconductors, or insulators.
- (b) It obtains the crystal structure and the lattice constant(s) of solids.
- (c) It calculates realistically various thermodynamic quantities such as the bulk and shear moduli, the specific heat, the thermal expansion coefficient, the electric susceptibility, etc. The accuracy of these calculations is usually of the order of 10% or better.
- (d) It calculates satisfactorily several magnetic properties of non-magnetic materials.
- (e) It obtains the optical properties of solids, such as optical absorption, index of refraction, etc., in fair agreement with the experimental data.

The implementation of the theoretical scheme within the framework of approximations **A1**–**A4** requires a reliable way of determining self-consistently the effective one-body potential, $\mathcal{V}(\mathbf{r})$; and of calculating the total energy, U_0 , of the system as a function of the positions of the ions and the concentration of electrons. A real breakthrough in addressing these issues occurred with the seminal papers of Hohenberg, Kohn, and Sham (Phys. Rev. B **136**, 864 (1964) and Phys. Rev. 4A **140**, 1133 (1965)), which led to the full development of the basic computational scheme known as density functional theory (DFT). The latter revolutionized the calculations of the structural and electronic properties of molecules and solids and its applications continue to expand.

8.3 Density Functional Theory

The DFT adopts approximation **A1** to start with; consequently, on the one hand, the part $\hat{H}_i$ in (8.2) does not influence the electronic motion, and on the other, the part $\hat{H}_{ei}$ has the form

$$\hat{H}_{ei} = \sum_{\ell=1}^{N_e} \mathcal{V}_i(\mathbf{r}_\ell), \quad (8.9)$$

where (by omitting spin-dependent terms)

$$\mathcal{V}_i(\mathbf{r}) = -e \sum_{j=1}^{N_a} \int \frac{d^3 r' \rho_i(\mathbf{r}' - \mathbf{R}_j)}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|}, \quad (8.10)$$

$\rho_i(\mathbf{r}' - \mathbf{R}_j)$ is the charge density of the ion located at $\mathbf{R}_j$; ρ_i is assumed known from atomic physics, and $\{\mathbf{R}_j\}$, the ion positions, are considered as fixed and not as dynamic variables as far as the electronic motion is concerned (because of **A1**).

The purely electronic part, $\hat{H}_e$, has a universal form given once and for all

$$\hat{H}_e = \hat{T}_e + \hat{H}_{ee}. \quad (8.11)$$

This means that the Hamiltonian $\hat{H}_e + \hat{H}_{ei} \equiv \hat{T}_e + \hat{H}_{ee} + \hat{H}_{ei}$, which determines the motion and all the properties of a given number N_e of electrons, is fully known, if the function $\mathcal{V}_i(\mathbf{r})$ is known.

The first step in the formulation of DFT is the following theorem:

The electronic concentration, $n_G(\mathbf{r})$, in the ground state Ψ_G

$$n_G(\mathbf{r}) \equiv N_e \int |\Psi_G(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_{N_e})|^2 d^3r_2 d^3r_3 \dots d^3r_{N_e} \quad (8.12)$$

uniquely determines $\mathcal{V}_i(\mathbf{r})$ and, hence, the full Hamiltonian $\hat{H}_e + \hat{H}_{ei}$.

The proof is based on disproving the hypothesis that there are two different $\mathcal{V}_i(\mathbf{r})$ s, $\mathcal{V}_i(\mathbf{r})$, and $\mathcal{V}'_i(\mathbf{r})$, which would produce the same $n_G(\mathbf{r})$. Let $\hat{H} = \hat{T}_e + \hat{H}_{ee} + \hat{H}_{ei}$ be the Hamiltonian associated with $\mathcal{V}_i(\mathbf{r})$ and $\hat{H}' = \hat{T}_e + \hat{H}_{ee} + \hat{H}'_{ei}$ be the one associated with $\mathcal{V}'_i(\mathbf{r})$; let Ψ_G and Ψ'_G be the corresponding ground states of $\hat{H}$ and $\hat{H}'$. Since the ground state minimizes the total energy, we have the following inequalities¹

$$\langle \Psi_G | \hat{H} | \Psi_G \rangle \equiv E_G < E_1 \equiv \langle \Psi'_G | \hat{H} | \Psi'_G \rangle, \quad (8.13)$$

$$\langle \Psi'_G | \hat{H}' | \Psi'_G \rangle \equiv E'_G < E'_1 \equiv \langle \Psi_G | \hat{H}' | \Psi_G \rangle \quad (8.14)$$

But

$$\begin{aligned} E_1 &= \langle \Psi'_G | \hat{H}' + (\hat{H}_{ei} - \hat{H}'_{ei}) | \Psi'_G \rangle \\ &= \langle \Psi'_G | \hat{H}' | \Psi'_G \rangle + \int d^3r n_G(\mathbf{r}) [\mathcal{V}_i(\mathbf{r}) - \mathcal{V}'_i(\mathbf{r})]. \end{aligned} \quad (8.15)$$

Similarly

$$E'_1 = \langle \Psi_G | \hat{H} + (\hat{H}'_{ei} - \hat{H}_{ei}) | \Psi_G \rangle = E_G + \int d^3r n_G(\mathbf{r}) [\mathcal{V}'_i(\mathbf{r}) - \mathcal{V}_i(\mathbf{r})]. \quad (8.16)$$

Adding together (8.13) and (8.14), and taking into account (8.15) and (8.16), we find

$$E_G + E'_G < E_1 + E'_1 = E'_G + E_G, \quad (8.17)$$

which is impossible. Hence, $\mathcal{V}_i(\mathbf{r}) = \mathcal{V}'_i(\mathbf{r})$.

The second step in the formulation of DFT is the construction in principle of an energy functional $E[n]$ of the electronic concentration, $n(\mathbf{r})$, such that $E[n]$ is minimum and equal to the ground state energy, E_G , when $n(\mathbf{r}) = n_G(\mathbf{r})$. $E[n]$ is defined as follows

¹ We assume that the ground states of $\hat{H}$ and $\hat{H}'$ are not degenerate. The proof can be extended to the degenerate case.

$$E[n] \equiv F[n] + \int d^3r n(\mathbf{r}) \mathcal{V}_i(\mathbf{r}), \quad (8.18)$$

$$F[n] \equiv \min \left\langle \Psi \left| \hat{T}_e + \hat{H}_{ee} \right| \Psi \right\rangle, \quad (8.19)$$

the minimization in (8.19) is with respect to all wavefunctions, Ψ , of N_e electrons that give the same concentration $n(\mathbf{r})$. Notice that $F(n)$ is a universal functional of $n(\mathbf{r})$, independent of $\mathcal{V}_i(\mathbf{r})$; hence, $F(n)$ needs to be determined once and for all. If Ψ_G is the ground state, and $n_G(\mathbf{r})$ is the corresponding concentration, we have

$$\begin{aligned} E[n_G] &= F[n_G] + \int d^3r n_G(\mathbf{r}) \mathcal{V}_i(\mathbf{r}) \\ &= \min \left\langle \Psi'_G \left| \hat{T}_e + \hat{H}_{ee} \right| \Psi'_G \right\rangle + \left\langle \Psi'_G \left| \hat{H}_{ei} \right| \Psi'_G \right\rangle, \\ &= \min \left\langle \Psi'_G \left| \hat{H} \right| \Psi'_G \right\rangle \end{aligned} \quad (8.20)$$

where by definition, Ψ'_G is a wavefunction that minimized the average value of $\hat{H}$ subject to the condition that it gives the ground state concentration. However, this is just the ground state wavefunction: $\Psi'_G = \Psi_G$. Hence, $E[n_G] = \left\langle \Psi_G \left| \hat{H} \right| \Psi_G \right\rangle = E_G$, which is valid even if the ground state energy is degenerate. Thus,

$$E[n_G] = E_G \leq E[n] = \left\langle \Psi \left| \hat{H} \right| \Psi \right\rangle, \quad (8.21)$$

where n is an arbitrary electron concentration. Thus, we reach the following important conclusion [8.1]:

The functional $E[n]$, as defined by (8.18) and (8.19), is minimized when the concentration $n(\mathbf{r})$ coincides with the ground state concentration $n_G(\mathbf{r})$; furthermore $E[n_G] = E_G$.

The third step is to find an expression for $E[n]$, which through the minimization theorem (and eventually, some approximations) will reduce the many-body problem to (8.3) and (8.4) [8.2]. Keeping in mind this goal of reducing the many-body problem to an effective one body, we shall express the yet-unknown concentration $n(\mathbf{r})$ in terms of N_e orthonormal single-particle wavefunctions, $\psi_\ell(\mathbf{r})$, $\ell = 1, \dots, N_e$ as follows:

$$n(\mathbf{r}) = \sum_{\ell=1}^{N_e} |\psi_\ell(\mathbf{r})|^2. \quad (8.22)$$

Given this expression for $n(\mathbf{r})$, we shall approximate the quantity $\left\langle \Psi \left| \hat{T}_e \right| \Psi \right\rangle$ by the corresponding expression for non-interacting particles

$$\left\langle \Psi \left| \hat{T}_e \right| \Psi \right\rangle \simeq -\frac{\hbar^2}{2m} \sum_{\ell=1}^{N_e} \int d^3r \psi_\ell^*(\mathbf{r}) \nabla^2 \psi_\ell(\mathbf{r}) \equiv T_{e0}[n]. \quad (8.23)$$

We are now in the position to write an expression for $E[n]$:

$$E[n] = T_{e0}[n] + \int d^3r n(\mathbf{r}) \mathcal{V}_i(\mathbf{r}) + \frac{e^2}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{4\pi\epsilon_0|\mathbf{r}-\mathbf{r}'|} + E_{xc}[n], \quad (8.24)$$

where the first term in the rhs of (8.24) is given by (8.23) and approximates the average kinetic energy; the second term gives the average value of the electron-ion interaction; the third term gives the average value of the *uncorrelated* el-el interaction; and the term $E_{xc}[n]$, called *exchange and correlations*, incorporates the corrections to the kinetic energy $T_{e0}[n]$ and the corrections to the el-el interaction due to their correlated motion, which increases on average the distance $|\mathbf{r}-\mathbf{r}'|$ in (8.24) (see Problem 4.6). The el-el correlations are due to both the Pauli principle (E_x) and the el-el interactions, (E_c): $E_{xc} = E_x + E_c$, where E_c incorporates the corrections to T_{e0} as well.

For the JM, the exchange term can be calculated exactly (see Problem 4.6) and the book by Kaxiras [SS83], pp. 49–54):

$$E_x = \int d^3r n e_x, \quad (8.25)$$

$$\varepsilon_x = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} \frac{e^2 n^{1/3}}{4\pi\epsilon_0} = -\frac{0.458}{\bar{r}_s} E_0. \quad (8.26)$$

For the general case, where the concentration is a function of $\mathbf{r}$ (and not a constant as in the JM), we assume that approximately E_x is still given by (8.25) and (8.26) with n replaced by $n(\mathbf{r})$. This replacement is known as the local density approximation (LDA) for E_x . The LDA is also employed for the term E_c giving:

$$E_c = \int d^3r n(\mathbf{r}) \varepsilon_c[n(\mathbf{r})]. \quad (8.27)$$

There is no exact expression for $\varepsilon_c[n]$; not even for the JM. Instead, there are several proposals² for an approximate expression $\varepsilon_c[n(\mathbf{r})]$ (see the book by Kaxiras [SS83], p. 64; see also Problem 4.6, (4.114) and [8.4]). The simplest one assumes that ε_c is proportional to ε_x ,

$$\varepsilon_c \simeq k\varepsilon_x, \quad (8.28)$$

where k is usually written as $(3/2)\alpha - 1$ with α close to but lower than 1 ($\alpha \simeq 3/4$ is a typical choice). Equation (8.28) with $k = (3/2)\alpha - 1$ is called

² For example, the proposal by Perdew and Zunger [8.3] is as follows.

$$\begin{aligned} \varepsilon_c/E_0 &= A_1 + A_2\bar{r}_s + [A_3 + A_4\bar{r}_s] \ln \bar{r}_s, \bar{r}_s < 1, \\ &= B_1 [1 + B_2\sqrt{\bar{r}_s} + B_3\bar{r}_s]^{-1}, \bar{r}_s \geq 1. \end{aligned}$$

$$A_1 = -0.048, A_2 = -0.0116, A_3 = 0.0311, A_4 = 0.002, B_1 = -0.1423, B_2 = 0.52645, B_3 = 0.1667, \text{ and } n^{-1} = (4\pi/3) a_B^3 \bar{r}_s^3$$

the $X - \alpha$ approximation. It must be pointed out that there are schemes that go beyond the LDA by including not only the local value of $n(\mathbf{r})$ but also its gradient through the quantity $s \equiv |\nabla n(\mathbf{r})|/2k_F n$, with $k_F(\mathbf{r}) = (3\pi^2 n(\mathbf{r}))^{1/3}$ (*generalized gradient approximation*, GGA).

Quite often we employ another generalization of LDA in which the spin is displayed explicitly by assuming that $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$ are not necessarily equal. This generalization, which is called local spin-density approximation (LSDA), is required for magnetic materials. The LSDA replaces the factor $[n(\mathbf{r})]^{4/3}$ in the integrals for E_x and E_c by $2^{1/3} [n_\uparrow(\mathbf{r})^{4/3} + n_\downarrow(\mathbf{r})^{4/3}]$. In superconductivity, an extension of the DFT has been developed (see Chap. 23, Sect. 23.9).

The final step in the DFT formulation is to minimize the expression (8.24) for $E[n]$ with respect to $n(\mathbf{r})$ subject to the auxiliary condition that

$$\int d^3r n(\mathbf{r}) = N_e. \quad (8.29)$$

This conditional minimization is achieved by setting the functional derivative of $E[n] - \mu \int d^3r n(\mathbf{r})$ with respect to $n(\mathbf{r})$ equal to zero:

$$\frac{\delta T_{e0}}{\delta n} + \mathcal{V}_i(\mathbf{r}) + e^2 \int \frac{d^3r' n(\mathbf{r}')}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{xc}[n]}{\delta n} - \mu = 0, \quad (8.30)$$

where μ , the chemical potential, acts as a Lagrange multiplier in the process of conditional minimization. Notice that for non-interacting fermions moving in an external field $\mathcal{V}(\mathbf{r})$, the same conditional minimization would lead to an equation similar to (8.30):

$$\frac{\delta T_{e0}}{\delta n} + \mathcal{V}(\mathbf{r}) - \mu = 0. \quad (8.31)$$

Hence, the electronic problem in a solid can be mapped to that of non-interacting fermions moving in an external field $\mathcal{V}(\mathbf{r})$ given by the following relation

$$\mathcal{V}(\mathbf{r}) = \mathcal{V}_i(\mathbf{r}) + e^2 \int d^3r' \frac{n(\mathbf{r}')}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{xc}[n]}{\delta n}, \quad (8.32)$$

where, e.g., within LDA and the $X - \alpha$ approximation,

$$\frac{\delta E_{xc}}{\delta n} = 2\alpha\epsilon_x = -\frac{3}{2} \left(\frac{3}{\pi}\right)^{1/3} \alpha \frac{e^2 [n(\mathbf{r})]^{1/3}}{4\pi\epsilon_0}. \quad (8.33)$$

8.4 Outline of an Advanced Scheme for Calculating the Properties of Solids

Based on **A1–A4**, DFT, and LDA (or some other approximation for E_{xc}) we outline in this section a step-by-step procedure for calculating the lattice structure, the lattice constant(s), the ground state electronic concentration, $n_G(\mathbf{r})$, and various other properties of solids.

- Step 1 Separate each atom to an ion and detached electrons. The separation must be such that the ions contain only those electrons that are so tightly bound that they are a priori certain that they would be practically unaffected by the formation of the solid.
- Step 2 Choose some reasonable periodic positions $\{\mathbf{R}_j\}$ for the ions.
- Step 3 Calculate the charge distribution, $\rho_i(\mathbf{r}' - \mathbf{R}_j)$, for each kind of ions using DFT.
- Step 4 Calculate the ionic potential, $\mathcal{V}_i(\mathbf{r})$, according to (8.10).
- Step 5 Choose an initial concentration $n_0(\mathbf{r})$ of the electrons; e.g., this initial guess could be obtained from the sum of their concentrations in isolated atoms.
- Step 6 Calculate the electronic potential,

$$\mathcal{V}_H(\mathbf{r}) \equiv \frac{e^2}{4\pi\epsilon_0} \int d^3r' n_0(\mathbf{r}') |\mathbf{r} - \mathbf{r}'|^{-1}.$$

- Step 7 Choose some approximation for $E_{xc}[n]$ to obtain $\mathcal{V}_{xc} = \delta E_{xc} / \delta n_0$.
- Step 8 Solve Schrödinger's equation

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + \mathcal{V}(\mathbf{r}) \psi = E \psi, \quad (8.34)$$

where

$$\mathcal{V}(\mathbf{r}) = \mathcal{V}_i(\mathbf{r}) + \mathcal{V}_H(\mathbf{r}) + \mathcal{V}_{xc}(\mathbf{r}). \quad (8.35)$$

- Step 9 Find a new $n_1(\mathbf{r})$, using (8.22).

$$n_1(\mathbf{r}) = 2 \sum_{\ell=1}^{N_e/2} |\psi_\ell(\mathbf{r})|^2, \quad (8.36)$$

where the sum in (8.36) is over the lowest (in energy) $N_e/2$ eigenfunctions of (8.34) and the factor two accounts for the two orientations of the electronic spin.

- Step 10 If the new $n_1(\mathbf{r})$ is different from $n_0(\mathbf{r})$, go back to step 5 with a new guess $n_2(\mathbf{r}) = an_0(\mathbf{r}) + bn_1(\mathbf{r})$, where $a + b = 1$ and repeat the procedure of steps 5–10, until you achieve self-consistency $n_s(\mathbf{r}) \simeq n_{s-1}(\mathbf{r})$.
- Step 11 Having obtained convergence in the loop “steps 5–10”, i.e., after you have obtained the electronic concentration, $n(\mathbf{r})$, calculate the total ground state energy, U_0 (still treating the ions as immobile).

$$U_0 = T_{e0} + \int \mathcal{V}_i(\mathbf{r}) n(\mathbf{r}) d^3r + \frac{1}{2} \int \mathcal{V}_H(\mathbf{r}) n(\mathbf{r}) d^3r + \int \epsilon_{xc}[n] n(\mathbf{r}) d^3r + U_i, \quad (8.37)$$

where U_i is the Coulomb interaction among the ions.

- The energy U_0 depends on the lattice structure and the lattice constant(s) chosen in step 2.
- Step 12 Repeat the procedure from steps 2 to 11 by changing the lattice constants for the chosen lattice structure until you obtain the minimum value of U_0 for this lattice structure.
- Step 13 Repeat the procedure from steps 2 to 12 for various candidate lattice structures; the one among them that gives the *lowest minimum value* of U_0 is most probably the *actual* lattice structure.³
- Step 14 Step 12 for the *actual* lattice structure has determined the variation of U_0 vs. the lattice constants, and consequently, the U_0 vs. volume. Hence, the bulk modulus, at zero temperature, $B \equiv V\partial^2 U_0/\partial V^2$, has also been determined.
- Step 15 By repeating the steps 2–12 for the *actual* lattice structure and for *appropriate* small displacements of the ions from their equilibrium positions, we obtain the variations of U_0 as functions of the various strain components; this allows the calculation of the elastic constants, and in turn, approximately, the “spring constants”, $k_{\ell n, ij}$, appearing in (8.5) and (8.6); then, the eigenoscillations and eigenfrequencies, $\omega_s(\mathbf{q})$, of the ionic motion can be obtained (with the help of **A4**).

Having the phononic and the electronic band structure, $\omega_s(\mathbf{q})$ and $E_n(\mathbf{k})$, and the corresponding eigenoscillations and eigenfunctions, one can proceed to calculate various thermodynamic and transport properties as in Chaps. 4, 5, and 7. Notice that the DFT does not guarantee that, by populating states above the $(N_e/2)$ lowest ψ_1 states (the two to take into account the two spin-orientations), we shall obtain the excited states of the many-body system. Indeed, for semiconductors the size of the gap is systematically underestimated by the DFT as a result of the fact that the character of the single particle states in the CB is quite different from that of the VB.

Concluding this section, we must point out that the procedure based on steps 2–13, although the most straightforward, is not the most efficient. Several other versions of the density functional approach have been developed (some of them are available even commercially) which cut down substantially the calculational effort. Among them worth mentioning for its physical insight is the Car–Parrinello method [8.5].

8.5 Beyond the Four Basic Approximations

As it was mentioned before, the basic calculational scheme described in Sects. 8.2–8.4, in spite of its impressive successes, cannot account by itself alone for all the phenomena appearing in various solids. There are several of

³ One, on a purely theoretical basis, cannot exclude the possibility that another more complicated lattice structure or a disordered one may produce even lower energy. However, since the lattice structure can be determined experimentally, this problem does not appear in practice.

them forcing us to go beyond the basic computational scheme outlined earlier. To obtain a qualitative understanding and a quantitative explanation of these phenomena, we follow several approaches depending on each particular case.

Quite often we start with the solution obtained within the **A1**–**A4** framework and then we calculate its modifications induced by the term(s) that violates (violate) one or more of the four approximations. There is a systematic mathematical technique called *perturbation theory*, for obtaining these modifications. An important example, where this technique has been applied, was the calculation of the electrical resistivity of metals in Sect. 5.4. (There, we took into account the scattering of electrons by the moving ions, i.e., we went beyond **A1** and **A4**.)

There are cases where, through additional approximations, we reduce the problem, or at least, some aspects of it, again within the four approximations. A typical example of this approach is in the study of strongly disordered systems; the electrons in such systems are treated, through an approach called *coherent potential approximation* (CPA, see Chap. 18, Sect. 18.8.1), as moving in an effective complex *periodic* potential self-consistently determined.

There are also cases where unusual phenomena are due to particular electronic correlations occurring in the actual ground state; these correlations neither appear within the scheme described in Sects. 8.2–8.4 nor are derivable through a perturbation approach. These key correlations, e.g. the formation of ‘Cooper pairs’ leading to superconductivity (see below), have to be identified and quantitatively characterized, usually by a combination of experimental work and more advanced many-body theoretical techniques. If this task is implemented, these key correlations can be incorporated *ad hoc* in the DFT approach, which is then capable of calculating numerical values in good agreement with the experimental data. Ferromagnetism (and other magnetic phases) and phonon-based superconductivity are typical examples, as we shall see in Part 6 of this book.

The explanation of some mechanical properties, such as plastic deformations and/or fracture of materials, involves macroscopic stresses and processes occurring both at the atomic and at the mesoscopic scale. Thus, their quantitative understanding, besides a microscopic approach as in Sects. 8.2–8.4, requires its “seamless” connection to a mesoscopic theory coupled in turn with a macroscopic phenomenological theory (e.g., theory of elasticity) involving stresses and strains.

In the rest of this section, we shall mention very briefly some important phenomena associated with violations of one or more of the approximations **A1**–**A4**. These phenomena shall be reexamined in the fifth and sixth parts of this book.

8.5.1 Periodicity Broken or Absent

Point Defects, Transport Properties, and Bound States

Point defects in a crystalline solid are caused by foreign atoms and by missing or misplaced host atoms. Foreign atoms may substitute for host atoms (*substitutional impurities*) or may be placed in between host atoms (*interstitial impurities*). A host atom may be missing, leaving behind a lattice point empty (*vacancy*); two vacancies next to each other form a divacancy, and so on. A host atom placed in a nonlattice point forms an *interstitial defect*. The combination of a vacancy and an interstitial is called a *Frenkel defect*, while a lone vacancy without the presence of an accompanying interstitial is called a *Schottky defect*.

In Chaps. 5 and 7 (see Sect. 5.3), we have seen that point defects scatter the Bloch wave, and as a result, produce a nonzero contribution to the resistivity or to other transport properties (see (5.38) and subsequent comments as well as Fig. 5.3); these point defects for very low temperatures dominate the value of the conductivity.⁴ Besides scattering, point defects may bind electrons around them creating thus levels in the gap. Some of these levels, as we have seen in Chap. 7, are of paramount importance in controlling the conductivity of semiconductors, while others, called *deep levels*, are detrimental to the functioning of semiconductor devices. Electronic transitions between such bound levels in the gap of ionic solids, called *color centers*, are responsible for the color of these solids. Finally, vacancies in ionic solids facilitate *ion transport*, which is the main contribution to the electrical conductivity of these materials.

It must be pointed out that point defects appear randomly within the solid. We do not know their exact positions; only their average concentration, n_s , is known. The latter is assumed to be very low, in the sense that the average separation $d_s \simeq n_s^{-1/3}$ of the nearest neighbor point defects is much larger than the square root of the scattering cross-section, σ_s , i.e., $d_s \gg \sigma_s^{1/2}$, or equivalently, $\ell \gg d_s$, where ℓ is the mean free path as given by (5.36).

Problem 8.1ts. Show that the concentration of Schottky defects, n_s , under conditions of thermodynamic equilibrium, is given by the following formula:

$$\frac{n_s}{n_L - n_s} = \frac{n_s}{n_a} \simeq \exp\left(-\frac{\varepsilon_V}{k_B T}\right), \quad (8.38)$$

where ε_V is the energy for the creation of a lone vacancy, n_L is the concentration of lattice sites, and $n_a \simeq n_L$ is the concentration of atoms of the material. Similarly, the concentration n_F for Frenkel defects is given by

⁴ For heavily doped semiconductors, where the substitutional impurities are charged, the defect mean free path dominates the value of the mobility even at elevated temperatures.

$$\frac{n_F}{(n_L n_I)^{1/2}} = \exp\left(-\frac{\varepsilon_F}{2k_B T}\right), \quad (8.39)$$

where ε_F is the energy needed for the creation of the Frenkel defect and n_I is the concentration of interstitial sites.

Hints: Minimize the free energy $G = U + PV - TS$, where PV is considered negligible, $S = k_B \ln \Gamma$ and

$$\Gamma = N_L! / N_S! (N_L - N_S)! \quad (8.40)$$

for the Schottky defect, while for the Frenkel defect

$$\Gamma = N_L! N_I! / (N_F! (N_L - N_F)! N_F! (N_I - N_F)!). \quad (8.41)$$

Problem 8.2t. For ionic solids $C^+ A^-$, a Schottky vacancy in the cation sublattice must be accompanied by a nearby anion Schottky vacancy to preserve electrical neutrality. Show that the concentration $n_S^\pm$ of cation (or anion) vacancies is given by

$$n_S^\pm = n_a^\pm \exp\left(-\frac{\varepsilon'_V}{2k_B T}\right), \quad (8.42)$$

where ε'_V is the energy needed for the creation of a pair of vacancies, one in each sublattice.

To obtain the *ionic conductivity*, σ , in ionic insulators, usually we find first the diffusion coefficient, D , and then through the Einstein relation

$$D = \frac{\sigma}{q^2} \frac{k_B T}{n}, \quad (8.43)$$

we end up with σ . Equation (8.43) is valid at high temperature, low concentration; q is the electric charge of each particle acting as a carrier of electricity and n is the concentration of such particles. The diffusion coefficient is defined through the so-called *Fick's law*.

$$\mathbf{j}_n \equiv -D \nabla n, \quad (8.44)$$

where the number current-density, $\mathbf{j}_n$, is related to the electric current-density, $\mathbf{j}$, by the relation $\mathbf{j} = q \mathbf{j}_n$. To prove (8.43), we use (5.110), (5.109), and (5.108) by setting $\phi = 0$ and q instead of $-e$. We have then

$$\mathbf{j}_n = \frac{\mathbf{j}}{q} = -\frac{1}{q} \sigma \frac{\nabla \mu}{q} = -\frac{1}{q^2} \sigma \frac{\partial \mu}{\partial n} \nabla n. \quad (8.45)$$

In (8.45), it was assumed that in the chemical potential $\mu(n, T)$ only n is a function of the position $\mathbf{r}$. Comparing (8.44) with (8.45), we find that

$$D = \frac{\sigma}{q^2} \frac{\partial \mu}{\partial n} \xrightarrow{T \rightarrow 0K} \frac{\sigma}{2q^2 \rho_{FV}}. \quad (8.46)$$

To obtain the last expression, we have taken into account that $\rho_{\text{FV}} \equiv \rho_{\text{F}}/V$, $\mu = E_{\text{F}}$, and $n = (2/V) \int^{E_{\text{F}}} \rho(E) dE$ as $T \rightarrow 0\text{K}$. In the opposite limit of finite temperature and very low concentration $n = N/V$, the Fermi distribution in (C.44) can be replaced by the Boltzmann distribution and then $n = \exp(\beta\mu) \phi(T)$ from which it follows that $(\partial n / \partial \mu) = \beta n \equiv n/k_{\text{B}}T$. Substituting this last relation in (8.46), we obtain (8.43).

To calculate the diffusion coefficient D of an ion, we introduce its period of oscillation, $t_0 = 1/f$, and the energy barrier E_{b} associated with the jumping of an ion from its initial position $\mathbf{r}$ to the neighboring position $\mathbf{r} + \mathbf{a}$; $\mathbf{a}$ is parallel to the vector ∇n and its magnitude, $|\mathbf{a}|$, is equal to the distance between two nearest neighboring planes normal to ∇n and passing through the points $\mathbf{r}$ and $\mathbf{r} + \mathbf{a}$. The probability dp that the ion will jump from $\mathbf{r}$ to $\mathbf{r} + \mathbf{a}$ during the time interval dt is equal to $(dt/t_0) \exp(-E_{\text{b}}/k_{\text{B}}T)$, where t_0^{-1} is the ionic frequency f . Hence, its average velocity, $\mathbf{v}$, is equal to $\mathbf{a} dp/dt = f \mathbf{a} \exp(-E_{\text{b}}/k_{\text{B}}T)$. It follows that the number current-density from $\mathbf{r}$ to $\mathbf{r} + \mathbf{a}$ is $\mathbf{j}_n = n(\mathbf{r}) f \mathbf{a} \exp(-E_{\text{b}}/k_{\text{B}}T)$. The opposite flux from $\mathbf{r} + \mathbf{a}$ to $\mathbf{r}$ is given by $n(\mathbf{r} + \mathbf{a}) f \mathbf{a} \exp(-E_{\text{b}}/k_{\text{B}}T)$. The net number current-density is therefore

$$\begin{aligned} \mathbf{j}_n &= f \mathbf{a} \exp(-E_{\text{b}}/k_{\text{B}}T) [n(\mathbf{r}) - n(\mathbf{r} + \mathbf{a})] \\ &= -f a^2 \exp(-E_{\text{b}}/k_{\text{B}}T) \nabla n. \end{aligned}$$

Hence,

$$D = f a^2 \exp(-E_{\text{b}}/k_{\text{B}}T). \quad (8.47)$$

The presence of vacancies or interstitials significantly reduces the energy barrier, and consequently, increases dramatically the diffusion and the ionic conductivity. In table 8.1, we give some data regarding the quantities entering in (8.47).

Line Defects (Dislocations) and Mechanical Properties

Line defects, in particular the so-called *dislocations*, are crucial for mechanical properties such as plastic deformations and/or fracture of crystalline materials [8.6–8.11]. They are also important for the growth of crystals and the quality of interfaces. In Fig. 8.1, we show the simplest dislocation, called *edge dislocation*. It can be thought of as the termination (in a straight line) of a lattice plane within the crystal, or equivalently, as the “gedanken” insertion of an extra half lattice plane in the crystal. The importance of this dislocation becomes apparent if we consider the elementary plastic deformation due to the permanent slip of the upper half crystal in Fig. 8.1 with respect to the lower one. If the slip takes place in the direction of the CC' line (the x -axis) and at the plane defined by the CC' line (and the z -axis), the required stress would be much smaller than the one associated with any other parallel plane. This is clear, since the breaking of the bonds between the row of atoms 1 and

Table 8.1. Diffusion coefficient, $D = D_0 \exp(-E_b/k_B T)$, energy barrier, E_b , and formation energy ε'_v of a pair of vacancies in ionic crystals

Material	Diffusing atom or ion	$D_0 \equiv f a^2$ (in $\text{cm}^2 \text{s}^{-1}$)	E_b (in eV)	ε'_v (in eV)
Cu	Cu ^a	0.2	2.04	—
Cu	Zn	0.34	1.98	—
Ag	Ag ^a	0.40	1.91	—
Ag	Cu	1.2	2.00	—
Ag	Au	0.26	1.98	—
U	U ^a	2×10^{-3}	1.20	—
Na	Na ^a	0.24	0.45	—
Si	Al	8.0	3.47	—
Si	Ga	3.6	3.51	—
Si	In	16.0	3.90	—
Si	As	0.32	3.56	—
Si	Sb	5.6	3.94	—
Si	Li	2×10^{-3}	0.66	—
Si	Au	1×10^{-3}	1.13	—
Ge	Ge ^a	10.0	3.1	—
NaCl	Na ⁺	—	0.86	2.02
LiF	Li ⁺	—	0.65	2.68
LiCl	Li ⁺	—	0.41	2.12
LiBr	Li ⁺	—	0.31	1.80
LiI	Li ⁺	—	0.38	1.34
Cl	K ⁺	—	0.89	2.1–2.4
AgCl	Ag ⁺	—	0.39 (0.10) ^b	1.4 ^{bb}
AgBr	Ag ⁺	—	0.25 (0.11) ^b	1.5 ^b

^aSelf-diffusion^bThese values are for interstitial Ag⁺ ions

1' and the establishment of bonds between the row of atoms 0 and 1' do not require much force. Thus, the edge dislocation can easily propagate from the row of atoms 0 to the row of atoms 1, and then to the row of atoms 2, and so on, until the far right surface of the crystal; the result is an elementary plastic deformation of the crystalline solid. Many such parallel elementary deformations lead to a macroscopic plastic deformation.

Similarly, the *existence* and/or *easy creation* and *movement* of dislocations favor ductile behavior and disfavor breaking. The latter is directly connected to the existence of microcracks at the end of which the stress is much larger than its average value⁵ (Fig. 8.2a). The increase of the stress leads eventually to either one of two paths. (a) The bonds at the very end of the microcrack break, the crack propagates, and the solid fractures. (b) There is a slip along

⁵ The stress at the edge of a microcrack is proportional to $1/\sqrt{R}$, where R is the radius of curvature at the edge.

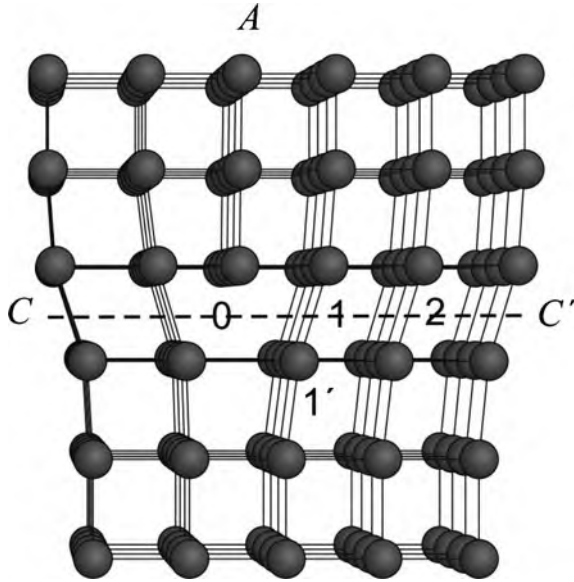


Fig. 8.1. The edge dislocation along a straight line parallel to the z -axis (normal to the page) and passing through the lattice points 0 is created by the termination at the points 0 of the half lattice plane OA (after Kittel [SS74])

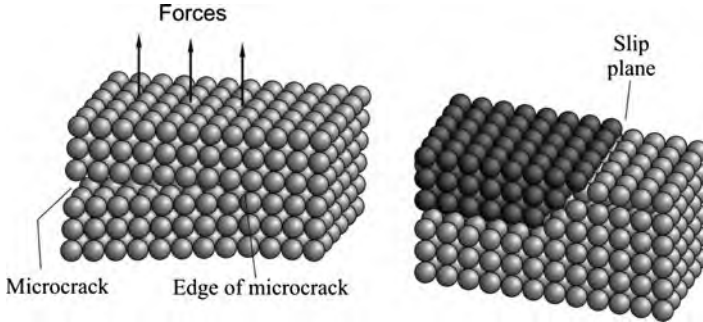


Fig. 8.2. (a) A microcrack and (b) a slip along a plane passing through the edge of the microcrack reduces the excessive local stress there; hence, the breaking of the solid may be avoided [8.6]

a plane almost normal to the crack, passing through its edge (Fig. 8.2b); this smoothens up the edge, i.e., it increases the radius of curvature, and hence, reduces the local stress avoiding thus the breaking. This break opposing process, shown in Fig. 8.2b, is facilitated by the presence and easy movement of dislocations.

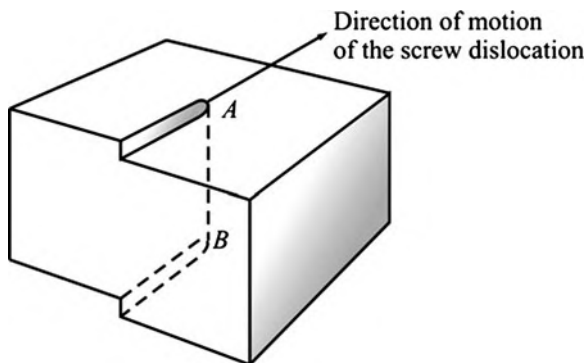


Fig. 8.3. Screw dislocation (line AB). The direction of slip (or glide) is parallel to the screw dislocation (i.e., to line AB), while the direction of motion of the dislocation is normal to the dislocation and lies in the plane of slip ([SS74], p. 604)

Another common dislocation, called *screw dislocation*, is shown in Fig. 8.3. One situation where this kind of dislocations plays an important role is in the growing of crystals by deposition of the material's atoms from an atmosphere of supersaturated vapor.

If the surface of the crystal is flat at the atomic scale, the sticking coefficient of the atoms is very low. In contrast, the sticking coefficient at steps or – even better – corners is very high (it may approach unity). Hence, screw dislocations, by providing steps and corners, lead to a spiral crystal growth that can exceed the rate at an atomically flat surface by many orders of magnitude.

Besides edge and screw dislocations, there are more general ones the definition of which is as follows:

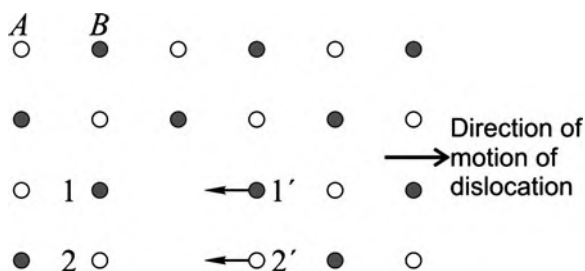
A **dislocation** is a linear region of a crystal⁶ near which the positions of the atoms differ significantly from those of a perfect crystal, while far away from it they coincide with those of a perfect crystal. Each dislocation is associated with a so-called **Burgers vector**, which is defined as follows. We consider a large closed path far away from the dislocation (without enclosing it) consisting of Bravais vectors joining points in the Bravais lattice. We repeat exactly the same sequence of Bravais vectors but this time enclosing the dislocation; the path in this second case is not closed. The vector from the initial point to the final one is called Burgers vector and it is usually denoted by $\mathbf{b}$.

Problem 8.3t. Show that the Burgers vector is perpendicular to the edge dislocation (along the direction x of Fig. 8.1), while it is parallel to the screw dislocation (along the line AB of Fig. 8.3).

⁶ which is either closed or terminates at points where the periodicity is violated, e.g., at the external surfaces. Dislocations by their very definition are associated with crystalline materials.

Table 8.2. Comparison of the critical stress τ_c for plastic deformation with the shear modulus μ_s

Material	μ_s (bars)	τ_c (bars)	μ_s/τ_c
Sn, monocrystal	1.9×10^5	13	15,000
Ag, monocrystal	2.8×10^5	6	45,000
Al, monocrystal	2.5×10^5	4	60,000
Al, pure, polycrystal	2.5×10^5	260	900
Al, commercial	2.5×10^5	990	250
Duraluminum	2.5×10^5	3,600	70
Fe, polycrystal	7.7×10^5	1,500	500
Steel, Fe-C	8×10^5	6,500	120
Steel, Fe-Ni-Cr	8×10^5	12,000	65

**Fig. 8.4.** In an ordered binary alloy AB the motion of the edge dislocation shown above does not restore the alternating AB structure, since pairs of similar atoms (1, 1'), (2, 2'), (3, 3') etc. will be next to each other. The presence of a second neighboring dislocation (i.e., atoms 1, 2, 3, etc. missing) gives the possibility to restore and maintain the AB configuration if the two dislocations move in tandem

We have pointed out before that the plastic deformation of materials is greatly facilitated by the *presence* and *easy movement* (*high mobility*) of dislocations. Indeed, as shown in Table 8.2, the critical stress, τ_c , for plastic deformation is usually much smaller than the theoretical value of $\mu_s/30$ appropriate for an absolutely perfect crystal (see Problem 8.5).

The main method to increase τ_c is by decreasing the mobility of dislocations. There are four mechanisms for inhibiting the motion of dislocations:

- Creation within the metal of particles of mesoscopic dimensions, which act as traps of dislocations (e.g., creation of iron carbide particles in the interior of iron turns it to steel).
- Insertion of foreign atoms that preferably go near the dislocations (because there is more empty space around them to accommodate the foreign atoms). These foreign atoms inhibit the motion of dislocations.
- Creation of short- or long-range order in alloys, which forces the dislocations to move in pairs reducing thus their mobility (see Fig. 8.4).

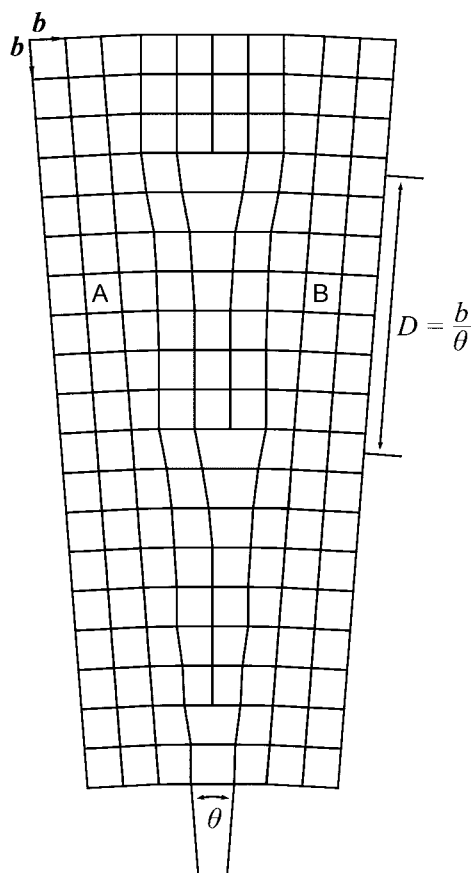


Fig. 8.5. Low-angle θ boundary between grain A and grain B created by a series of neighboring edge dislocations (after Kittel [SS74])

- (d) Work-hardening or strain-hardening, through which the concentration of dislocations becomes so high that their interlocking greatly reduces their mobility. This is the mechanism behind the breaking of a thin sheet of metal or a thin wire by repeated bending; the large local increase of the dislocation concentration reduces their mobility, and consequently, pushes up the critical stress for plastic deformation, τ_c , beyond the critical value for breaking. In other words, the metal or alloy at the bending region ceases to be ductile and becomes brittle.

We mention finally that a bundle of neighboring edge dislocations can give rise to boundaries between microcrystallites of slightly different orientation (*low-angle grain boundaries*). Figure 8.5 shows how this may happen.

Besides low-angle grain boundaries, dislocations are also involved in *stacking faults*, by facilitating the displacements (by non-Bravais vectors) of

consecutive lattice planes. For example, in the fcc perfect lattice, the lattice planes normal to the direction (1,1,1) follow an ABCABCABC... sequence (see Fig. 3.15); a possible stacking fault is as follows: ABABC ABCABC...; another one is the so-called *twinning*: ABCABCABCBCACBAC BA... By inspection of Fig. 3.15, find out what lattice displacements give rise to each of these two stacking faults.

More about dislocations and mechanical failure of materials are presented in the book by Kaxiras [SS83] and references therein.

Surfaces, Interfaces, and Devices

All solids terminate at surfaces. Thus surfaces are always present. Furthermore, the interaction of a solid with its environment takes place mainly through its surface or even exclusively through its surface. Important phenomena such as catalysis, oxidation, crystal growth, etc. occur at surfaces and are controlled by them. Thus, there is a great need to study various properties of surfaces such as their atomic structure and composition, their interactions with external fields and external particles (electrons, ions, atoms, molecules), and the electronic and ionic motion at and near them. Hence, the study of surfaces has grown to a big field called *surface science*, involving both special experimental techniques (see Table 8.3) and theoretical methods designed to face the challenge of the broken periodicity, associated with the very presence of surfaces.

Under ordinary conditions surfaces are very rough and contain foreign molecules loosely bound (*physisorption*) or strongly bound (*chemisorption*). Clean and flat (at the atomic scale) surfaces require special techniques and ultrahigh vacuum (UHV). Even then, the few external lattice planes are subject to *relaxation* and/or *reconstruction*.

Surfaces, besides modifying Bloch waves, can create bound states as well, i.e., states that decay exponentially as the distance from the surface becomes large. These surface states may refer to individual electrons or to collective excitations such as *surface plasmons* and *surface phonons*.

Of great technological interest are the *interfaces* between different material (*heterojunction*) or between the same material with opposite doping in the two sides of the interface (*homojunction*). The reason is that interfaces are of crucial importance for the design and functioning of all electronic devices (rectifiers, photovoltaics, transistors, integrated circuits, solid state lasers, etc.). In Fig. 8.6, some artificial structures of technological interest are shown (schematically).

Heterojunctions are usually under considerable strain and stress with dislocations being an important factor in determining the quality of the junction. Their behavior in the absence or presence of external voltages or under illumination is what determines the performance of the electronic devices.

It must be pointed out that interfaces are also important from the basic physics point of view. Very clean heterojunctions can trap electrons creating

Table 8.3. Experimental techniques for the study of surfaces^a

Acronym ^b	Incident particle field	Emitted particle(s)	Main use
LEED	Electron	Electron	Determination of surface crystal structure
Auger or AES	Electron	Electron	Identification of foreign atoms
APS	Electron	Photon	Identification of foreign atoms
RHEED	Electron	Electron	Determination of surface crystal structure
EELS	Electron	Electron	Determination of energy vs. wavevector for surface waves
UPS	Photon	Electron	Determination of work function, W
XPS	Photon	Electron	Work function, W
ARPES	Photon	Electron	Information re-occupied surface states
ESCA	Photon	Electron	Identification of foreign atoms
SEXAFS	Photon	Absorption measurement	Determination of local environment
IPS	Electron	Photon	Information re non-occupied surface states
FIM	Electric field	Ions	Atomic scale imaging of the surface
FEM	Electric field	Electron	Atomic scale imaging of the surface
STM	Voltage	Electric current	Atomic scale imaging of the surface
AFM	Mechanical force	Movement	Atomic scale imaging of the surface
HREM	Electron	Electron	Atomic scale imaging of the surface

^aFor a short description of these techniques, see the book by Burns [SS77], pp. 692–702

^bFor the full name, see Table H.3

thus a two-dimensional electron gas in which one can test experimentally a wealth of theoretical results. *Various topics of surfaces and interfaces shall be examined in a later chapter.*

Disordered Systems and Localization

This extensive and diverse category of materials includes *glasses* (where the disorder is exclusively, or mainly, positional), *alloys* (where the disorder is mainly compositional), and *amorphous films* (where the disorder is positional

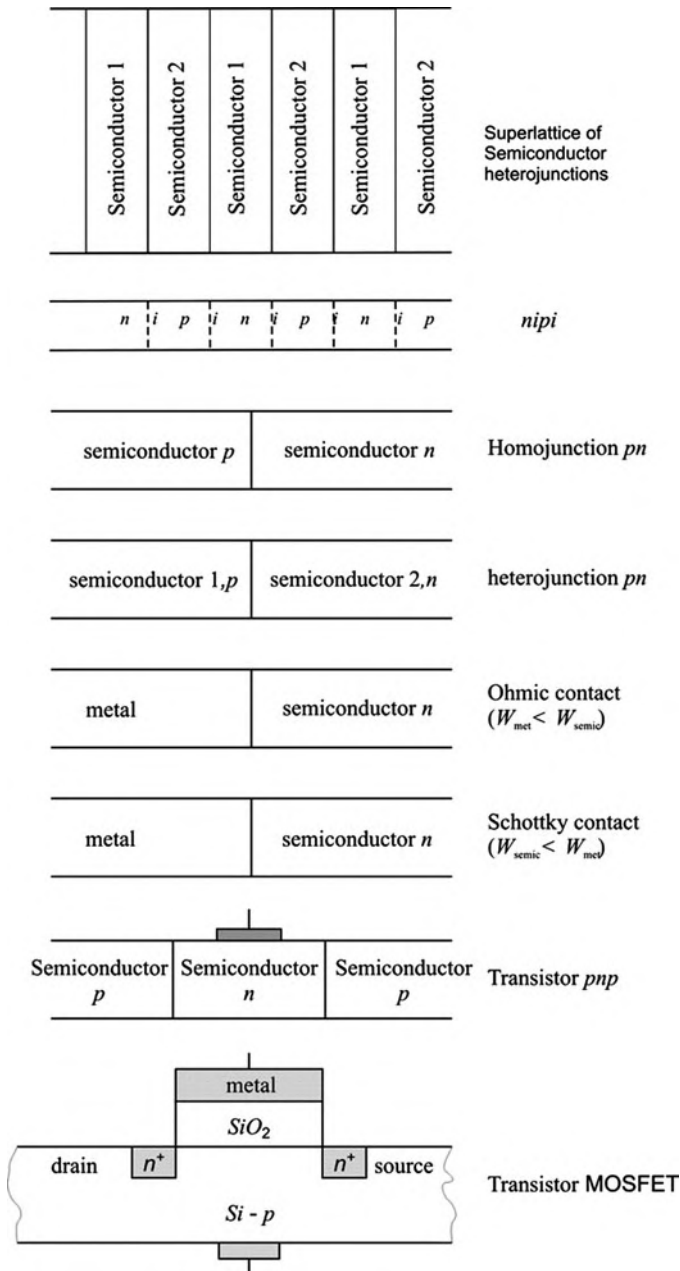


Fig. 8.6. Artificial structures of technological interest involving one or more interfaces (W : work function)

as in glasses but appears as a result of the preparation techniques and the thinness of the film); it also includes some *artificial structures* where the disorder, in spite of being very small, is responsible for the appearance of unexpected novel phenomena. A disordered system emerges also in the case where the concentration of point defects substantially exceeds a certain limit (see Sect. 8.5.1). For example, if the concentration of n and p dopants in semiconductors becomes relatively high, the impurity level in the gap (see Fig. 7.6) gives rise to a narrow band called *impurity band*, which is highly disordered (positionally).

The novel element that disorder introduces is the lack of knowledge regarding the positions of atoms (in glasses and amorphous films) or which type of atom occupies a given lattice point (in crystalline alloys), etc. This lack of detailed knowledge forces us to adopt a probabilistic approach.⁷ This means that, instead of knowing the exact values of the matrix elements of the Hamiltonian, we know only their probability distribution. For example, in binary alloys, $A_x B_{1-x}$, instead of knowing that a given lattice point is occupied by atom A (and hence, the diagonal matrix element being ε_A), we only know the probability, p_A , that this point is occupied by atom A (e.g., $p_A = x$) or by atom B (e.g., $p_B = 1 - x$); hence, the probability of the diagonal matrix elements being ε_A is p_A and being ε_B is p_B .

The novel basic phenomenon associated with disordered systems is the appearance of square-integrable bound eigenstates called **localized eigenstates** (usually in the tails of each band), separated by critical energies called **localization edges**, from the inner part of the band, where the eigenstates are propagating and the spectrum is continuous. (In the localized regions the spectrum is what the mathematicians call *dense point spectrum*; this means that the number of states $R(E)$ (for an infinite system) is *continuous* but nowhere *differentiable*). This dense point spectrum is quite unusual because in all familiar cases continuous spectra are associated with propagating or extended eigenstates and discrete (i.e. non-dense) spectra are associated with bound eigenstates. The physical mechanism responsible for localization and related phenomena is the coherent *multiple scattering*, i.e., the fact that a scattered wave can be scattered again and again and it can interfere (constructively or destructively) with the original wave and other scattered or multiscattered waves (see Sects. 8.6, 8.7, and 18.8.2). Multiple scattering effects are important when the concentration, n_s , of scatterers is high and the individual scattering cross-section, σ_s , is large, i.e., when $\ell \ll n_s^{-1/3}$, where $\ell = 1/n_s \sigma_s$. Notice that the last formula for the mean free path was obtained in Chap. 5 by implicitly neglecting the multiple scattering effects. The argument in favor of this neglect is that constructive and destructive interference effects cancel out, as a result of the randomness in the phases due to the positional and/or compositional randomness of the scatterers. A more careful analysis, to be presented in a later chapter, shows that this cancellation is not complete:

⁷ That is why disordered systems are also referred to as random systems.

destructive interference effects systematically win over the constructive ones. Thus, the multiple scattering effects reduce both the mean free path and the conductivity, and eventually, trap the eigenstates in clusters of neighboring scatterers leading to the phenomenon of localization and the vanishing of the conductivity at $T = 0$ K (if the Fermi level is in the region of localized states).

8.5.2 Electron–Electron Correlations, Quasi-Particles, Magnetic Phases, and Superconductivity

In Problem 2.1, we have shown that a system of two *interacting* particles can be transformed to two *non-interacting* quasi-particles: one has a mass $M = m_1 + m_2$ and coordinate $\mathbf{R} = (m_1\mathbf{r}_1 + m_2\mathbf{r}_2)/M$, and the other has a mass m_1m_2/M and coordinate $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$. Similarly, we have shown that the system of *interacting* ions in a solid can be transformed (within the framework of **A3**) to a system of *non-interacting* phonons. If **A3** is relaxed, we expect to have a system of weakly interacting phonons. In general, we try to transform a system of strongly interacting particles to an equivalent system of weakly interacting quasi-particles. For example, the system of the strongly interacting electrons in a solid can be usually transformed to a system of weakly interacting “dressed” electrons and plasmons; each “dressed” electron consists of a bare electron at its core and a cloud of reduced electronic concentration around it that in combination with the positive ionic background screens the bare Coulomb interaction. The single-particle states $\psi_\ell(\mathbf{r})$ appearing within the framework of the DFT can be thought of as being occupied by non-interacting quasi-particles. This conceptual scheme of reducing approximately a strongly interacting many-body problem to a one-body problem works well when the quasi-particles can be brought in one-to-one correspondence with the actual particles. However, there are cases where this one-to-one correspondence is violated. Coulomb interactions or phonon-mediated attractions may create long-range correlations, which have no analog or correspondence in a non-interacting system. For example, in ferromagnetic materials, the time average magnetic moment, $\mathbf{m}$, of the primitive cell is non-zero in spite of the absence of an external magnetic field. For this to happen in a metal like iron, it is necessary to break the spin up–spin down symmetry through a particular correlation favoring single occupation of states. The quantity $\mathbf{m}$, which quantitatively characterizes the appearance of this long-range correlation, is called *order parameter*. Similarly, in traditional superconducting solids, a phonon-mediated attraction between two electrons *with the help of the rest of them* creates bound electron pairs (the so-called *Cooper pairs*) and reorganizes the ground state of the whole system, as well as its excited states. The order parameter in the superconducting phase is denoted by $\Delta(\mathbf{r})$ and it is connected to the bound pair binding energy; $\mathbf{r}$ is the center of mass of the pair. The DFT is capable of treating ferromagnetism, phonon-mediated superconductivity, and other such phases by incorporating in the energy functional extra terms involving the corresponding order parameter.

Superconductivity is a complex and impressive phenomenon occurring in most metals and alloys (and in other materials) at *very low temperatures* (the highest observed temperature for superconducting transition under normal pressure is 138 K in the thallium-doped compound $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$). The main characteristics of the superconducting state of matter are its zero DC resistivity and its expulsion of the magnetic field $\mathbf{B}$ from the interior of a superconductor (i.e., perfect diamagnetism). Both of these unexpected properties stem from the approximate relation (valid in the gauge $\nabla \cdot \mathbf{A} = 0$)

$$\mathbf{j} = -\frac{e^2 n_s}{mc} \mathbf{A}, \quad (8.48)$$

where n_s is the concentration of “superconducting” electrons to be exactly defined in Chap. 23 (in SI c must be deleted). Equation (8.48) implies that $d\mathbf{j}/dt$, and hence, the electronic acceleration is proportional to the electric field $\mathbf{E}$ (see (A.21)), which means absence of friction. Equation (8.48), known as *London equation*, is for the “superconducting” electrons what Ohm’s equation, $\mathbf{j} = (e^2 n \tau / m) \mathbf{E}$, is for the “normal” electrons (the London equation is further examined in Sects. 22.4 and 22.6). For the traditional phonon-mediated superconductors, there are three crucial steps leading to (8.48):

(a) *Attraction between two electrons inside the solid.*

Indeed, by combining (5.7) with (5.19) and (5.20), and omitting the imaginary part of $\varepsilon(k, \omega)$, we have for the Fourier transform of the dynamically screened Coulomb interaction

$$\mathcal{V}_s(\mathbf{k}, \omega) = \frac{4\pi e^2}{4\pi\epsilon_0 k^2 \varepsilon(k, \omega)} = \frac{4\pi e^2 (\omega^2 - \omega_t^2)}{4\pi\epsilon_0 (ak^2 + k_s^2) (\omega^2 - \omega_k^2)}, \quad (8.49)$$

$$\mathcal{V}_s(\mathbf{k}, \omega) = \frac{4\pi e^2}{4\pi\epsilon_0 (ak^2 + k_s^2)} - \frac{4\pi e^2 (\omega_k^2 - \omega_t^2)}{4\pi\epsilon_0 (ak^2 + k_s^2) (\omega_k^2 - \omega^2)}, \quad (8.50)$$

where $a = 1 + \chi_b$, $\omega_k = c_\ell k$ is given by (5.20), and $\omega_t = c_t k$; $\hbar k = \hbar |\mathbf{k}_1 - \mathbf{k}_2|$ is the momentum transfer between the two electrons of the pair and $\hbar\omega = |\varepsilon_1 - \varepsilon_2|$ is the energy transfer. We see that the first term in (8.50) is a repulsive electron-screened Coulomb interaction, while the second is a phonon-mediated (because of $\omega_k = c_\ell k$ and $\omega_t = c_t k$) interaction, which, for $\omega < \omega_k$, is negative, i.e., attractive. Hence, phonons for small values of the difference $|\varepsilon_1 - \varepsilon_2|$, i.e., for electrons very close to the Fermi level, create an attraction that may be stronger than the screened Coulomb repulsion.

(b) *Creation of bound pairs (Cooper pairs) in the presence of the Fermi sea of electrons.*

Consider a pair of electrons each with energy just above the Fermi level. For $T = 0$ K, all states with energy less than the Fermi level are occupied by the other electrons, and hence, are unavailable. The result of this unavailability, as we shall see in a later chapter, is that the relative motion of the two electrons

is effectively two-dimensional. However, in 2D, any attractive potential always creates at least one bound state (see Problem 2.11); for weak potential $\mathcal{V}_s$, the binding energy, ε_b , is given by the expression

$$\varepsilon_b = E_m \exp\left(-\frac{1}{\rho |\varepsilon|}\right) \quad (8.51)$$

where, as we shall show in Sects. 23.2–23.4, $E_m \simeq 4\hbar\omega_D$ (in the current case of phonon-mediated attraction), ρ is the DOS at the Fermi level multiplied by V_o/V , $|\varepsilon| = \lambda/\rho$, and λ is the dimensionless electron–phonon coupling defined in Chap. 5; V_o is the equivalent volume of the potential well. Notice that (8.51) is non-analytic in ε , showing that the processes leading to the formation of Cooper pairs are non-perturbative.

- (c) *“Condensation” of Cooper pairs (being bosons) into a coherent quantum state.*

Since the “condensed” Cooper pairs move in a fully correlated way as a single entity, collision of a minute fraction of them at each moment is unable to degrade the flow of the whole coherent entity; hence, the continuation of the perpetual motion of “condensed” pairs without the application of any external force. As the temperature is raised from absolute zero, some of the Cooper pairs break into individual electrons; thus, the concentration, $n_c = 2n_s$, of Cooper pairs is a decreasing function of temperature and vanishes at the temperature T_c of superconducting transition. The latter is of the order of ε_b ; more explicitly,

$$T_c \simeq 1.13 \Theta_D \exp\left(-\frac{1}{\lambda}\right), \quad (8.52)$$

where Θ_D is the Debye temperature: $\Theta_D \simeq \hbar\omega_D/k_B$.

Equation (8.52) has been obtained by Bardeen, Cooper, and Schrieffer (BCS) in their classic paper [8.12] on the theory of superconductivity. More accurate formulae and calculational schemes for obtaining T_c have been developed since then.

8.5.3 Electron–Phonon Interactions, Transport Properties, Superconductivity, and Polarons

We have already seen that electron–phonon interactions (i.e., violation of **A1**) are essential for metallic resistivity at high temperatures; furthermore, this type of interaction provides a well-documented mechanism for an indirect electron–electron attraction,⁸ which is crucial for the phenomenon of superconductivity.

⁸ For the so-called high T_c superconductors, it is not clear to what extent the indirect electron attraction is due to phonons or to other mechanisms possibly in combination with phonons.

We mentioned before that electrons in metals are “dressed” by a cloud of holes (missing electrons) that follow the bare electron in its motion. Similarly, each mobile electron in all kinds of solids carries with it a lattice polarization, i.e., a cloud of phonons as a result of el-ph interaction. The composite particle, electron plus phonon cloud, is called *polaron*. In very good metals, we expect that the “dressing” by holes to be more important than the “dressing” by phonons; on the other hand, in ionic solids the phonon “dressing” will be by far the dominant mechanism. If the electron-phonon coupling is very strong ($\lambda \gtrsim 5$), the extent of the lattice deformation induced by a moving electron becomes of the order of the lattice constant and the electron is trapped within it; the resulting composite entity is called *small polaron*; it is very heavy and hardly moves. Such strong electron-phonon coupling may also lead to the trapping of two electrons within an atomic scale lattice deformation thus creating an entity called *small bipolaron*. The small bipolaron may be viewed as the ultimate “unfortunate fate” of a Cooper pair; the latter has typically an extent ξ_0 of the order of 10^3 Å. As the el-ph coupling increases, ξ_0 becomes smaller and smaller; eventually, when the length ξ_0 becomes of the order of interatomic distance, the Cooper pair would be transformed to an immobile small bipolaron and the material would become an insulator instead of a very high T_c superconductor. Molecular hydrogen under ordinary pressure may be viewed as the outcome of the instability of metallic hydrogen toward formation of small bipolarons, the latter being the hydrogen molecules.

Electron-phonon interaction does not influence only the properties of electrons; it affects phonons as well. For example, ultrasonic attenuation in metals is caused to a large extent by the interaction of the ultrasound with the conduction electrons (See [SS99], Chap. 17).

It must be stressed that the concept of a quasi-particle, be it bosonic (such as a phonon, a plasmon, or a Cooper pair), or fermionic (such as polarons, or hole-dressed electron), is not restricted to periodic media but it can be extended to alloys, amorphous materials and other disordered systems as well. In this case, because of the absence of translational symmetry, one is forced to employ further approximations or to resort to numerical solutions of finite systems (modern day computers can handle systems consisting of a few hundred particles).

8.5.4 Phonon-Phonon Interactions, Thermal Expansion, Melting, Structural Phase Transitions, Solitons, Breathers

The harmonic approximation (**A3**) was based on the assumption that the amplitude of ionic oscillations is very small. There are several situations where the harmonic approximation is violated and anharmonic effects become important; the latter are equivalent to phonon-phonon interactions (omitted within the framework of **A3**).

The most obvious and widespread violation of **A3** is the thermal expansion; if the ionic motion was truly harmonic, the thermal expansion of insulators would be zero, since $\partial\omega_D/\partial V$ would be zero (see (4.99) and (4.88)). More dramatic is the melting of solids: as the temperature rises, the amplitude of the ionic vibrations (especially of those associated with transverse phonons) increases, and at some critical temperature T_m , a first-order phase transition takes place associated with the melting of the lattice, the full collapse of **A3**, and the discontinuous vanishing of the shear modulus, μ_s .

Structural phase transition is another common case where anharmonic effects are of central importance. To be specific, let us consider Fig. 7.4, which show that as the ionicity of tetravalent compounds increases, the lattice structure changes from zincblende to, e.g., NaCl. This structural change can take place, if neighboring $x = \text{const.}$ planes move along opposite directions $(0, 1, \bar{1})$ and $(0, \bar{1}, 1)$ in an alternating way. At the transition point, such movement occurs spontaneously without any restoring force opposing it. Hence, under those circumstances, we have no small-amplitude oscillation but large permanent displacement. Even before we reach the critical value of ionicity for such a structural phase transition, the eigenfrequency of the corresponding lattice vibration would be reduced (signaling a weakening of the restoring force) and would tend to zero at the critical ionicity (at which the restoring force becomes zero). The conclusion is that a very low eigenfrequency (*soft mode*), which tends to zero as some parameter varies, is associated with large oscillations and eventually with permanent displacement leading to a structural phase transition.

Anharmonicity, i.e., a force that depends in a non-linear way on the ionic displacement, allows, under certain conditions, large-amplitude solutions of finite spatial extent that are robust and may propagate a long distance retaining their identity. Such non-linear ionic solutions are called *solitons* [8.13–8.15]. In addition, strong anharmonicity in discrete lattices may lead to spatially localized time-periodic solutions called *discrete breathers* [8.16, 8.17] or lattice solitons. Non-linearity makes the amplitude of these oscillations frequency dependent and discreteness induces gaps in the linearized (phonon) spectrum; these gaps are “home” of stable discrete breathers.

Finally, phonon–phonon scattering processes, which do not conserve the crystal momentum (called *Umklapp processes*), contribute to the thermal resistivity especially in insulators where phonons are the only entities transporting thermal energy.

8.5.5 Disorder and Many Body Effects in Coexistence

There are phenomena in mesoscopic and other systems at very low temperatures where disorder, el–el interactions, and el–ph interactions influence each other so that all play in tandem an important role. The physical interpretation and the quantitative understanding of these phenomena, where disorder

and many-body effects may reinforce or may compete with each other, pose challenging problems.

8.5.6 Quantum Informatics and Solid State Systems

The development of information-storing, retrieving, and processing devices based on the exploitation of coherence in quantum systems is one of the exciting prospects of current research efforts. The main obstacle in implementing quantum information processing devices is decoherence induced by interaction with the environment. Among the systems investigated as possible bits of quantum information (qubits), solid state systems such as quantum dots (see Sect. 19.7) and superconductors (see Sect. 8.5.2 and Chaps. 22 and 23) provide possible paths, actively pursued, towards the ultimate goal (8.18)–(8.22).

8.6 Key Points

- The four basic approximations (Born–Oppenheimer, one-electron, harmonic, and periodicity), which make the qualitative understanding and the quantitative calculations tractable, were presented.
- The DFT, which plays a key role in justifying the one-electron approximation and implementing the calculations of electronic properties, was also presented. An explicit recipe for obtaining the self-consistent effective one-electron potential was outlined.
- There are several phenomena, the explanation and quantitative calculation of which require us to go beyond the four basic approximations. This is usually achieved through perturbation theory or other natural extensions of the conceptual framework based on **A1–A4**. However, phenomena appear that require more advanced formalisms (and careful experiments) to identify the specialized correlations responsible for their existence and necessary for their quantitative treatment.
- Several such phenomena related to the violation of one or more of the four basic approximations were outlined:
 - (a) Breakdown of periodicity through *point defects* or line defects (*dislocations*) or at *surfaces* and *interfaces*, or finally, in *glasses*, *alloys*, *amorphous films*, etc.
 - (b) Specialized el–el correlations leading to phenomena such as *superconductivity*, *magnetic phases*, etc.
 - (c) Electron–phonon interactions creating attractive phonon-mediated el–el interactions, *polarons*, etc.
 - (d) Phonon–phonon interactions, i.e., violation of the harmonic approximation, being responsible for phenomena such as *melting*, *structural phase transitions*, etc.

8.7 Problems

- 8.1 Starting from (8.5), prove (8.6).
 8.2 Calculate the exchange energy E_x according to (8.25) and (8.26).
 8.3 Prove (8.33) within the framework of the $X - \alpha$ approximation.
 8.4 Show that $d_s \gg \sigma_s^{1/2}$ is equivalent to $\ell \gg d_s$.
 8.5 Consider Fig. 8.1 in the absence of dislocation. Argue that the shear stress τ vs. displacement x can be approximated by a sinusoidal relation

$$\tau = \left(\frac{\mu_s a}{2\pi d} \right) \sin \left(\frac{2\pi x}{a} \right), \quad (8.53)$$

where d is the interplanar spacing in the y -direction, while a is the lattice spacing in the x -direction. What is the critical shear stress, τ_c , for plastic deformation according to (8.53). How does this value compare with those in Table 8.2? (See Kittel, 8th ed., [SS74], p. 599.)

- 8.6 Using Maxwell's equations, the definition of $\mathbf{A}$, and (8.38), prove that the magnetic field, $\mathbf{B}$, is zero in the bulk of a superconductor (except at a thin surface layer where $\mathbf{B}$ drops exponentially from its value just outside the superconductor to zero in the bulk. (Consider a single plane surface separating the superconductor from the vacuum.)
 8.7 Prove (8.39) and (8.40).
 8.8 Examine the problem of a bound state within the framework of the simplest TBM, where

$$\hat{H}_0 = V_2 \sum_{nm} |n\rangle \langle m| \quad (8.54)$$

and the perturbation $\hat{H}_1$ is

$$\hat{H}_1 = -\varepsilon |0\rangle \langle 0|. \quad (8.55)$$

Use the resolvent (or Green's function) formulae (B.58)–(B.60) to show that the relation,

$$\langle 0 | \hat{G}_0(\varepsilon_b) \hat{H}_1 | 0 \rangle = 1,$$

determines the bound eigenenergy, ε_b . Express the matrix element $\langle n | \hat{G}_0(E) | n \rangle$ in terms of the unperturbed DOS per site, $\rho_0(E)$. What is the connection between the van Hove singularity of $\rho_0(E)$ at the band edge and the need or not of a critical value of ε for bound state formation?

Further Reading

- In the book by Kaxiras [SS83], a derivation of E_x as well as a clear presentation of DFT (pp. 58–66) is given (pp. 47–54).
- The subject of dislocations and failure of solids is treated in many books on solid state, such as Kittel [SS74], Kaxiras [SS83], Marder [SS82], etc.

More About Periodicity & its Consequences

Crystal Structure and Ionic Vibrations

Summary. We show how elastic scattering of external particles (usually photons or neutrons) by a crystal allows us to determine experimentally the lattice structure. We also show that the inelastic scattering of thermal neutrons due to phonon absorption or emission reveals the phononic dispersion relation; a comparison with the corresponding theoretical results is presented. Explicit expressions for these elastic and inelastic cross-sections are obtained.

9.1 Experimental Determination of Crystal Structures

The lattice structure of a crystalline solid is determined experimentally by the elastic scattering of *X-rays* or *neutrons*; in special cases, such as the surface lattice structure, *electron* elastic scattering is employed (see Table 8.1). X-ray photons, being *neutral*, weakly interacting with the solid, and having a *wavelength comparable to the lattice spacing*, are ideal for penetrating in the bulk of the solid and giving rise to constructive interference patterns; the latter are directly dependent on the lattice structure. Thermal neutrons (i.e., of energy around 25 meV) are also very suitable for determining the crystalline structure of solids; furthermore, thermal neutrons, in contrast to X-rays, can reveal the magnetic ordering as well, in cases where this does not coincide with the positional ordering of atoms, as in antiferromagnets. The main disadvantage of neutrons is that they are not easily available.

Let us consider a plane wave of X-rays or neutrons impinging upon an immobile particle (electron or nucleus) located at the origin; this particle acts as an elastic scattering center producing at large distances r a spherical outgoing wave. The wave function of the incident wave becomes then:

$$\psi(\mathbf{r}) = e^{i\mathbf{k}_i \cdot \mathbf{r}} + f(\theta, \phi) \frac{e^{ik_f r}}{r}, \quad (9.1)$$

where the initial wavevector, $\mathbf{k}_i$, determines the direction of propagation and the energy quantum of the undisturbed plane wave; $f(\theta, \phi)$ is the so-called

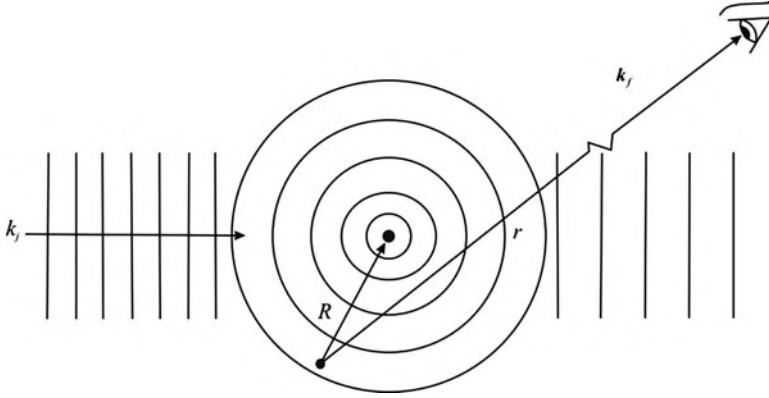


Fig. 9.1. A beam of external particles (photons, or neutrons) each of momentum $\hbar \mathbf{k}_i$ is scattered off a particle (electron or nucleus) located at $\mathbf{R}$. If the scattering is elastic the final energy $E_f = \hbar c k_f$ or $\hbar^2 k_f^2 / 2m_n$ for photons or neutrons respectively, is equal to the initial energy E_i ; $\hbar \mathbf{k}_f$ is the final momentum ($k_f = k_i$)

scattering amplitude along the direction θ, ϕ coinciding with the direction of the final wavevector $\mathbf{k}_f$; $|\mathbf{k}_f| = |\mathbf{k}_i|$ because of the elastic character of the scattering. If the scattering center is located at the point $\mathbf{R}$, (9.1) is modified as follows:

$$\psi(\mathbf{r}) = e^{i\mathbf{k}_i \cdot \mathbf{r}} + e^{i\mathbf{k} \cdot \mathbf{R}} f(\theta, \phi) \frac{e^{i\mathbf{k}_f \cdot \mathbf{r}}}{r}, \quad (9.2)$$

where $\mathbf{k} = \mathbf{k}_i - \mathbf{k}_f$ is the momentum transfer (over $\hbar$) to the scattering center (Fig. 9.1).

If there are many identical particles (acting as scattering centers) located at different points $\mathbf{R}$, the total scattering amplitude f_t is equal to¹

$$f_t = f \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}}. \quad (9.3)$$

Equation (9.3) can be recast as an integral by introducing the concentration of particles $n(\mathbf{r})$

$$\begin{aligned} n(\mathbf{r}) &= \sum_{\mathbf{R}} \delta(\mathbf{r} - \mathbf{R}), \\ f_t &= f \int_V d^3r \, n(\mathbf{r}) e^{i\mathbf{k} \cdot \mathbf{r}} \equiv f \tilde{n}^*(\mathbf{k}), \end{aligned} \quad (9.4)$$

where $V (\rightarrow \infty)$ is the volume in which all particles are located, and $\tilde{n}(\mathbf{k})$ is the Fourier transform of $n(\mathbf{r})$. Now, if $n(\mathbf{r})$ is a periodic function, i.e.,

¹ To arrive at (9.3) one has to omit the multiple scattering effects. If the latter were included, the f factor in the rhs of (9.3) would be replaced by a complicated function of f and $\{\mathbf{R}\}$, but the sum $\sum_{\mathbf{R}} \exp(i\mathbf{k} \cdot \mathbf{R})$ would remain unaffected.

if $n(\mathbf{r} + \mathbf{R}_n) = n(\mathbf{r})$, where $\{\mathbf{R}_n\}$ form a Bravais lattice, we have the following relation for any $\mathbf{R}_n$

$$\tilde{n}(\mathbf{k}) = \tilde{n}(\mathbf{k})e^{-i\mathbf{k} \cdot \mathbf{R}_n}. \quad (9.5)$$

Problem 9.1t. Prove (9.5) by taking into account the periodicity of $n(\mathbf{r})$ and (9.4).

Equation (9.5) implies that $\tilde{n}(\mathbf{k})$ is zero unless $\exp(-i\mathbf{k} \cdot \mathbf{R}_n)$ is equal to one; but $\exp(-i\mathbf{k} \cdot \mathbf{R}_n) = 1$ for any $\mathbf{R}_n$ means that $\mathbf{k}$ is a vector $\mathbf{G}$ of the reciprocal lattice. Thus, the total scattering amplitude from a periodic system is in general zero; only in some particular directions (if any) determined by $\mathbf{k}_f$ (which have to satisfy the relation, $\mathbf{k}_f = \mathbf{k}_i + \mathbf{G}_m$) there are scattered beams called *diffracted beams*. In other words,

$$f_t \sim \tilde{n}^*(\mathbf{k}) = 0, \quad \mathbf{k} \neq \mathbf{G}. \quad (9.6)$$

Taking the inverse Fourier transform of (9.4), and in view of (9.6), we arrive at the following theorem:

Any periodic function $n(\mathbf{r})$ can be expanded in a Fourier series (not in a Fourier integral) as follows

$$n(\mathbf{r}) = \frac{1}{V_{pc}} \sum_{\mathbf{G}} S_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}}, \quad (9.7)$$

where

$$S_{\mathbf{G}} = \int_{V_{pc}} d^3r \, n(\mathbf{r}) e^{-i\mathbf{G} \cdot \mathbf{r}} = \frac{\tilde{n}(\mathbf{G})}{N_{pc}}. \quad (9.8)$$

The integration in (9.8) is over the volume V_{pc} of any primitive cell; $S_{\mathbf{G}}$ is the same for all primitive cells, and hence, the last relation in (9.8) is equivalent to (9.4), since N_{pc} is the total number of primitive cells in the periodic system. The quantity $S_{\mathbf{G}}$ is called the *structure factor* of the primitive cell. The proof of (9.7) and (9.8) follows immediately by writing $n(\mathbf{r})$ in terms of its Fourier transform

$$n(\mathbf{r}) = \int \frac{d^3k}{(2\pi)^3} \tilde{n}(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{r}}, \quad (9.9)$$

$$= \frac{1}{V} \sum_{\mathbf{k}} \tilde{n}(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{r}}, \quad (9.10)$$

and taking into account (9.6).

We repeat once more that an incoming monochromatic wave scattered elastically by a periodic system gives rise only to one or more diffracted beams in some particular directions and only² when the difference between the incoming wavevector $\mathbf{k}_i$ and the scattered wavevector $\mathbf{k}_f$ is equal to a vector of the reciprocal lattice

² It is possible to have zero scattering even if the difference $\mathbf{k}_i - \mathbf{k}_f$ is equal to a vector $\mathbf{G}$ of the reciprocal lattice; this happens if the integral in (9.8) is zero for

$$\mathbf{k}_i - \mathbf{k}_f = \mathbf{G}. \quad (9.11)$$

From (9.11), it follows that

$$2\mathbf{k}_i \cdot \mathbf{G} = G^2, \quad (9.12)$$

or

$$k_{iG} = \frac{G}{2}, \quad (9.13)$$

where k_{iG} is the projection of $\mathbf{k}_i$ on $\mathbf{G}$: $k_{iG} \equiv \mathbf{k}_i \cdot \mathbf{G}/G$.

Problem 9.2t. Prove (9.12) and (9.13) by transferring $\mathbf{k}_i$ in (9.11) to its rhs, squaring the resulting equation, and taking into account that $\mathbf{k}_i^2 = \mathbf{k}_f^2 = k^2$.

In a similar way we show that

one or more reciprocal vectors. To pursue this matter further let us assume that the concentration $n(\mathbf{r})$ can be written as a sum of terms each one of which is in one-to-one correspondence with the atoms of the solids

$$n(\mathbf{r}) = \sum_{\mathbf{R}} \sum_s n_s(\mathbf{r} - \mathbf{R} - \mathbf{r}_s),$$

where $\mathbf{R}$ is the vector defining each primitive cell, and $\mathbf{R} + \mathbf{r}_s$ is the position of the s^{th} atom, in the $\mathbf{R}$ primitive cell. Substituting in the integral defining S_G we have

$$S_G = \frac{1}{N_{pc}} \sum_{\mathbf{R}} \sum_s \int_V d^3r n_s(\mathbf{r} - \mathbf{R} - \mathbf{r}_s) e^{-i\mathbf{G} \cdot \mathbf{r}},$$

where the integral is now over the whole space and as a result, the total number, N_{pc} , of primitive cells appears in the denominator. By introducing the vector $\boldsymbol{\rho} \equiv \mathbf{r} - \mathbf{R} - \mathbf{r}_s$, the exponential can be written as follows

$$\exp(-i\mathbf{G} \cdot \mathbf{r}) = \exp(-i\mathbf{G} \cdot \boldsymbol{\rho}) \exp(-i\mathbf{G} \cdot \mathbf{R}) \exp(-i\mathbf{G} \cdot \mathbf{r}_s).$$

Since $\exp(-i\mathbf{G} \cdot \mathbf{R}) = 1$ and $d^3r = d^3\rho$, we have

$$S_G = \frac{1}{N_{pc}} \sum_{\mathbf{R}} \sum_s e^{-i\mathbf{G} \cdot \mathbf{r}_s} g_s = \sum_s e^{-i\mathbf{G} \cdot \mathbf{r}_s} g_s, \\ g_s \equiv \int_V d^3\rho n_s(\boldsymbol{\rho}) e^{-i\mathbf{G} \cdot \boldsymbol{\rho}},$$

and the integration is over the whole space. The quantity g_s is called **atomic form factor**. A reasonable estimate of g_s for X-rays or charged particles can be obtained by equating $n_s(\boldsymbol{\rho})$ with the concentrations of electrons in isolated atoms. This equation shows how S_G can be zero in the case where there are more than one atom in the primitive cell. For example, let us assume that we have two identical atoms ($g_1 = g_2 = g$) within the primitive cell, one at $\mathbf{r}_1 = 0$, and the other at $\mathbf{r}_2$ such that for a particular $\mathbf{G}$, $\mathbf{G} \cdot \mathbf{r}_2 = \pi$. Then, $S_G = g(1 + e^{-i\pi}) = g(1 - 1) = 0$ for this particular $\mathbf{G}$. In problem 9.2, we discuss what happens if one considers the unit cell of a lattice instead of the primitive cell.

$$2\mathbf{k}_f \cdot \mathbf{G} = -G^2, \quad (9.14)$$

$$k_{fG} = -\frac{G}{2}, \quad (9.15)$$

where k_{fG} is the projection of $\mathbf{k}_f$ on $\mathbf{G}$.

Equation (9.13) means that the tip of the initial wavevector $\mathbf{k}_i$ lies on a plane perpendicular to $\mathbf{G}$ and passing through its middle point. In other words, to have diffracted beams at all in a periodic system, it is necessary that the tip of the incoming monochromatic wavevector lies on a Bragg plane. Similarly, (9.15) means that the tip of the final wavevector lies on the Bragg plane perpendicular to $-\mathbf{G}$ and passing through its middle point. Thus, (9.11) together with $k_f^2 = k_i^2$ is equivalent to

$$\mathbf{k}_i = \frac{\mathbf{G}}{2} + \mathbf{a}, \quad (9.16)$$

$$\mathbf{k}_f = -\frac{\mathbf{G}}{2} + \mathbf{a}, \quad (9.17)$$

where $\mathbf{a} = \mathbf{k}_i - (\mathbf{G}/2)$ lies on the Bragg plane defined by $\mathbf{G}$, and hence, it is perpendicular to $\mathbf{G}$ as shown in Fig. 9.2. From this figure it follows that $\sin \theta = (G/2)/k$, or $2 \sin \theta = \lambda G/2\pi$, where λ is the wavelength of the incoming monochromatic beam. In Problem 9.3s, the readers are asked to show that

$$G = 2\pi n/d_p, \quad (9.18)$$

where n is a positive integer and d_p is the distance between nearest neighbor planes of the *direct lattice* that are perpendicular to $\mathbf{G}$. Replacing this expression of $\mathbf{G}$ in the equation $2 \sin \theta = \lambda G/2\pi$ we find the well-known Bragg result

$$2d_p \sin \theta = n\lambda. \quad (9.19)$$

If the orientation of the crystalline solid relative to the incoming monochromatic beam is chosen randomly, it is almost certain that the tip of $\mathbf{k}_i$ will

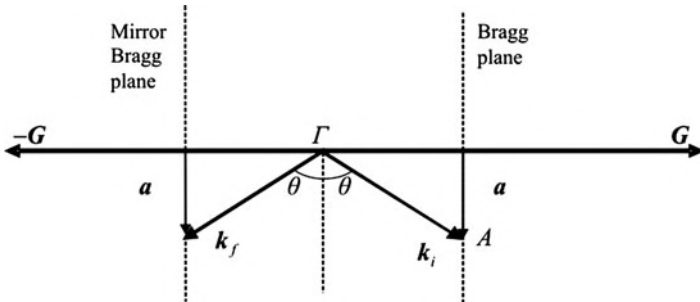


Fig. 9.2. Incoming wavevector $\mathbf{k}_i$ and wavevector $\mathbf{k}_f$ of the elastically diffracted beam; the tip of $\mathbf{k}_i$ has to lie on a Bragg plane, while the tip of $\mathbf{k}_f$ lies on the mirror Bragg plane. The Γ point is the origin ($\mathbf{k} = 0$) of the reciprocal space

not lie on a Bragg plane and thus no diffracted beam will appear. However, if the crystal will be rotated relative to $\mathbf{k}_i$, the reciprocal lattice and the Bragg planes being rigidly attached to it will also be rotated. Hence, as the rotation continues, the tip of the constant vector $\mathbf{k}_i$, at some point would lie on a Bragg plane, provided that $2|\mathbf{k}_i|$ is larger than the minimum nonzero value of $|\mathbf{G}|$. This inequality can be recast in the form

$$\lambda \leq c_1 d, \quad (9.20)$$

where d is the distance between nearest neighbor atoms in the lattice and c_1 is a numerical constant of the order of unity ($c_1 = 2\sqrt{2/3} = 1.633$ for **bcc** and **fcc**, and $c_1 = 4\sqrt{2/3} = 3.266$ for **hcp**). If we take as typical values $c_1 \simeq 1.6$ and $d \simeq 2.5\text{\AA}$, we have $\lambda \lesssim 4\text{\AA}$ or

$$\hbar\omega \gtrsim 3.1\text{ keV} \quad \text{for X-rays}, \quad (9.21)$$

$$\varepsilon \gtrsim 5.1\text{ meV} \quad \text{for neutrons}, \quad (9.22)$$

$$\varepsilon \gtrsim 9.4\text{ eV} \quad \text{for electrons}. \quad (9.23)$$

Actually, considerably larger values of $\hbar\omega$ or ε are used in order to produce more than one diffracted beams. For this to happen, the tip of $\mathbf{k}_i$ (point A in Fig. 9.2) must lie on more than one Bragg planes.

To summarize our analysis: For a monochromatic wave, propagating within a periodic system, to give rise to any diffracted³ beam (i.e., to undergo any scattering at all), the following conditions must be satisfied:

1. The wavelength must be smaller than a distance of the order of the interatomic spacing (see (9.19)).
2. The initial wavevector $\mathbf{k}_i$ placed with one end at the origin of the reciprocal space must have the other end on a Bragg plane. If the tip of $\mathbf{k}_i$ lies on two or more Bragg planes there would be in general two or more diffracted beams. With the first condition satisfied, the second can be met by:
 - (a) A proper rotation of the crystalline solid with respect to the incoming beam, the latter being of fixed direction (Ewald's method).
 - (b) The powder method, according to which the crystal is broken into micrograins of random orientation. Some of these micrograins would satisfy condition (2), producing thus diffracted beams.
 - (c) An intense nonmonochromatic initial beam of large spectral width, so that some of its $\mathbf{k}_i$ components would satisfy condition (2).

From a diffracted beam, we determine the direction of $\mathbf{k}_f$ (its magnitude is known since $k_f = k_i$). Having $\mathbf{k}_f$ and $\mathbf{k}_i$, we can find $\mathbf{G} = \mathbf{k}_i - \mathbf{k}_f$. Having various $\mathbf{G}$'s, we can use (3.14) to obtain by inversion the direct lattice.

³ Diffraction must not be confused with reflection and refraction, which are surface or interface phenomena. On the contrary, diffraction is a bulk phenomenon completely unrelated to surfaces and interfaces.

The basic equation, $\mathbf{k} = \mathbf{G}$, where $\mathbf{k} \equiv \mathbf{k}_i - \mathbf{k}_f$, can be written in an equivalent way by multiplying it with the basic vectors, $\mathbf{a}_i$ ($i = 1, 2, 3$) of the direct lattice and taking into account (3.15) and (3.17):

$$\mathbf{a}_i \cdot \mathbf{k} = 2\pi m_i, \quad i = 1, 2, 3, \quad (9.24)$$

where m_i are integers such that $|m_1| + |m_2| + |m_3| \geq 1$. Equations (9.24) are known as *Laue's equations*. For a given $m_1 \neq 0$, $\mathbf{k}$ lies on the surface of a cone the axis of which coincides with $\mathbf{a}_1$. Similarly, $\mathbf{k}$ must also lie on the surface of two other cones, the axes of which coincide with $\mathbf{a}_2$ and $\mathbf{a}_3$ respectively (assuming m_2 and $m_3 \neq 0$). Hence, for (9.24) to be satisfied, the three cones corresponding to $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ must have a common intersection. For this improbable coincidence to take place the magnitude of $\mathbf{k}_i$ must exceed a minimum value so that $a_i k > 2\pi$ and an appropriate orientation of $\mathbf{k}_i$ relative to the crystal must be chosen, as it was discussed before. The main physical conclusion of this section is as follows:

A periodic medium, during a scattering event, can only emit or absorb a crystal wavevector necessarily equal to a vector of the reciprocal lattice. This statement is valid not only during the interaction of a periodic medium with a single external wave, but in the more general case involving two or more interacting waves such as those shown in Fig. 9.3. In other words, during scattering events taking place within a periodic medium, the total crystal momentum is conserved *up to a vector of the reciprocal lattice* (times $\hbar$):

$$\sum_i \mathbf{k}_i = \sum_f \mathbf{k}_f + \mathbf{G}. \quad (9.25)$$

In (9.25) the sum over $i(f)$ is over all the initial (final) wave vectors.

If $\mathbf{G} = 0$, the scattering process is called *normal*.

If $\mathbf{G} \neq 0$, the scattering process, following its German name, is called *Umklapp*.

Equation (9.25) generalizes (9.11) and it can be proved in a similar way. Its physical meaning is that a periodic system, during a scattering event, can absorb (or emit) a crystal momentum equal to $\hbar$ times a vector of the reciprocal lattice. Recall that a uniform system cannot absorb or emit any nonzero momentum.

9.2 Experimental Determination of the Frequency vs. Wavevector Relation for Phonons

The main experimental technique for determining phonon dispersion relations, $\omega = \omega_s(\mathbf{q})$, is *inelastic neutron scattering*. Neutrons are ideal for this purpose: First, they penetrate well inside the solid (and thus sample the bulk phonons), because they are neutral and their interaction with matter is not as strong as that of external charged particles (which stay close to the surface and thus

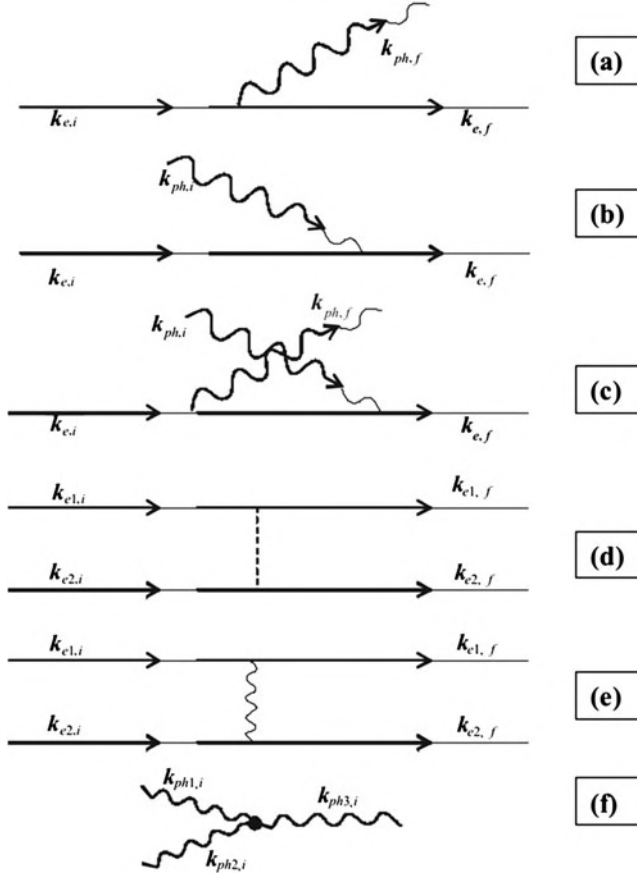


Fig. 9.3. Examples of scattering processes involving electrons and/or phonons. ((a) and (b)): Inelastic scattering of an electron due to the emission (*Stokes event*) or absorption (*anti-Stokes event*) respectively of a phonon. (c): A phonon is emitted by an electron which subsequently absorbs another phonon. (d): Two electrons are scattered off each other as a result of their Coulomb interaction. (e): Two electrons interact by exchanging a phonon. (f): As a result of a third-order process in the ionic displacement potential two phonons disappear giving rise to a third phonon

sample the surface phonons). Second, the maximum of the wavevector, k_i , required to cover the whole BZ, $k_i \simeq 10^8 \text{ cm}^{-1}$, corresponds to a neutron energy of only 2 meV, i.e., smaller than a typical phonon energy (of a few tens of meV). Thus, a neutron of $k_i \simeq 10^8 \text{ cm}^{-1}$ by absorbing a phonon of energy, let us say, of 25 meV will come out of the sample with an energy of 27 meV clearly distinguishable from the initial energy of 2 meV. To appreciate this point, consider an alternative possibility: a photon as an incident particle (instead of a neutron) of the same wavenumber $k_i \simeq 10^8 \text{ cm}^{-1}$; its energy ($\hbar\omega = \hbar ck_i$) would be now 1,973.269 eV, i.e., in the X-rays range.

By absorbing the same phonon of 0.025 eV, the photon would come out with an energy 1,973.294 eV, hardly distinguishable from the initial photon energy (an extreme resolution of 10^{-5} to 10^{-6} is required for separating in this case the elastic from the inelastic peak). If one is to employ optical photons in the range of around 2 eV (from a laser beam), their wavenumber would be in the range of around 10^5 cm^{-1} , i.e., about 1% of the BZ. Thus, these photons, in contrast to the neutrons, can be used to obtain the phonon frequency only at the center of the BZ and its immediate vicinity. Usually, the inelastic scattering of an optical photon accompanied by the emission or absorption of an *acoustic phonon* is called *Brillouin scattering*, while the one associated with the emission or absorption of an *optic phonon* is called *Raman scattering*.

The inelastic scattering of an external particle (be it neutron or photon, etc) due to the emission or absorption of a phonon obeys the conservation laws for the (crystal) momentum and the energy

$$\hbar \mathbf{k}_f - \hbar \mathbf{k}_i = \pm \hbar \mathbf{q}, \quad (9.26)$$

$$\varepsilon_f - \varepsilon_i = \pm \hbar \omega_s(\mathbf{q}), \quad (9.27)$$

where the upper signs refer to the absorption and the lower to the emission of a phonon; $\hbar \mathbf{k}_f$, $\hbar \mathbf{k}_i$ are the final and initial momenta of the external particle, and ε_f , ε_i are the corresponding energies (for a neutron $\varepsilon_j = \hbar^2 k_j^2 / 2m_n$, $j = f, i$ and m_n is the neutron mass); finally $\mathbf{q}$ is the crystal wavevector of the absorbed or emitted phonon of polarization s and eigenfrequency $\omega_s(\mathbf{q})$ (notice that $\mathbf{q}$ is not restricted to the first BZ, i.e., $\mathbf{q} = \mathbf{q}_{1\text{BZ}} + \mathbf{G}$ where $\mathbf{G}$ is any vector of the reciprocal lattice).

Knowing the initial $\mathbf{k}_i$ and measuring the final $\mathbf{k}_f$, we determine both $\mathbf{q}$ (from (9.26)) and $\omega_s(\mathbf{q})$ (from (9.27) taking into account that $\varepsilon_j = \hbar^2 k_j^2 / 2m_n$, $j = f, i$); in other words, we determine the dispersion relation $\omega = \omega_s(\mathbf{q})$. Actually, what we do is to fix the energy, ε_i , of each incident particle and the direction of the initial beam (this is equivalent of fixing $\mathbf{k}_i$); then for each chosen scattering direction we measure the scattering intensity (i.e., the number of scattered particles per unit time) as a function of the final energy. Having the final direction and energy, the final wavevector $\mathbf{k}_f$ is determined. However, for an arbitrary value of $\mathbf{k}_f$ and with fixed $\mathbf{k}_i$, (9.26) and (9.27) cannot in general be both satisfied, since we have only three independent unknowns (the three components of $\mathbf{q}$) and four equations (Equation (9.26), being a vector equation, is equivalent to three independent equations). Hence, for arbitrarily chosen final direction and arbitrary final energy, we do not expect to find any scattered particle, i.e., we expect the inelastic scattering intensity to be zero. Only for a few values of ε_f (given the final direction of the scattered beam), we expect to have a nonzero scattering intensity (see Pr.9.5s). Hence, for a chosen final direction, we expect the measured scattering intensity, I , as a function of ε_f to be as in Fig. 9.4. Notice that in Fig. 9.4, the scattering intensity has a nonzero background in contrast to what we concluded a few lines before. The origin of this nonzero background can be

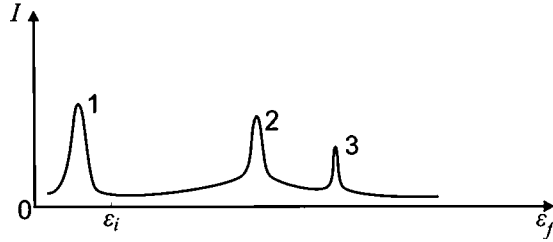


Fig. 9.4. Schematic plot of the scattering intensity, I , at a chosen direction vs. the final energy ε_f of the scattered particle. The initial momentum $\hbar\mathbf{k}_i$, and hence, the initial energy, ε_i , are fixed. Peak 1 is due to the creation of a phonon (*Stokes line*, $\varepsilon_{f1} < \varepsilon_i$), while peaks 2 and 3 to the absorption of phonons (*anti-Stokes lines*, $\varepsilon_{f2}, \varepsilon_{f3} > \varepsilon_i$)

traced back to multiphonon scattering processes, i.e., to processes where more than one phonons are absorbed and/or emitted. For example, if two phonons are involved, we have six independent variables, $\mathbf{q}_1, \mathbf{q}_2$, to satisfy still four equations (three for the conservation of (crystal) momentum and one for the conservation of energy). Of course, since the external particle–phonon interaction, I_i , is in general weak, we expect an n -phonon process to be of the order I_i^n , i.e., very weak for $n \geq 2$. Another point to notice in Fig. 9.4 is that the anti-Stokes and Stokes lines are not δ -functions but peaks of finite height and nonzero width. The latter is due to finite instrumental resolution, to a nonzero width $\delta\varepsilon_i$ of the external “monochromatic” beam, and to a finite lifetime of phonons (remember that A.3 is only an approximation).

To fully analyze the experimental data (schematically presented in Fig. 9.4), we need a theory for the intensity and line shape of each Stokes and anti-Stokes lines. This is briefly presented in Sect. 9.4. Here we only mention that for the same phonon

$$I_{\text{Stokes}}/I_{\text{antiStokes}} = (1 + \bar{n}_{\text{ph}})/\bar{n}_{\text{ph}}, \quad (9.28)$$

where $\bar{n}_{\text{ph}}$ is the number of thermally excited phonons, $\bar{n}_{\text{ph}} = [\exp(\beta\hbar\omega_s(\mathbf{q})) - 1]^{-1}$. Thus, the anti-Stokes lines tend to disappear at very low temperatures, where $\bar{n}_{\text{ph}} \rightarrow \exp(-\beta\hbar\omega_s)$. Equation (9.28) follows immediately, since the probability of absorption is proportional to the already existing number of phonons, $\bar{n}_{\text{ph}}$, while the probability of emission is proportional to the factor $1 + \bar{n}_{\text{ph}}$ characteristic of the Bose–Einstein statistics (contrast this factor to the $1 - \bar{n}$ factor in the case of Fermi statistics).

Besides inelastic scattering (of monochromatic neutron beam for sampling the whole BZ, or of laser to sample only the center of the BZ), *photon absorption by phonons* can also give information regarding transverse optical phonon eigenfrequencies at the center of the BZ. The process is shown in Fig. 9.5.

Conservation of energy and (crystal) momentum requires that

$$\omega = \omega_s(\mathbf{q}), \quad (9.29)$$

$$\mathbf{k} = \mathbf{q}. \quad (9.30)$$

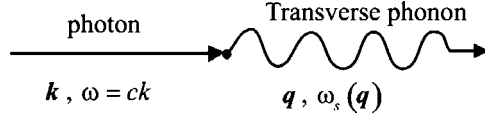


Fig. 9.5. Absorption of a photon of wavevector $\mathbf{k}$ by a transverse⁴ phonon of wavevector $\mathbf{q}$ ($\mathbf{q}$ is not necessarily in the first BZ). The photon wavevector $|\mathbf{k}| = \omega/c$ is practically zero; hence the phonon $\mathbf{q}$ is practically at the center of the BZ, unless another particle is involved in the process so that both energy and momentum are conserved

The first equation implies that ω is equal to a typical phonon frequency, i.e., $\hbar\omega \simeq 35 \text{ meV}$, which in turn implies that $k \simeq 50 \text{ cm}^{-1}$, i.e., 6 to 7 orders of magnitude smaller than a typical size of the first BZ. Hence, the conservation laws together with the transverse nature of photons imply that the only phonons that can give rise to photon absorption⁵ are transverse optic phonons of $\mathbf{q} \simeq 0$. Such phonons exist in materials where the bonding is not fully homopolar, e.g., ionic solids and ionic compound semiconductors (see Table 7.6 p. 206).

By combining (D.8) (or (D.9)) pp. 724, 725 giving the absorption coefficient α' (or α), with (7.86), giving the phonon contribution to the dielectric function in ionic solids, we can obtain an explicit expression of the phonon absorption coefficient α in ionic crystals:

$$\alpha = \frac{\omega\varepsilon_2}{c} = \frac{\omega}{c}\varepsilon_\infty \text{Im} \left\{ \frac{\omega^2 - \omega_{\text{LO}}^2}{\omega^2 - \omega_{\text{TO}}^2} \right\}, \quad (9.31)$$

$$\alpha = \frac{\pi\varepsilon_\infty}{2c} (\omega_{\text{LO}}^2 - \omega_{\text{TO}}^2) \delta(\omega - \omega_{\text{TO}}), \quad \omega \simeq \omega_{\text{TO}}. \quad (9.32)$$

In reality the delta function will be replaced by a Lorentzian

$$\delta(\omega - \omega_{\text{TO}}) \rightarrow \frac{1}{\pi} \frac{\gamma}{(\omega - \omega_{\text{TO}})^2 + \gamma^2}, \quad \omega \simeq \omega_{\text{TO}}, \quad (9.33)$$

where γ is the width of the absorption line.

Since the photon by being absorbed gives rise to a TO phonon, the opposite process can also take place, i.e., a TO phonon can disappear giving rise to a photon and so on again and again. Hence, the coupled photon–TO phonon system will appear as a “mixed” particle, partly photon and partly TO phonon. This “mixed” bosonic quasi-particle is called TO phonon-*polariton*.⁶ Actually, the dispersion relation of the polariton is obtained by solving the exact

⁴ Since photons are of transverse nature, they can interact only with transverse phonons.

⁵ Photon absorption can take place through electron excitation as well (see, e.g., Sects. 7.7 and 7.11 in particular Fig. 7.7).

⁶ The term polariton is used in a more general way as the mixed state of a photon and a bosonic excitation within a solid (e.g., the mixed state of a photon and an exciton is also called polariton).

equation

$$\omega^2 = \frac{c^2 k^2}{\varepsilon(\mathbf{k}, \omega)}, \quad (9.34)$$

which incorporates the coupling of photon with TO phonon and gives the collective oscillations of the coupled system consisting of EM fields and material body. What we have done before is as follows: We have set $c = \infty$ in the exact equation (9.34) (this is equivalent of decoupling the TO phonon from the photon) and in the framework of this approximation we determined the TO phonon dispersion relation, $\omega_s(\mathbf{k})$, from the equation $\varepsilon(\mathbf{k}, \omega) = \infty$. By recoupling the TO phonon with the photon we restored the finite value of c , and hence, we returned (following a rather complicated detour) to the original equation (9.34).

9.3 Theoretical Calculation of the Phonon Dispersion Relation and the Corresponding Normal Modes

According to (8.5) and (8.6), to proceed with the calculation of the eigenfrequencies $\omega_s(\mathbf{q})$, we need the effective spring constants $\kappa_{\mathbf{l}\mathbf{n},ij}$ or the quantities $A_{\mathbf{l}\mathbf{n},ij}$. Instead of the quantities $\kappa_{\mathbf{l}\mathbf{n},ij}$, it is slightly more convenient to introduce the quantities $D_{\mathbf{l}\mathbf{n},ij}$ defined as follows:

$$D_{\mathbf{l}\mathbf{n},ij} = -\kappa_{\mathbf{l}\mathbf{n},ij} = -A_{\mathbf{l}\mathbf{n},ij}, \quad \mathbf{l} \neq \mathbf{n}, \quad (9.35)$$

$$D_{\mathbf{l}\mathbf{l},ij} \equiv \sum_{\mathbf{n} \neq \mathbf{l}} \kappa_{\mathbf{l}\mathbf{n},ij} = \omega^2 m_{\ell} \delta_{ij} - A_{\mathbf{l}\mathbf{l},ij}. \quad (9.36)$$

According to these definitions

$$\sum_{\mathbf{n}} D_{\mathbf{l}\mathbf{n},ij} = 0. \quad (9.37)$$

In terms of the quantities, $D_{\mathbf{l}\mathbf{n},ij}$, (8.6) takes the more elegant form

$$-F_{\mathbf{l}i} = \omega^2 m_{\ell} u_{\mathbf{l}i} = \sum_{\mathbf{n},j} D_{\mathbf{l}\mathbf{n},ij} u_{\mathbf{n}j}. \quad (9.38)$$

Since by definition $F_{\mathbf{l}i}$ is equal to $-\partial\Delta/\partial u_{\mathbf{l}i}$, where Δ is the potential energy due to ionic displacements from their equilibrium positions, we have, in view of (9.38), that

$$\Delta = \frac{1}{2} \sum_{\mathbf{l}i} \sum_{\mathbf{n},j} u_{\mathbf{l}i} D_{\mathbf{l}\mathbf{n},ij} u_{\mathbf{n}j}. \quad (9.39)$$

Hence

$$D_{\mathbf{l}\mathbf{n},ij} = \frac{\partial^2 \Delta}{\partial u_{\mathbf{l}i} \partial u_{\mathbf{n}j}}. \quad (9.40)$$

For a periodic system with more than one atom per primitive cell we have that

$$\mathbf{l} = \mathbf{R} + \mathbf{r}_v, \quad (9.41)$$

and

$$\mathbf{n} = \mathbf{R}' + \mathbf{r}_{v'}, \quad (9.42)$$

where $\mathbf{R}$, $\mathbf{R}'$ are lattice vectors and the vectors $\mathbf{r}_v$, $\mathbf{r}_{v'}$, are determining the positions of the atoms within the $\mathbf{R}$, $\mathbf{R}'$ primitive cells respectively. Periodicity implies that

$$D_{\mathbf{ln},ij} = D_{vv',ij}(\mathbf{R} - \mathbf{R}'), \quad (9.43)$$

and

$$u_{\mathbf{n}j}^{(qs)} = w_{v'j}^{(qs)} e^{i\mathbf{q}\cdot\mathbf{R}'}, \quad (9.44)$$

where $u_{\mathbf{n}j}^{(qs)}$ is the j Cartesian component of the complex normalized displacement of the atom located at the position $\mathbf{R}' + \mathbf{r}_{v'}$, under the condition that only the normal mode $\mathbf{q}s$ has been excited. Substituting (9.43) and (9.44) in (9.38), we obtain the following equation

$$m_v \omega_{\mathbf{q}s}^2 w_{vi}^{(qs)} = \sum_{vj} \tilde{D}_{vv',ij}(\mathbf{q}) w_{v'j}^{(q,s)}, \quad (9.45)$$

for the unknown Cartesian components of the vectors $\mathbf{w}_v (v = 1, \dots, p)$ where p is the number of atoms in the primitive cell. The quantity $\tilde{D}_{vv',ij}(\mathbf{q})$ is called the *dynamical matrix* and it is given by the following relation:

$$\tilde{D}_{vv',ij}(\mathbf{q}) = \sum_{\mathbf{R}} D_{vv',ij}(\mathbf{R}) e^{-i\mathbf{q}\cdot\mathbf{R}}. \quad (9.46)$$

To simplify this cumbersome expressions with the many indices we shall use a compact notation where x stands for all indices $\mathbf{R}, v, i$ and x' for $\mathbf{R}', v', j$; similarly we denote the set $\mathbf{q}, s, s$ by Q .

Then

$$u_{\mathbf{n}j}^{(qs)} \equiv u_Q(x'), \quad (9.47)$$

$$u_{\mathbf{n}}^{(qs)} \equiv u_Q(x), \quad (9.48)$$

$$u_Q(x') = w_Q(v'j) e^{i\mathbf{q}\cdot\mathbf{R}'}, \quad (9.49)$$

and

$$m_v \omega_Q^2 u_Q(x) = \sum_{vj} \tilde{D}_{vv',ij}(\mathbf{q}) u_Q(x'). \quad (9.50)$$

The eigensolutions, $u_Q(x)$, are orthogonal

$$\sum_x m_v u_Q^*(x) u_{Q'}(x) = M_0 \delta_{QQ'} \quad (9.51)$$

and normalized in such a way that, when there is only one atom per primitive cell, to have $|\mathbf{w}| = 1$;⁷ this normalization implies that M_0 is the total mass

⁷ Notice that the normalization (9.51) makes $u_Q(x)$ and $w_Q(v'j)$ dimensionless; then N_Q and N_Q^* in (9.52) will have necessarily dimension of length.

of the solid $M_0 = N_a \bar{m}$, where N_a is the total number of atoms in the solid, $\bar{m}$ is the average mass per atom, $\bar{m} = (\sum_{v=1}^p m_v) / p$, and p is the number of atoms in each primitive cell.

The most general (unforced) ionic vibration can be written as a linear combination of the complex orthonormal eigenmodes (and their complex conjugate, to secure the reality of all displacements):

$$u(x, t) = \sum_Q N_Q u_Q(x) e^{-i\omega_Q t} + \sum_Q N_Q^* u_Q^*(x) e^{i\omega_Q t}. \quad (9.52)$$

Notice that $u(x, t)$ is indeed real as it should. The Cartesian component of the momentum of the ion at the point $\mathbf{R} + \mathbf{r}_v$ is obtained by taking the time derivative of (9.52) and multiplying by m_v :

$$p(x, t) = \sum_Q m_v (-i\omega_Q) N_Q u_Q(x) e^{-i\omega_Q t} + \sum_Q m_v (i\omega_Q) N_Q^* u_Q^*(x) e^{i\omega_Q t}. \quad (9.53)$$

The total energy, E , of the vibrating ionic system is equal to twice the time-averaged kinetic energy $\langle E_k \rangle = \sum_x \langle p(x, t)^2 \rangle / 2m_v$. The result is

$$E = M_0 \sum_Q (N_Q N_Q^* + N_Q^* N_Q) \omega_Q^2. \quad (9.54)$$

In (9.54) we have kept the ordering of $N_Q N_Q^*$ and $N_Q^* N_Q$, because, by quantizing the vibrations, N_Q , N_Q^* become noncommuting operators (see Problem 9.7s, where the quantization procedure is outlined).

To summarize the content of this section so far, we point out that by solving the homogeneous linear system (9.50) of $3p$ equations with the $3p$ unknowns, w_{vi} ($v = 1, \dots, p$, $i = x, y, z$), we determine the $3p$ normal modes (see (9.49)) and the corresponding eigenfrequencies, $\omega_s(\mathbf{q})$ ($s = 1, \dots, 3p$) for each value of the crystal momentum $\hbar \mathbf{q}$. In Fig. 9.6 we plot the $\omega_s(\mathbf{q})$ vs. $\mathbf{q}$ ($s = 1, 2, 3$) for the three phononic branches in Cu ($p = 1$; compare with the six phononic branches in Si ($p = 2$) and GaAs ($p = 2$) shown in Figs. 7.9 and 7.10 respectively).

Notice that the eigenoscillations and the corresponding eigenfrequencies $\omega_s(\mathbf{q})$ remain invariant under the transformation, $\mathbf{q} \rightarrow \mathbf{q}' = \mathbf{q} + \mathbf{G}$, where $\mathbf{G}$ is any vector of the reciprocal lattice:

$$\omega_s(\mathbf{q}) = \omega_s(\mathbf{q} + \mathbf{G}), \quad s = 1, \dots, 3p. \quad (9.55)$$

Furthermore, if there is a plane of mirror symmetry passing through the origin, and *parallel* to a face of the Brillouin Zone, then

$$\frac{\partial \omega_s}{\partial q_{\perp}} = 0, \quad (9.56)$$

at every point $\mathbf{q}$ of this face, where $q_{\perp}$ is the component of $\mathbf{q}$ perpendicular to this face. Furthermore, if at some point, $\mathbf{q}$, of this face the parallel component,

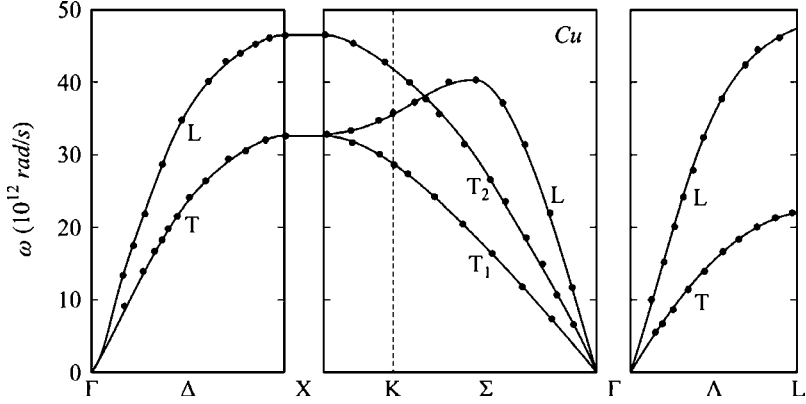


Fig. 9.6. Phonon dispersion relation, $\omega_s(\mathbf{q})$ vs. $\mathbf{q}$, $s = 1, 2, 3$, as determined by inelastic neutron scattering, for the three main directions of the Brillouin zone of copper

$(\partial\omega_s/\partial\mathbf{q})_{\parallel}$, of the group velocity $\partial\omega_s/\partial\mathbf{q}$ is zero (for symmetry reasons or accidentally), then the group velocity at this point is zero:

$$\frac{\partial\omega_s}{\partial\mathbf{q}} = 0. \quad (9.57)$$

Equation (9.56) is a direct consequence of (9.55) and the assumed mirror symmetry.

Knowledge of $\omega_s(\mathbf{q})$ allows us to obtain the partial, $\tilde{\phi}_s(\omega)$, and the total, $\tilde{\phi}(\omega) = \sum_{s=1} \tilde{\phi}_s(\omega)$, phononic DOS according to (7.82). Notice that, when $v_s(\mathbf{q}) \equiv \partial\omega_s/\partial\mathbf{q}$ is zero, the integrand in (7.82) blows up; then $\tilde{\phi}_s(\omega)$ develops analytic singularities known as *van-Hove singularities* (see Fig. 9.7 and problem 9.17).

Having the classical results for the eigenmodes and having quantized the energy, the next step is to express the displacement and the momentum of each atom in terms of creation and annihilation operators for phonons (see Pr.9.8).

All this, of course, assumes that the spring constants $\kappa_{vv',ij}(\mathbf{R} - \mathbf{R}')$, or equivalently, the matrix elements $D_{vv',ij}(\mathbf{R} - \mathbf{R}')$ are known. However, the calculation of $\kappa_{vv',ij}(\mathbf{R} - \mathbf{R}')$ requires to displace several pairs of atoms from their equilibrium positions, and calculate for each displaced pair the energy difference Δ . (See (9.40).) This calculation is in general far from easy, because the displaced atoms break locally the periodic symmetry and thus they render the direct application of Bloch's theorem inadmissible. Given this difficulty, one quite often opts for the calculation of the second “best thing,” i.e., the calculation of the elastic constants. We have already seen that for a homogeneous and isotropic solid there are two independent elastic constant: the hydrostatic bulk modulus, B , and the shear modulus, μ_s . In crystals the

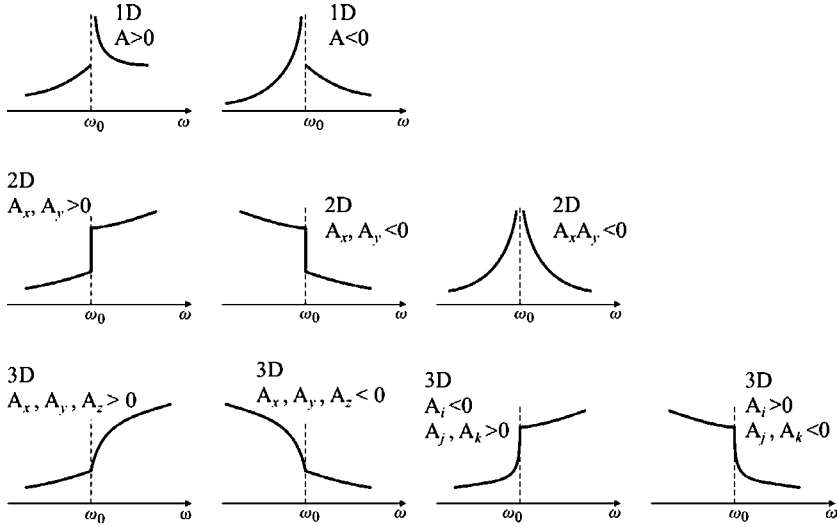


Fig. 9.7. Behavior of the phononic DOS, $\tilde{\phi}_s(\omega)$ vs. ω near a van Hove singular point ω_0 , where $(\partial\omega_s/\partial q)_{q=q_0} = 0$ and $\omega_0 = \omega_s(\mathbf{q}_0)$. The symbols 1D, 2D, 3D denote one-, two-, and three-dimensional systems respectively. The quantities A_l are by definition equal to $(\partial^2\omega_s/\partial q_l^2)_{q=q_0}$ ($l = x, y, z$), where x, y, z are along the directions of the principal axes at the point $\mathbf{q}_0$

elastic constants are defined in a similar way as in isotropic homogeneous solids. We define first the strain tensor u_{ij}

$$u_{ij} \equiv \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right), \quad i, j = x, y, z, \quad (9.58)$$

where in the discrete lattice case $\partial u_i / \partial x_j \equiv [u_i(\mathbf{R}_n + \mathbf{a}_j) - u_i(\mathbf{R}_n)] / a_j$; $u_i(\mathbf{R}_n + \mathbf{a}_j)$ and $u_i(\mathbf{R}_n)$ are the i components of the displacements of the primitive cells centered at $\mathbf{R}_n + \mathbf{a}_j$ and $\mathbf{R}_n$ respectively;⁸ the displacements of each primitive cell at $\mathbf{R}_n$ are such as to retain the periodicity in the deformed lattices as shown in the two examples in Fig. 9.8. The calculation of the energy difference, Δ , between the deformed and the original lattice is of similar difficulty as the calculation of the energy of any periodic system (although the required accuracy is higher). Having the energy difference, Δ , and the strain tensor, u_{ij} , we define the elastic constants, $c_{ij\kappa\ell}$, as the coefficients of the leading approximation of Δ/V in terms of u_{ij} :

$$\frac{\Delta}{V} \equiv \frac{1}{2} \sum_{ijkl} c_{ijkl} u_{ij} u_{kl}. \quad (9.59)$$

⁸ The basic vectors $\mathbf{a}_j$ ($i = x, y, z$) are assumed orthogonal to each other; otherwise instead of $\mathbf{a}_j$ one has to use the projection of $\mathbf{a}_j$ along the x , or y , or z direction.

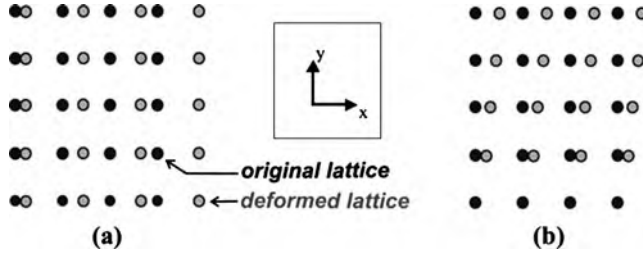


Fig. 9.8. (a) Each atom in the first column is displaced by u along the x direction; in the second column by $2u$ in the third by $3u$, etc; the deformed lattice is still periodic but of lower symmetry with lattice constant along the x direction equal to $a_x + u$; in this case $u_{xx} = u/a_x$. (b) Each atom in the second row from the bottom is displaced by u' in the x direction; in the third row by $2u'$; in the fourth row by $3u'$ etc; the deformed lattice is still periodic but no longer orthogonal; in this case $u_{xy} = u'/a_y$

Notice that $c_{ij\kappa\ell}$ have the dimensions of pressure, as they should. Since there are six independent u_{ij} (recall that $u_{ij} = u_{ji}$), there are 21 combinations of $u_{ij}u_{kl}$ (six of the form u_{ij}^2 and fifteen of the form $u_{ij}u_{kl} \equiv u_{kl}u_{ij}$ with $ij \neq kl$, i.e., as many as the combinations of two different objects out of six). In a triclinic lattice, where there are no rotation and inversion symmetries, all 21 combinations $u_{ij}u_{kl}$ have in general different coefficients, c_{ijkl} ; however, in the absence of any point symmetry, the orientation of the orthogonal Cartesian system is arbitrary. This arbitrariness, which involves three angles (two for the direction of the z -axis and one for the rotation around it), can be exploited to arbitrarily fix three out of 21 c_{ijkl} . Thus, there are 18 independent elastic constants in triclinic crystals; in the other extreme, in lattices of cubic symmetry, there are only three independent elastic constants: $c_{xxxx} = c_{yyyy} = c_{zzzz} \equiv c_{11}$; $c_{xxyy} = c_{yyzz} = c_{zzxx} \equiv c_{12}$; and $c_{xyxy} = c_{yzyz} = c_{zxzx} \equiv c_{44}$; the ones involving odd number of identical indices are zero because of mirror symmetry. Thus, for cubic lattices,

$$\begin{aligned} \frac{\Delta}{V} = & \frac{1}{2}c_{11}(u_{xx}^2 + u_{yy}^2 + u_{zz}^2) + c_{12}(u_{xx}u_{yy} + u_{yy}u_{zz} + u_{zz}u_{xx}) \\ & + 2c_{44}(u_{xy}^2 + u_{yz}^2 + u_{zx}^2). \end{aligned} \quad (9.60)$$

For other classes of lattices the numbers of independent elastic constants are shown in Table 9.1.

For cubic lattices and uniform compression, where $u_{xx} = u_{yy} = u_{zz}$ and $u_{xy} = u_{yz} = u_{zx} = 0$, (9.60) becomes

$$\begin{aligned} \frac{\Delta}{V} = & \frac{1}{2}c_{11}3u_{xx}^2 + c_{12}3u_{xx}^2 = \frac{1}{2}(c_{11} + 2c_{12})\frac{1}{3}(u_{xx} + u_{yy} + u_{zz})^2 \\ = & \frac{1}{2}\frac{c_{11} + 2c_{12}}{3}(\nabla \cdot \mathbf{u})^2. \end{aligned} \quad (9.61)$$

Table 9.1. Number of independent elastic constants

Lattice symmetry	No of independent elastic constants
Triclinic	18
Monoclinic	12
Orthorhombic	9
Tetragonal	6
Rhombohedral	6
Hexagonal	5
Cubic	3
Spherical	2

Comparing (9.61) with the definition of bulk modulus, B (see (E.12) and (E.13)), we find that B in cubic crystals satisfy the relation

$$B = \frac{c_{11} + 2c_{12}}{3}. \quad (9.62)$$

In Table 9.2 we give the elastic constants c_{11} , c_{12} , and c_{44} (in Mbars = 10^{11} N/m² = 10^{12} dyn/cm²) for some cubic monocrystalline solids as well as the bulk modulus, B , and the Lamé coefficients, λ , μ_s for the corresponding polycrystalline solids. We point out that there is no simple way to obtain the Lamé coefficients for a polycrystalline solid given the elastic constants of the corresponding monocrystalline solid. The reason is that λ and μ_s depend not only on c_{ijkl} but also on the size, shape, and orientation of the crystalline grains making up the polycrystalline material. In Table 9.2, we have calculated also the bulk modulus, B , of each monocrystalline solid according to (9.62), which is practically the same as the bulk modulus of the corresponding polycrystalline material.

In the case of one atom per primitive cell we find, by comparing (9.39) with (9.59), a relation between the elastic constants and $D_{ij}(\mathbf{R})$ ([SS75], pp. 443–445):

$$c_{ijkl} = -\frac{1}{8V_{\text{pc}}} \sum_{\mathbf{R}} [R_i D_{j\ell}(\mathbf{R}) R_k + R_j D_{i\ell}(\mathbf{R}) R_k + R_i D_{jk}(\mathbf{R}) R_\ell + R_j D_{ik}(\mathbf{R}) R_\ell]. \quad (9.63)$$

Notice that (9.63) gives the elastic constants in terms of the dynamic matrix $D_{ij}(\mathbf{R})$ and not vice versa. As we shall see in Chap. 13 one can construct approximate but physically reasonable models with only a few “spring” constants such that (9.63) can be inverted. Depending on the type of materials, several direct methods have been developed to obtain the “spring” constants or even directly the dispersion relations $\omega_s(\mathbf{q})$ vs. $\mathbf{q}$. (See Chap. 12).

Table 9.2. The elastic constants c_{11} , c_{12} , c_{44} , and the bulk modulus, $B' = (c_{11} + 2c_{12})/3$, for some cubic monocrystalline solids (in Mbars = 10^{11} N/m² = 10^{12} dyn/cm²). Shown also are the bulk modulus, B , and the Lamé coefficients λ and μ_s for some of the corresponding polycrystalline solids

Solid	Monocrystalline ^a				Polycrystalline		
	c_{11}	c_{12}	c_{44}	B'	B	λ	μ_s
<i>Cu</i>	1.69	1.22	0.753	1.37	1.38	1.06	0.48
<i>Ag</i>	1.23	0.92	0.453	1.02	1.04	0.86	0.27
<i>Au</i>	1.90	1.61	0.423	1.71	1.78	1.58	0.30
<i>Na</i>	0.07	0.061	0.045	0.064	–	–	–
<i>K</i>	0.037	0.032	0.019	0.034	–	–	–
<i>Al</i>	1.08	0.62	0.283	0.77	0.87	0.68	0.28
<i>C</i>	10.4	1.70	5.5	4.6	–	–	–
<i>Si</i>	1.65	0.64	0.792	0.98	0.98	0.54	0.67
<i>Ge</i>	1.29	0.48	0.671	0.75	–	–	–
<i>Pb</i>	0.49	0.414	0.148	0.44	0.46	0.42	0.06
<i>V</i>	2.30	1.20	0.432	1.57	–	–	–
<i>Ta</i>	2.62	1.56	0.826	1.91	–	–	–
<i>Nb</i>	2.45	1.32	0.284	1.70	–	–	–
<i>Fe</i>	2.30	1.35	1.17	1.67	1.68	1.13	0.82
<i>Ni</i>	2.47	1.53	1.22	1.84	1.82	1.08	0.80
<i>GaAs</i>	1.18	0.53	0.59	0.75	–	–	–
<i>NaCl</i>	0.485	0.125	0.127	0.245	–	–	–

^a In the special case where $c_{11} = c_{12} + 2c_{44}$, the cubic symmetry is reduced to spherical (i.e., isotropic) symmetry. Indeed by setting $c_{12} = \lambda$ and $c_{44} = \mu_s$ and consequently $c_{11} = \lambda + 2\mu_s$, (9.57) is reduced to (E.11). Furthermore, if the forces are central (i.e., the force $\mathbf{F}_{nm}$ between atoms at $\mathbf{R}_n$ and $\mathbf{R}_m$ is parallel to $\mathbf{R}_n - \mathbf{R}_m$), the so-called *Cauchy relation* is valid: $c_{12} = c_{44}$. (See the solution of problem 9.12s)

9.4 The Debye–Waller Factor and the Inelastic Cross-Section

Phonons reduce the strength of the diffracted beams in a crystalline solid by a factor known as the Debye–Waller factor. To simplify the derivation, we shall assume that there is only one atom per primitive cell. In the presence of phonons, the position of an atom is not simply $\mathbf{R}$ (as in (9.3)), but $\mathbf{R} + \mathbf{u}(\mathbf{R}, t)$, where $\mathbf{u}(\mathbf{R}, t)$ is given in problem 9.8 at the end of this chapter. Hence, the total scattering amplitude f_t is given now by the following expression⁹

$$f_t = f \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{u}}. \quad (9.64)$$

Expanding the last exponential factor in powers of the small quantity $\mathbf{k} \cdot \mathbf{u}$, we have

⁹ Actually, the expression for the differential inelastic scattering cross section depends on the frequency $\hbar\omega = \varepsilon_i - \varepsilon_f$ as well (see (9.79) till (9.92)).

$$e^{i\mathbf{k}\cdot\mathbf{u}} = 1 + i\mathbf{k}\cdot\mathbf{u} - \frac{1}{2}(\mathbf{k}\cdot\mathbf{u})^2 + \dots \quad (9.65)$$

For simplicity we assume that only one phonon, the one characterized by $\mathbf{q}_s$, is present; then, according to the results of Pr.9.8, $\mathbf{u}(\mathbf{R}, t)$ is

$$\mathbf{u}(\mathbf{R}, t) = \mathbf{b}_{q,s} e^{i(q\mathbf{R} - \omega_{qs}t)} a_{qs} + \mathbf{b}_{q,s}^* e^{-i(q\mathbf{R} - \omega_{qs}t)} a_{qs}^\dagger, \quad (9.66)$$

where

$$\mathbf{b}_{q,s} = \frac{1}{\sqrt{N_a}} \left(\frac{\hbar}{2m\omega_{qs}} \right)^{1/2} \mathbf{w}_{qs}, \quad (9.67)$$

and $|\mathbf{w}_{qs}| = 1$. Combining (9.64) to (9.66) we obtain

$$\begin{aligned} f_t = f \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} [1 + i\mathbf{k}\cdot\mathbf{b}_{qs} e^{i\phi} a_{qs} + i\mathbf{k}\cdot\mathbf{b}_{qs}^* e^{-i\phi} a_{qs}^\dagger \\ - \frac{1}{2} (\mathbf{k}\cdot\mathbf{b}_{qs} e^{i\phi} a_{qs} + \mathbf{k}\cdot\mathbf{b}_{qs}^* e^{-i\phi} a_{qs}^\dagger)^2 + \dots], \end{aligned} \quad (9.68)$$

where $\phi = \mathbf{q}\cdot\mathbf{r} - \omega_{qs}t$.

The term $(\mathbf{k}\cdot\mathbf{u})^2$ is equal to

$$(\mathbf{k}\cdot\mathbf{u})^2 = (\mathbf{k}\cdot\mathbf{b}_{qs})^2 e^{2i\phi} a_{qs} a_{qs} + (\mathbf{k}\cdot\mathbf{b}_{qs}^*)^2 e^{-2i\phi} a_{qs}^\dagger a_{qs}^\dagger + |\mathbf{k}\cdot\mathbf{b}_{qs}|^2 (a_{qs} a_{qs}^\dagger + a_{qs}^\dagger a_{qs}). \quad (9.69)$$

The average value of $a_{qs} a_{qs}$ and $a_{qs}^\dagger a_{qs}^\dagger$ for eigenstates of the number operator $a_{qs}^\dagger a_{qs}$ are zero and

$$\langle a_{qs}^\dagger a_{qs} \rangle = n_{qs}, \quad (9.70)$$

while

$$\langle a_{qs} a_{qs}^\dagger \rangle = 1 + \langle a_{qs}^\dagger a_{qs} \rangle = 1 + n_{qs}, \quad (9.71)$$

where n_{qs} is the average number of phonons in the normal mode $\mathbf{q}_s$.

Hence,

$$\langle (\mathbf{k}\cdot\mathbf{u})^2 \rangle = |\mathbf{k}\cdot\mathbf{b}_{qs}|^2 (1 + 2n_{qs}). \quad (9.72)$$

Taking into account (9.65) and (9.72) and the relation $\phi = \mathbf{q}\cdot\mathbf{r} - \omega_{qs}t$, we can reexpress (9.68) as follows

$$\begin{aligned} f_t = f \left[\sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \left(1 - \frac{1}{2} (\mathbf{k}\cdot\mathbf{u})^2 \right) + i\mathbf{k}\cdot\mathbf{b}_{qs} a_{qs} e^{-i\omega_{qs}t} \sum_{\mathbf{R}} e^{i(\mathbf{q}+\mathbf{k})\cdot\mathbf{R}} \right. \\ \left. + i\mathbf{k}\cdot\mathbf{b}_{qs}^* a_{qs}^\dagger e^{i\omega_{qs}t} \sum_{\mathbf{R}} e^{i(\mathbf{k}-\mathbf{q})\cdot\mathbf{R}} \right] = f N_a \left[\delta_{\mathbf{k},\mathbf{G}} \left(1 - \frac{1}{2} (\mathbf{k}\cdot\mathbf{u})^2 \right) \right. \\ \left. + i\mathbf{k}\cdot\mathbf{b}_{qs} a_{qs} e^{-i\omega_{qs}t} \delta_{\mathbf{q}+\mathbf{k},\mathbf{G}} + i\mathbf{k}\cdot\mathbf{b}_{qs}^* a_{qs}^\dagger e^{i\omega_{qs}t} \delta_{\mathbf{k}-\mathbf{q},\mathbf{G}} \right]. \end{aligned} \quad (9.73)$$

Thus, the average differential scattering cross section $d\sigma/d\Omega = \langle f_t^\dagger f_t \rangle$, keeping terms up to second order in $|\mathbf{b}_{qs}|$, is equal to

$$\begin{aligned} \langle f_t^\dagger f_t \rangle = |f|^2 N_a^2 \left[\sum_{\mathbf{G}} \delta_{\mathbf{k},\mathbf{G}} \left(1 - \langle (\mathbf{k}\cdot\mathbf{u})^2 \rangle \right) + |\mathbf{k}\cdot\mathbf{b}_{qs}|^2 n_{qs} \sum_{\mathbf{G}} \delta_{\mathbf{q}+\mathbf{k},\mathbf{G}} \right. \\ \left. + |\mathbf{k}\cdot\mathbf{b}_{qs}|^2 (1 + n_{qs}) \sum_{\mathbf{G}} \delta_{\mathbf{k}-\mathbf{q},\mathbf{G}} \right]. \end{aligned} \quad (9.74)$$

The first term in brackets in (9.74) reduces the elastic differential cross section $|f|^2 N_a^2$ (in the absence of ionic displacements) by a factor $1 - 2W$, where $2W$ is given by

$$2W = \langle (\mathbf{k} \cdot \mathbf{u})^2 \rangle. \quad (9.75)$$

Actually, as we shall see, if one keeps all orders in $|\mathbf{b}|$, the reduction factor, instead of $1 - 2W$, becomes

$$\exp(-2W).$$

(See (9.89).) This factor is known as the *Debye–Waller factor*. The second term in brackets in (9.74) corresponds to the inelastic¹⁰ scattering associated with the absorption of a phonon, $\mathbf{q}s$, while the last term is associated with the creation of a phonon $\mathbf{q}s$.

If the displacement $\mathbf{u}(\mathbf{R}, t)$ is due to an arbitrary phonon excitation (as in Problem 9.8), the second and third term in the bracket of (9.74) will involve a summation over $\mathbf{q}s$ and

$$2W = \langle (\mathbf{k} \cdot \mathbf{u})^2 \rangle = \sum_{\mathbf{q}s} |\mathbf{k} \cdot \mathbf{b}_{\mathbf{q}s}|^2 (1 + 2n_{\mathbf{q}s}), \quad (9.76)$$

or, taking into account (9.67)

$$2W = \frac{1}{N_a} \frac{\hbar}{2m} \sum_{\mathbf{q}s} \frac{1}{\omega_{\mathbf{q}s}} |\mathbf{w}_{\mathbf{q}s} \cdot \mathbf{k}|^2 (1 + 2n_{\mathbf{q}s}) = \frac{\hbar k^2}{6mN_a} \sum_{\mathbf{q}} \sum_s \frac{1 + 2n_{\mathbf{q}s}}{\omega_{\mathbf{q}s}}. \quad (9.77)$$

In arriving at the last expression we have taken into account that $|\mathbf{w}_{\mathbf{q}s}| = 1$ and that $|\mathbf{w}_{\mathbf{q}s} \cdot \mathbf{k}|^2 = k^2 \cos^2 \theta$; finally the average of $\cos^2 \theta$ over the solid angle is $1/3$. The readers may fill up the missing steps in the derivation of (9.77) and calculate $2W$ when $n_{\mathbf{q}s}$ is given by the thermal equilibrium distribution at temperature T .

If we have retained the time dependence of $\mathbf{u}(\mathbf{R}, t)$, then instead of the relation

$$\frac{d\sigma}{d\Omega} = \langle f_t^* f_t \rangle = |f|^2 \sum_{\mathbf{r}_\ell} \sum_{\mathbf{r}'_\ell} \left\langle e^{-i\mathbf{k} \cdot (\mathbf{r}_\ell - \mathbf{r}'_\ell)} e^{-i\mathbf{k} \cdot (\mathbf{u}_\ell - \mathbf{u}'_\ell)} \right\rangle, \quad (9.78)$$

which follows immediately from (9.64), we should have an expression for the inelastic differential cross-section $d^2\sigma/d\Omega d\varepsilon_f$ of the following form

$$\frac{d^2\sigma}{d\Omega d\varepsilon_f} = \frac{1}{\hbar} \frac{k_f}{k_i} |f|^2 S(\mathbf{k}, \omega), \quad (9.79)$$

where, the quantity $S(\mathbf{k}, \omega)$ called *dynamical structure factor* of the crystal, is given by

¹⁰ If we had included initially the frequency, $\hbar\omega = \varepsilon_i - \varepsilon_f$, the inelastic scattering cross section would have contained a factor $\delta(\omega + \omega_{\mathbf{q}s})$, and a factor $\delta(\omega - \omega_{\mathbf{q}s})$ in the second and the third term of (9.74) respectively.

$$S(\mathbf{k}, \omega) = \sum_{\mathbf{r}_\ell} \sum_{\mathbf{r}'_\ell} e^{-i\mathbf{k} \cdot (\mathbf{r}_\ell - \mathbf{r}'_\ell)} \left\langle \int \frac{dt}{2\pi} e^{i\omega t} e^{-i\mathbf{k} \cdot \hat{\mathbf{u}}'_\ell(t)} e^{i\mathbf{k} \cdot \hat{\mathbf{u}}'_\ell(0)} \right\rangle, \quad (9.80)$$

where $t = t_\ell - t'_\ell$. Notice that (9.79) and (9.80) reduce to (9.78), if the time dependence of $\hat{\mathbf{u}}_\ell(t)$ is omitted, since, in this case, $k_i = k_f$ (the scattering is elastic), $d\sigma/d\Omega = \int d\varepsilon_f (d^2\sigma/d\Omega d\varepsilon_f)$, and $\int (dt/2\pi) \exp(i\omega t) = \delta(\omega)$.

Problem 9.3t. Taking into account (9.4), prove that $S(\mathbf{k}, \omega)$ is the Fourier transform of the so-called *density correlation function*, $D(\mathbf{r}, t; \mathbf{r}', 0) \equiv \langle \hat{n}(\mathbf{r}, t) \hat{n}(\mathbf{r}', 0) \rangle / 2\pi$ where $\hat{n}(\mathbf{r}, t)$ is the number-density operator at the point $\mathbf{r}$ and the time t :

$$S(\mathbf{k}, \omega) = \int d^3r \int d^3r' dt \exp[-i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}') + i\omega t] D(\mathbf{r}, t; \mathbf{r}', 0), \quad (9.81)$$

To evaluate (9.80), we shall use the following relation

$$\langle e^{\hat{A}} e^{\hat{B}} \rangle = e^{\frac{1}{2} \langle \hat{A}^2 + 2\hat{A}\hat{B} + \hat{B}^2 \rangle}, \quad (9.82)$$

which is valid for operators $\hat{A}, \hat{B}$ which are linear functions of the displacements $\hat{u}_\ell(t)$ and the momenta $\hat{p}_\ell(t)$ of a harmonic crystal.¹¹ We have then

$$\begin{aligned} \langle e^{-i\mathbf{k} \cdot \hat{\mathbf{u}}_\ell(t)} e^{i\mathbf{k} \cdot \hat{\mathbf{u}}'_\ell(0)} \rangle &= e^{-\frac{1}{2} \langle [\mathbf{k} \cdot \hat{\mathbf{u}}_\ell(t)]^2 \rangle - \frac{1}{2} \langle [\mathbf{k} \cdot \hat{\mathbf{u}}'_\ell(0)]^2 \rangle} \\ &\quad \times e^{\langle [\mathbf{k} \cdot \hat{\mathbf{u}}_\ell(t)] [\mathbf{k} \cdot \hat{\mathbf{u}}'_\ell(0)] \rangle}. \end{aligned} \quad (9.83)$$

We have already shown in (9.76) that

$$\langle [\mathbf{k} \cdot \hat{\mathbf{u}}_\ell(t)]^2 \rangle = \langle (\mathbf{k} \cdot \hat{\mathbf{u}})^2 \rangle = \sum_{q,s} |\mathbf{k} \cdot \mathbf{b}_{qs}|^2 (1 + 2n_{qs}) = 2W. \quad (9.84)$$

Similarly we can show that

$$\begin{aligned} I &\equiv \langle [\mathbf{k} \cdot \hat{\mathbf{u}}_\ell(t)] [\mathbf{k} \cdot \hat{\mathbf{u}}'_\ell(0)] \rangle \\ &= \sum_{qs} |\mathbf{k} \cdot \mathbf{b}_{qs}|^2 \left[(1 + n_{qs}) e^{i\mathbf{q} \cdot (\mathbf{r}_\ell - \mathbf{r}'_\ell)} e^{-i\omega_{qs} t} + n_{qs} e^{-i\mathbf{q} \cdot (\mathbf{r}_\ell - \mathbf{r}'_\ell)} e^{i\omega_{qs} t} \right]. \end{aligned} \quad (9.85)$$

Substituting (9.85) and (9.84) in (9.83), and the latter in (9.80), we obtain after a straightforward algebra the following result for $S(\mathbf{k}, \omega)$:

$$S(\mathbf{k}, \omega) = N_a e^{-2W} \sum_{\mathbf{R}} e^{-i\mathbf{k} \cdot \mathbf{R}} \int \frac{dt}{2\pi} e^{i\omega t} e^I, \quad (9.86)$$

where $\mathbf{R} \equiv \mathbf{r}_\ell - \mathbf{r}'_\ell$.

¹¹ For a proof, see Mermin [9.1].

Since in general the quantity I is small (because the displacements $|\mathbf{u}_\ell(t)|$ and $|\mathbf{u}'_\ell(0)|$ are small), we can expand $\exp(I)$ in a power series of I

$$\exp(I) = \sum_{n=0}^{\infty} \frac{1}{n!} I^n = 1 + I + \frac{1}{2} I^2 + \cdots, \quad (9.87)$$

where the zero order term corresponds to no-phonon creation or annihilation giving the elastic results for S

$$S^{(0)}(\mathbf{k}, \omega) = N_a^2 e^{-2W} \delta(\omega) \sum_{\mathbf{G}} \delta_{\mathbf{k}, \mathbf{G}}. \quad (9.88)$$

To obtain the differential elastic scattering cross-section, we have to integrate $S^{(0)}$ over $d\varepsilon_f = \hbar d\omega$ and to multiply by $|f|^2$. The latter is given by

$$\begin{aligned} f &= -a, \text{ for neutron-nucleus scattering } (a \text{ is the so-called scattering length}) \\ &= \frac{e^2}{4\pi\varepsilon_0 m_e c^2} \mathbf{e}_i \cdot \mathbf{e}_f, \text{ for phonon-free electron scattering}^{13} \\ &= -\frac{m}{2\pi\hbar^2} \frac{4\pi Qe}{4\pi\varepsilon_0 k^2}, \quad \text{for a particle of mass } m \text{ and charge } Q \text{ scattered by} \\ &\quad \text{Coulomb forces} \\ &= -\frac{m_e}{2\pi\hbar^2 n_a} \tilde{v}(\mathbf{k}), \quad \text{for electrons scattered by a pseudopotential.} \end{aligned}$$

Hence, for the elastic neutron scattering by a crystal we have

$$\frac{d\sigma}{d\Omega} = N_a^2 a^2 e^{-2W} \sum_{\mathbf{G}} \delta_{\mathbf{k}, \mathbf{G}}. \quad (9.89)$$

Equation (9.89) for the elastic cross-section is an explicit result that incorporates the basic result (9.6) and the Debye–Waller reduction factor, $\exp(-2W)$. Furthermore, this cross-section is proportional to the square of the number of particles (N_a in the present case is equal to the number of primitive cells); this is a consequence of the coherence of the scattering, i.e., of the fact that the scattered waves are in phase.

The first order term in (9.87) gives the cross-section associated with the creation or annihilation of one phonon at a time. Employing the result (9.85) and performing the summation over $\mathbf{R}$ and integration over t in (9.86), we obtain

$$\frac{d^2\sigma}{d\Omega d\varepsilon_f} = \frac{1}{\hbar} \frac{k_f}{k_i} |f|^2 N_a^2 e^{-2W} \sum_s |\mathbf{k} \cdot \mathbf{b}_{ks}|^2 A, \quad (9.90)$$

where

¹³ $\mathbf{e}_i$, $\mathbf{e}_f$ are the photon unit polarization vectors before and after the scattering respectively.

$$A \equiv (1 + n_{qs}) \delta(\omega - \omega_{qs}) \left(\sum_{\mathbf{G}} \delta_{\mathbf{q}-\mathbf{k}, \mathbf{G}} \right) + n_{qs} \delta(\omega + \omega_{qs}) \left(\sum_{\mathbf{G}} \delta_{\mathbf{q}+\mathbf{k}, \mathbf{G}} \right); \quad (9.91)$$

$\omega = (\varepsilon_i - \varepsilon_f)/\hbar$. Taking into account (9.67) we can rewrite (9.90) as follows:

$$\frac{d^2\sigma}{d\Omega d\varepsilon_f} = N_a \frac{k_f}{k_i} |f|^2 e^{-2W} \sum_s \frac{1}{2m_a \omega_{qs}} |\mathbf{k} \cdot \mathbf{w}_{qs}|^2 A. \quad (9.92)$$

Equation (9.92) gives the intensity of the peaks shown in Fig. 9.4 and verifies the relation (9.28).

The higher-order terms, I^n , $n = 2, 3, \dots$ are responsible for the background appearing schematically in Fig. 9.4

9.5 Key Points

- The momentum exchange of a particle interacting with a periodic system is necessarily equal to a vector $\mathbf{G}$ of the reciprocal lattice (times $\hbar$). Measuring this momentum exchange, we determine the reciprocal lattice, and hence, the direct one.
- The inelastic scattering of a monochromatic beam of neutrons of momentum $\hbar\mathbf{k}_i$ (and energy $\varepsilon_i = \hbar^2 k_i^2 / 2m_n$) due to a phonon absorption or emission leads to a final momentum and energy given by the following expressions as a result of momentum and energy conservation:

$$\begin{aligned} \hbar\mathbf{k}_f &= \hbar\mathbf{k}_i \pm \hbar\mathbf{q}, \\ \varepsilon_f &= \varepsilon_i \pm \hbar\omega_s(\mathbf{q}). \end{aligned}$$

The upper sign is for absorption and the lower for emission of a phonon, $\mathbf{q}, s$; $\mathbf{q}$ is the phonon's wavevector (not necessarily in the 1st BZ) and $\hbar\omega_s(\mathbf{q})$ is its energy. Measuring $\mathbf{k}_i$ and $\mathbf{k}_f$ (and consequently, knowing $\varepsilon_i = \hbar^2 k_i^2 / 2m_n$ and $\varepsilon_f = \hbar^2 k_f^2 / 2m_n$), we determine $\mathbf{q}$ and $\omega_s(\mathbf{q})$.

- A photon can be absorbed or emitted by a transverse phonon if both energy and momentum are matched giving rise to a composite bosonic quasiparticle called polariton.
- The ionic displacement $\mathbf{u}_{qs}(\mathbf{R}, t)$ corresponding to a phonon $\mathbf{q}s$ is given by the following expression (assuming one atom per primitive cell)

$$\mathbf{u}_{qs}(\mathbf{R}, t) = \left(\frac{\hbar}{2N_a m \omega_{qs}} \right)^{1/2} \left[\mathbf{w}_{qs} e^{i(\mathbf{q} \cdot \mathbf{R} - \omega_{qs} t)} a_{qs} + \mathbf{w}_{qs}^* e^{-i(\mathbf{q} \cdot \mathbf{R} - \omega_{qs} t)} a_{qs}^\dagger \right],$$

where the quantities $\mathbf{w}_{qs}$ and ω_{qs} satisfy the relation $|\mathbf{w}_{qs}| = 1$ and

$$\sum_j D_{ij}(\mathbf{q})(w_{qs})_j = m\omega_{qs}(w_{qs})_i;$$

$D_{ij}(\mathbf{q})$ is called the dynamical matrix and it is related to the spring constants k_{ij} . The quantities $a_{\mathbf{q}s}$ and $a_{\mathbf{q}s}^\dagger$ in the quantum version are phonon annihilation and creation operators respectively. The average energy E is given by

$$E = \sum_{\mathbf{q}s} \hbar \omega_{\mathbf{q}s} (\langle a_{\mathbf{q}s}^\dagger a_{\mathbf{q}s} \rangle + \frac{1}{2}),$$

and the eigenvalues of $a_{\mathbf{q}s}^\dagger a_{\mathbf{q}s}$ are $0, 1, 2, \dots$. In this way one can derive the so-called Debye-Waller factor.

- Points at which $\partial \omega_{\mathbf{q}s} / \partial \mathbf{q} = 0$ produce singularities in the phononic DOS (known as phononic van Hove singularities) the nature of which depends on the dimensionality.
- The inelastic scattering cross-section $d^2\sigma/d\Omega d\varepsilon_f$ of a particle by the ions (or atoms) of a crystalline solid has the following form

$$\frac{d^2\sigma}{d\Omega d\varepsilon_f} = \frac{1}{\hbar} \frac{k_f}{k_i} |f|^2 S(\mathbf{k}, \omega), \mathbf{k} = \mathbf{k}_i - \mathbf{k}_f, \hbar\omega = \varepsilon_i - \varepsilon_f;$$

$S(\mathbf{k}, \omega)$, the dynamical structure factor, can be written as a sum of terms $S = S_0 + S_1 + S_2 + \dots$, where $S_0 \sim \delta(\omega) \sum_{\mathbf{G}} \delta_{\mathbf{k}, \mathbf{G}}$ gives the zero phonon (i.e., the elastic) part, S_1 gives the single phonon emission or absorption part, and so on; f depends on the interaction of the scattered particle by an ion (or atom).

9.6 Problems

- 9.1s Prove (9.2).
- 9.2s Calculate the structure factor of the *unit* cell of the **bcc** and **fcc** lattices. How is this structure factor connected to the structure factor of the primitive cell of the same lattices?
- 9.3s Prove (9.18).
- 9.4 Calculate the structure factor of the primitive cell of Si.
- 9.5s Solve (9.26) and (9.27) for a one-dimensional “solid” of the type examined in Sect. 6.1 when the incident beam consists of monochromatic neutrons.
- 9.6 Calculate the dispersion relation of the polariton associated with the dielectric function shown in (7.88).
- 9.7s Quantize the ionic vibrations by going through the following steps:
- (a) Express N_Q and N_Q^* in terms of $u(x, 0)$ and $p(x, 0)$. To do so, multiply (9.52) by $m_v u_Q^*(x)$ and (9.53) by $u_Q^*(x)$ and sum over x . Employ the orthonormality relation, (9.51). The final result is

$$N_Q = \sum_x \frac{m_v u_Q^*(x)}{2M_0} \left(u(x, 0) + \frac{ip(x, 0)}{m_v \omega_Q} \right), \quad (9.93)$$

$$N_Q^* = \sum_x \frac{m_v u_Q(x)}{2M_0} \left(u(x, 0) + \frac{ip(x, 0)}{m_v \omega_Q} \right). \quad (9.94)$$

- (b) Quantize the vibration system by treating $u(x, t)$ and $p(x, t)$ as hermitean operators obeying the standard commutation relations

$$[\hat{u}(x, t), \hat{p}(x', t)] = i\hbar\delta_{xx'}, \quad (9.95)$$

$$[\hat{u}(x, t), \hat{u}(x', t')] = 0, \quad (9.96)$$

$$[\hat{p}(x, t), \hat{p}(x', t')] = 0. \quad (9.97)$$

By combining (9.93), (9.94) with (9.95)–(9.97) and writing $\hat{N}_Q^\dagger$ instead of $\hat{N}_Q^*$, show that $\hat{N}_Q$ and $\hat{N}_Q^\dagger$ become nonhermitean operators obeying the following commutation relations.

$$[\hat{N}_Q, \hat{N}_{Q'}^\dagger] = \frac{\hbar}{2M_0\omega_Q}\delta_{QQ'}, \quad (9.98)$$

$$[\hat{N}_Q, \hat{N}_{Q'}] = 0, \quad (9.99)$$

$$[\hat{N}_Q^\dagger, \hat{N}_{Q'}^\dagger] = 0. \quad (9.100)$$

- (c) Introduce the operator

$$a_Q = (2M_0\omega_Q/\hbar)^{1/2} \hat{N}_Q, \quad (9.101)$$

and its adjoint $a_Q^\dagger$ and show that the eigenvalues of $a_Q^\dagger a_Q$ are the nonzero integers $0, 1, 2, \dots$; $a_Q^\dagger$ is a phonon Q creation operator and a_Q is a phonon Q annihilation operator.

- (d) Show that the Hamiltonian of the vibrating system in view of (9.54) and (9.101) becomes

$$\hat{H} = \sum_Q \hbar\omega_Q \left(a_Q^\dagger a_Q + \frac{1}{2} \right). \quad (9.102)$$

9.8 Express the operators $\hat{u}(x, t)$ and $\hat{p}(x, t)$ in terms of operators a_Q and $a_Q^\dagger$ and vice versa. In particular, for the case of one atom per unit cell, show that

$$\hat{u}(\mathbf{R}, t) = \frac{1}{\sqrt{N_a}} \sum_{qs} \left(\frac{\hbar}{2m\omega_{qs}} \right)^{1/2} \left[\mathbf{w}_{qs} e^{i(\mathbf{q}\cdot\mathbf{R} - \omega_{qs}t)} a_{qs} + \mathbf{w}_{qs}^* e^{-i(\mathbf{q}\cdot\mathbf{R} - \omega_{qs}t)} a_{qs}^\dagger \right].$$

9.9s Show that

$$\begin{aligned} a_Q^\dagger |\dots n_Q \dots\rangle &= \sqrt{n_Q + 1} |\dots n_Q + 1 \dots\rangle, \\ a_Q |\dots n_Q \dots\rangle &= \sqrt{n_Q} |\dots n_Q - 1 \dots\rangle, \end{aligned}$$

where $|\dots n_Q \dots\rangle$ is an eigenstate of $a_Q^\dagger a_Q$ with n_Q phonons of type $Q \equiv \mathbf{q}, s$.

- 9.10 For the case of one atom per primitive cell and taking into account (9.37) and the relations $D_{lnij} = D_{nlji}$ (because of (9.40)) and $D_{ij}(\mathbf{R} - \mathbf{R}') = D_{ij}(\mathbf{R}' - \mathbf{R})$, since the Bravais lattice possesses inversion symmetry), show that

$$D_{ij}(\mathbf{q}) = \sum_{\mathbf{R}} \sin^2 \frac{\mathbf{q} \cdot \mathbf{R}}{2} D_{ij}(\mathbf{R}).$$

- 9.11 Based on (9.45) and (9.37), show that there are three normal modes for which $\omega_{qs} \rightarrow c(\theta, \varphi) \cdot \mathbf{q}$ as $\mathbf{q} \rightarrow 0$; for $p > 1$, show that there are $3p - 3$ modes for which $\omega \neq 0$ as $q \rightarrow 0$.
- 9.12s Prove Cauchy's relation (see footnote in Table 9.2, p. 263).
- 9.13s Calculate the dispersion relations, $\omega_s = \omega_s(\mathbf{q})$, $s = 1, 2$ for the eigenoscillations of the two-dimensional system the unit cell of which is shown in Fig. 9.9.
- 9.14 Show that the total phononic DOS as $\omega \rightarrow 0$ is given by

$$\phi(\omega) = \frac{3V}{2\pi^2} \frac{\omega^2}{\bar{c}^3},$$

where

$$\frac{3}{\bar{c}^3} = \frac{1}{\bar{c}_1^3} + \frac{1}{\bar{c}_2^3} + \frac{1}{\bar{c}_3^3},$$

$$\frac{1}{\bar{c}_s^3} = \frac{1}{4\pi} \int \frac{d\Omega_{\mathbf{q}}}{c_s^3(\theta, \phi)}, \quad s = 1, 2, 3.$$

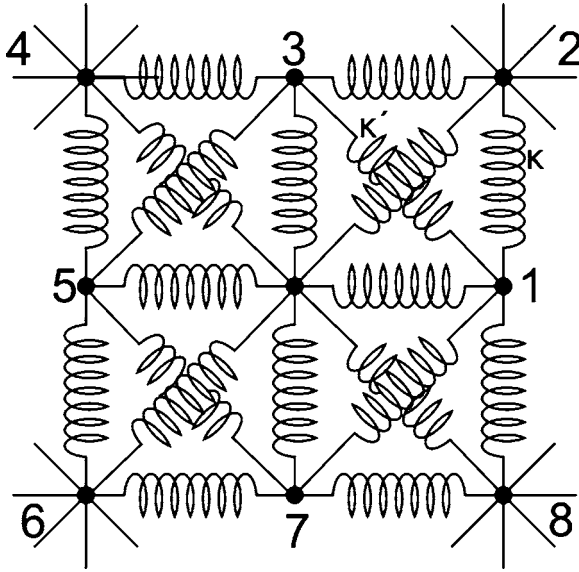


Fig. 9.9. The unit cell of a 2D system of springs (two types of spring constants) and masses (all of them equal to each other)

- 9.15 Prove (9.51).
- 9.16s Calculate the quantity $2W$ if the solid is in thermal equilibrium at temperature T . What are the explicit expressions for $2W$ at high temperatures ($T \gg \Theta_D$) and low temperatures ($T \ll \Theta_D$)? Can you obtain these expressions (apart from the numerical factor) by dimensional analysis or by other physical arguments?
- 9.17 Verify the results shown in Fig. 9.7 and determine the analytical behavior of the DOS near each type of van-Hove singularities.

Further Reading

- See the book by Ashcroft and Mermin [SS75] Chaps. 22, 23, 24, and Appendices L, M, N and the book by Kittel [SS74], Chap. 2.

Electrons in Periodic Media. The Role of Magnetic Field

Summary. We examine the conditions under which a periodic Hamiltonian can be approximated by a free-electron Hamiltonian with an appropriately defined effective mass; under certain approximations, the center $\mathbf{k}$ of a wavepacket of Bloch functions follows a trajectory obeying the Newtonian equation $\hbar\dot{\mathbf{k}} = \mathbf{F}_{\text{add}}$, where $\mathbf{F}_{\text{add}}$ is an additional non-periodic force due to external fields and/or impurities, etc. From the trajectory in $\mathbf{k}$ space, we find the trajectory in real space using the relation, $d\mathbf{r}/dt = \mathbf{v}_{n\mathbf{k}} = \partial E_n(\mathbf{k})/\hbar\partial\mathbf{k}$. We demonstrate that this scheme achieves agreement with the experimental data regarding the cyclotron resonances, the de Haas–van Alphen effect, the Hall effect, and the magnetoresistance succeeding where the jellium model (JM) failed very badly.

10.1 Introduction

As we have seen in Chaps. 4 and 5, the JM produced several results. Some of them were in satisfying semiquantitative agreement with the corresponding experimental data, while others failed even qualitatively. Among the failures of the JM, one must mention its inability to account for:

- (a) The insulating or semiconducting behavior so common among solids (The LCAO approach of Chaps. 6 and 7 took care of this severe failure of the JM)
- (b) The big values of the specific heat coefficient γ_c observed in most transition metals
- (c) The positive value of the thermopower appearing in some materials
- (d) The small value of the electrical conductivity of semimetals in spite of the large value of their “free” electron concentration
- (e) The appearance of more than one cyclotron frequencies in most metals
- (f) The frequency dependence of the Hall coefficient and its positive value observed in some metals (e.g., Al)
- (g) The presence of more than one period in the de Haas–van Alphen effect

To remedy these problems, it is only natural to employ a more realistic model that will take into account the basic fact that each detached electron in a solid is subject to a nonzero force. In a crystalline solid, this force is, to a good approximation, periodic; as a result, the generic free electron relation, $E = \hbar^2 k^2 / 2m$, of the JM is replaced by the material specific¹ band structure relation, $E = E_n(\mathbf{k})$. Similarly, the simple DOS, $\rho(E) \sim E^{1/2}$, of the JM is replaced by a material-specific $\rho_n(E)$, which is in general a complicated, nonmonotonic function of the energy. Finally, the surfaces of equal energy are not spheres as in the JM, but complicated nonisotropic surfaces characteristic of each crystalline solid. In Fig. 10.1 we plot the DOS vs. E for four elemental solids (a transition metal (Pt), a simple metal (Al), a semimetal (Be), and a semiconductor (Ge)).

10.2 Dispersion Relations, Surfaces of Constant Energy, and DOS: A Reminder

We have seen in Sect. 3.4.1 that the electronic eigenfunctions in a periodic potential can be written as

$$\psi_{\mathbf{k}n}(\mathbf{r}) = w_{\mathbf{k}n}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (10.1)$$

where $w_{\mathbf{k}n}(\mathbf{r})$ is a periodic function of $\mathbf{r}$ of the same underlying Bravais lattice as that of the periodic potential; $\hbar\mathbf{k}$ is the crystal momentum, which can be restricted to any Brillouin zone without loss of generality; n is the so-called band index. The functions $w_{\mathbf{k}n}(\mathbf{r})$ for a given $\mathbf{k}$ and for $n = 1, 2, 3, \dots$ are determined by substituting (10.1) in Schrödinger's equation

$$\hat{H}\psi_{\mathbf{k}n}(\mathbf{r}) = E_n(\mathbf{k})\psi_{\mathbf{k}n}(\mathbf{r}). \quad (10.2)$$

Having the eigenenergy $E_n(\mathbf{k})$ for a given n as a function of $\mathbf{k}$ allows us to determine the partial DOS for the band n according to formula (4.17):

$$\rho_n(E) = \frac{V}{(2\pi)^3} \int \frac{dS_n}{|\nabla_{\mathbf{k}} E_n(\mathbf{k})|}, \quad (10.3)$$

where dS_n is the elementary area of the surface $S_n(E)$ in $\mathbf{k}$ -space defined as the set of $\mathbf{k}$ -points satisfying the equation

$$E_n(\mathbf{k}) = E \Rightarrow S_n(E). \quad (10.4)$$

For a given E and n , it is possible that no $\mathbf{k}$ vector may exist satisfying (10.4); if this is the case, no surface $S_n(E)$ exists and $\rho_n(E)$ is equal to zero. It is even possible that for a given, E , no n and no $\mathbf{k}$ may exist satisfying (10.4);

¹ Each crystalline material has its own band structure $E_n(\mathbf{k})$, which is different from that of any other material.

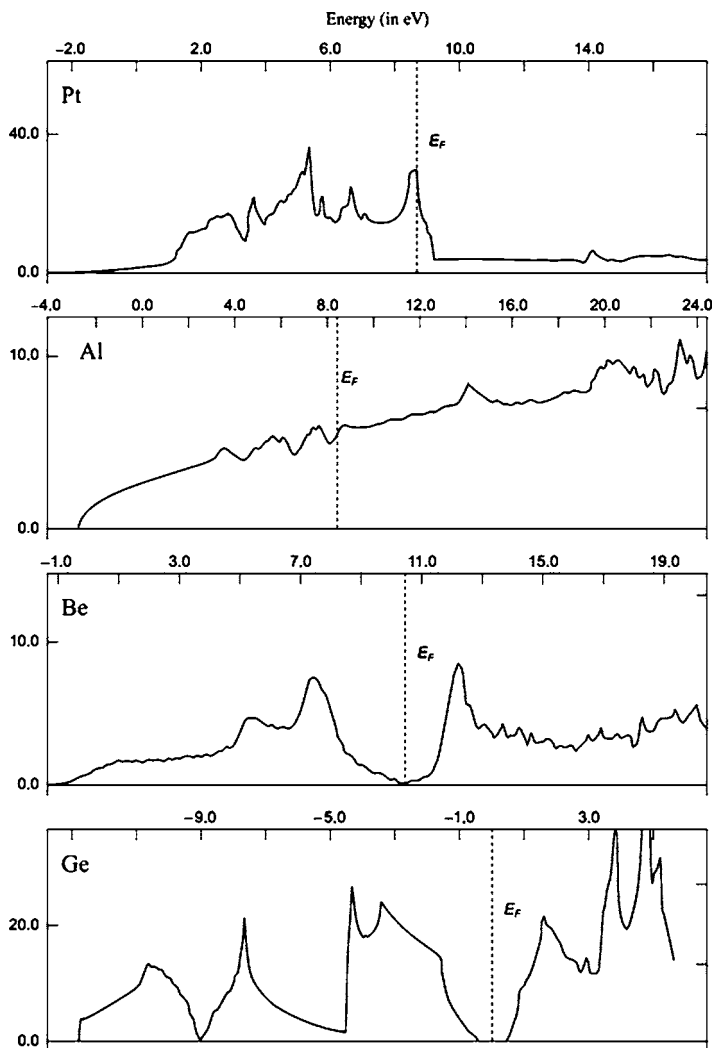


Fig. 10.1. The total DOS (per atom and per Ry) for four characteristic crystalline solids². Notice that, as we move from Pt to Ge, the DOS at E_F , ρ_F , goes from large value (29.9 for Pt), to value close to that of the JM, (5.46 for Al), to much smaller value (0.1 for Be), and, finally, to zero (for Ge)

then, for this given E , $\rho_n(E) = 0$ for all n , and consequently, this E belongs to a gap, since the total DOS at E ,

$$\rho(E) = \sum_n \rho_n(E), \quad (10.5)$$

² Similar DOSes should also exist for amorphous systems, but without singularities. Thus sharp gaps, for example, are smoothed.

is zero. In general, no more than a finite number of n 's contribute to the total electronic DOS for a given energy E . We remind the readers that the partial DOS is the derivative of the number of states $R_n(E)$ (with $E_n(\mathbf{k})$ less than E):

$$\rho_n(E) = dR_n(E)/dE. \quad (10.6)$$

Sometimes it is convenient to define the total number of states $\tilde{R}_n(E)$ with $E_n(\mathbf{k})$ higher than E . Obviously, the sum $R_n(E) + \tilde{R}_n(E)$ is equal to the total number of states within a Brillouin zone; this total number (ignoring the spin) is equal to $VV_{\text{BZ}}/(2\pi)^3$ according to the basic equation (4.11). However, $V = V_{\text{pc}}N_{\text{pc}}$, where V_{pc} is the volume of any primitive cell of the direct lattice and N_{pc} is the total number of primitive cells in the crystal. Thus, the total number of states for a given n is equal to $N_{\text{pc}}V_{\text{pc}}V_{\text{BZ}}/(2\pi)^3 = N_{\text{pc}}$; the last equation follows in view of (3.16). Thus,

$$R_n(E) + \tilde{R}_n(E) = N_{\text{pc}}, \quad (10.7)$$

and consequently,

$$\rho_n(E) = -d\tilde{R}_n(E)/dE. \quad (10.8)$$

Near the top of a band and in a few other cases, it is easier to calculate $\tilde{R}_n(E)$ rather than $R_n(E)$ or $\rho_n(E)$.

If in (10.4), we set the energy equal to the Fermi energy, $E = E_F$, the resulting surface, S_{nF} , in $\mathbf{k}$ -space is the part of the **Fermi surface** associated with the band n . The Fermi surface S_F is the union of all the parts S_{nF} of nonzero area: $S_F = \sum_n S_{nF}$. As in the case of phonons (see Fig. 9.7), the partial (and the total) DOS develop the so-called van Hove singularities at energies E associated with $\mathbf{k}$ -space surfaces $S_n(E)$ containing one or more points $\mathbf{k}_0$ such that $\nabla E_n(\mathbf{k})$ is zero at $\mathbf{k} = \mathbf{k}_0$. This is obvious, since the quantity $|\nabla E_n(\mathbf{k})|$ is in the denominator of the integrand in (10.3)

10.3 Effective Hamiltonian and Semiclassical Approximation

In Sect. 7.8 we considered the Hamiltonian, $\hat{H} = \hat{H}_0 + \hat{H}_1$, where $\hat{H}_0$ is the periodic crystal potential plus the kinetic energy, $\hat{p}^2/2m$, of the electron, and $\hat{H}_1$ is a nonperiodic perturbation due to impurities and/or defects and/or external fields, etc. We mentioned there that, under certain conditions, $\hat{H}$ can be approximated by $\hat{H}_{\text{eff}}$, where

$$\hat{H} \simeq \hat{H}_{\text{eff}} = -\frac{\hbar^2 \nabla^2}{2m^*} + \hat{H}_1. \quad (10.9)$$

To see how this drastic simplification was reached, we shall state first the following basic relation:

$$\hat{E}_n \left(-i \frac{\partial}{\partial \mathbf{r}} \right) \psi_{\mathbf{k}n}(\mathbf{r}) = E_n(\mathbf{k}) \psi_{\mathbf{k}n}(\mathbf{r}), \quad (10.10)$$

where $\hat{E}_n$ is the operator, which results by replacing $\mathbf{k}$ in $E_n(\mathbf{k})$ by the operator $-i\partial/\partial\mathbf{r}$. Equation (10.10) is valid only for the eigenfunctions and the corresponding eigenenergies of $\hat{H}_0$ belonging to the band n .

Problem 10.1t. Prove (10.10).

Hint: Since $E_n(\mathbf{k})$ is a periodic function of $\mathbf{k}$, it can be expanded in a Fourier series, according to (9.7), $E_n(\mathbf{k}) = \sum_{\mathbf{R}} \tilde{E}_n \mathbf{R} \mathbf{e}^{i\mathbf{R}\cdot\mathbf{k}}$, where the summation is over all vectors of the reciprocal of the reciprocal lattice, i.e., of the direct lattice. Take into account also that $\exp(+\mathbf{R}\cdot\nabla_{\mathbf{r}})\phi(\mathbf{r}) = \phi(\mathbf{r} + \mathbf{R})$, where $\phi(\mathbf{r})$ is any well-behaved function.

Equation (10.10) means that the operator $\hat{E}_n(-i\partial/\partial\mathbf{r})$ is “equivalent” to the Hamiltonian $\hat{H}_0$, as long as we restrict ourselves only to functions belonging to the band n . Indeed, for the band n the operators $\hat{H}_0$ and $\hat{E}_n(-i\partial/\partial\mathbf{r})$ have the same eigenfunctions and the same eigenenergies; hence, they are “equivalent”

$$\hat{E}_n(-i\partial/\partial\mathbf{r}) = \hat{H}_0, \quad \text{for } n\text{-band functions} \quad (10.11)$$

Now, if a perturbation $\hat{H}_1$ is added to our periodic potential, Schrödinger’s time-dependent equation for the wave function $\psi(\mathbf{r}, t)$ of an electron becomes

$$i\hbar \frac{\partial\psi}{\partial t} = (\hat{H}_0 + \hat{H}_1)\psi. \quad (10.12)$$

We assume that before the action of $\hat{H}_1$, ψ was a linear combination of eigenfunctions belonging exclusively to the band n . If $\hat{H}_1$ is such that it mixes eigenstates of the band n without appreciable transitions to other bands n' , then $\hat{H}_0$ in (10.12) can be replaced by $\hat{E}_n(-i\partial/\partial\mathbf{r})$ and the resulting error will not be significant:

$$i\hbar \frac{\partial\psi}{\partial t} \simeq [\hat{E}_n(-i\partial/\partial\mathbf{r}) + \hat{H}_1]\psi. \quad (10.13)$$

The assumption that $\hat{H}_1$ does not lead to appreciable transitions to other bands n' is valid when all of the following inequalities are satisfied ([SS75], pp. 219–220):

$$\hbar\omega \ll E_g(\mathbf{k}), \quad (10.14)$$

$$e|\mathbf{E}|a \ll E_g^2(\mathbf{k})/E_0, \quad (10.15)$$

$$\hbar\omega_c \ll E_g^2(\mathbf{k})/E_0, \quad (10.16)$$

where ω is the frequency of the external perturbation (or more generally, $\omega = 2\pi/t_0$, where t_0 is the characteristic time of variation of $\hat{H}_1$); $E_g(\mathbf{k})$ is the minimum value of the difference $|E_n(\mathbf{k}) - E_{n'}(\mathbf{k})|$; $\mathbf{E}$ is the electric field associated with the perturbation $\hat{H}_1$; a is the lattice constant; $E_0 = \hbar^2/m_e a^2$,

and $\omega_c = eB/mc$ is the cyclotron frequency³ in the presence of an external magnetic field B .

The inequality (10.14) makes sure that the energy of the external photon is not enough to kick up the electron to another band; (10.15) and (10.16) impose limits on the size of the electric and the magnetic field respectively. Equation (10.15) is satisfied almost always for metals, while for semiconductors and insulators it can be violated for very strong electric fields; this violation leads to the phenomenon of *dielectric breakdown* or the *Zener tunneling* occurring under reverse bias in heavily doped diodes (see Fig. 17.5). The magnetic field inequality, (10.16), is violated more easily leading to the phenomenon of *magnetic breakdown*.

The full simplification power of the approximate relation (10.13) is revealed near the lower or upper edge of a band where $E_n(\mathbf{k})$ has the simple form

$$E_n(\mathbf{k}) = E_{n0} + \frac{\hbar^2 \delta k_1^2}{2m_1^*} + \frac{\hbar^2 \delta k_2^2}{2m_2^*} + \frac{\hbar^2 \delta k_3^2}{2m_3^*}, \quad (10.17)$$

where m_1^* , m_2^* , m_3^* are the three values of the effective mass tensor along the three main axes and $\delta k_i = k_i - k_{i0}$. Equation (10.17) is further simplified to become (10.9), if $m_1^* = m_2^* = m_3^*$ and $k_{i0} = 0$. In the interior of a band and far from its edges, the function $E_n(\mathbf{k})$ is usually rather complicated and the resulting operator $\hat{E}_n(-i\partial/\partial\mathbf{r})$ is inconvenient for calculations. In this case, we are looking for further simplification through the (additional) so-called *semiclassical approximation*, which replaces the quantum wave propagation by a semiclassical trajectory. The basis of this approach is to form a wave packet by an appropriate linear combination of Bloch functions of fixed band index n and crystal wave vectors belonging to a 3-D neighborhood centered at the chosen $\mathbf{k}$; the extent δk of this neighborhood in all directions must be much smaller than the size π/a of the first BZ, where a is the lattice constant. The inequality $\delta k \ll \pi/a$ is necessary in order to treat approximately the wavepacket as a classical particle of momentum $\hbar\mathbf{k}$; on the other hand, this inequality implies that the extent, δr , of this wavepacket in real space is much larger than a/π ; in other words, the size of this semiclassical “particle” is much larger than the atomic scale. Hence, it is necessary for this “particle”, since it will move in the presence of $\hat{H}_1$, to be much smaller than the characteristic length, λ , of the spatial variation of $\hat{H}_1$ as well as the radius of curvature, R , of its trajectory:

$$a \ll \delta r \ll \lambda, R. \quad (10.18)$$

The inequality $\delta r \ll \lambda$ assures that the perturbative potential $\hat{H}_1$ is spatially constant over the extent of the wavepacket; this is necessary for the statement “the semiclassical particle (corresponding to the wavepacket centered at $\mathbf{r}$) experiences a potential $\hat{H}_1(\mathbf{r})$ ” to make sense. Similarly, the inequality

³ In G-CGS system. To perform the transition from the G-CGS system to the SI one, replace the velocity of light c by the number 1 in all equations of this chapter involving the magnetic field

$\delta r \ll R$ is necessary to make the concept of trajectory approximately valid. Under these conditions, the wave packet behaves as a classical particle subject to the Newtonian mechanics in the form of Hamilton's equations

$$\mathbf{v} = \frac{\partial H(\mathbf{p}, \mathbf{r})}{\partial \mathbf{p}}, \quad (10.19)$$

$$\dot{\mathbf{p}} = -\frac{\partial H(\mathbf{p}, \mathbf{r})}{\partial \mathbf{r}}, \quad (10.20)$$

where in the present case $\mathbf{p} = \hbar \mathbf{k}$ is the momentum, and $H(\mathbf{p}, \mathbf{r}) = E_n(\mathbf{p}/\hbar) + H_1(\mathbf{r})$. These last relations follow from (10.13) and the basic rule connecting classical mechanics with quantum mechanics, according to which we pass from one to the other with the replacement, $\mathbf{p} \Leftrightarrow \hat{\mathbf{p}} \equiv -i\hbar \nabla_{\mathbf{r}}$. Implementing this rule in the present case, (10.19) and (10.20) become

$$\mathbf{v}_{n\mathbf{k}} = \frac{\partial E_n(\mathbf{k})}{\hbar \partial \mathbf{k}}, \quad (10.21)$$

$$\dot{\mathbf{k}} = -\frac{\partial H_1(\mathbf{r})}{\hbar \partial \mathbf{r}} = \frac{1}{\hbar} \mathbf{F}_{\text{add}}. \quad (10.22)$$

Thus, under the inequalities, (10.14), (10.15), (10.16), and (10.18), the wave packet made of Bloch functions $\psi_{\mathbf{k}'n}(\mathbf{r})$ of a fixed band index n and of $\mathbf{k}'$ s belonging to a region centered at $\mathbf{k}$ and of “radius” δk behaves as a classical particle. Its initial velocity is given by (10.21), i.e., it coincides with the group velocity $\partial \omega_n(\mathbf{k})/\partial \mathbf{k}$, where $\omega_n(\mathbf{k}) = E_n(\mathbf{k})/\hbar$. Furthermore, this group velocity satisfies the exact quantum mechanical relation

$$\langle \hat{\mathbf{v}} \rangle_{\mathbf{k}n} \equiv \langle \psi_{\mathbf{k}n} | \hat{\mathbf{v}} | \psi_{\mathbf{k}n} \rangle = \frac{\partial E_n(\mathbf{k})}{\hbar \partial \mathbf{k}}, \quad (10.23)$$

For a proof of (10.23), see Problem 10.1. The initial wavevector $\mathbf{k}$ changes with time according to Newton's law, $\hbar \dot{\mathbf{k}}(t) = \mathbf{F}$, and the role of force $\mathbf{F}$ is played *not* by the total force $\mathbf{F}_{\text{per}} + \mathbf{F}_{\text{add}}$ but by the additional force $\mathbf{F}_{\text{add}}$. Thus, under the stated inequalities, the time evolution of $\mathbf{k}$ is as in the free-electron model; the only difference is that the energy-vs.- $\mathbf{k}$ relation does not have the simple form $E = \hbar^2 k^2/2m$ but the actual $E_n(\mathbf{k})$. As a result of this, in the acceleration $\dot{\mathbf{v}}_n$ the effective mass tensor m_{eff} appears instead of the free-electron mass,

$$\begin{aligned} \dot{v}_{ni} &= \frac{\partial}{\partial t} \left(\frac{\partial E_n(\mathbf{k})}{\hbar \partial k_i} \right) = \frac{1}{\hbar} \sum_{j=1}^3 \frac{\partial^2 E_n(\mathbf{k})}{\partial k_j \partial k_i} \frac{dk_j}{dt} \\ &= \sum_{j=1}^3 (m_{\text{eff}}^{-1})_{ij} \hbar \dot{k}_j = \sum_{j=1}^3 (m_{\text{eff}}^{-1})_{ij} F_{\text{add},j}. \end{aligned} \quad (10.24)$$

For external electromagnetic fields, the additional force F_{add} is given by the well-known Lorentz formula (see (A.1)):

$$\mathbf{F}_{\text{add}} = -|e|\left(\mathbf{E} + \frac{\mathbf{v}}{c} \times \mathbf{B}\right), \text{ G-CGS}^4. \quad (10.25)$$

10.4 Semiclassical Trajectories in the Presence of a Magnetic Field

Combining (10.22) and (10.25) with the electric field $\mathbf{E} = 0$, we have

$$d\mathbf{k}/dt = -\frac{|e|\hbar}{c} \mathbf{v}_k \times \mathbf{B}, \text{ G-CGS},^1 \quad (10.26)$$

Equation (10.26) implies that $d\mathbf{k}$ is perpendicular to both $\mathbf{B}$ and $\mathbf{v}_k$ (hence, tangential to the surface of constant energy, $E_n(\mathbf{k}) = \text{const} = E_n(\mathbf{k}_0)$, where $\mathbf{k}_0$ is the initial value of $\mathbf{k}(t)$, $\mathbf{k}_0 = \mathbf{k}(0)$). It follows that $d\mathbf{k}$ lies at every time on a curve defined by the intersection of the surface $E_n(\mathbf{k}) = E_n(\mathbf{k}_0)$ and a plane perpendicular to the vector $\mathbf{B}$ and passing through the initial point, $\mathbf{k}_0$. This curve is the trajectory of the semiclassical particle in $\mathbf{k}$ -space. From the trajectory in $\mathbf{k}$ -space, we can obtain the trajectory of the particle in real space by the following formula:

$$\mathbf{r}(t) = \mathbf{r}_\perp(t) + \mathbf{r}_\parallel(t) = \mathbf{r}_\perp(t) + \mathbf{B}_0(\mathbf{r}(t) \cdot \mathbf{B}_0), \quad (10.27)$$

$$\mathbf{r}_\perp(t) = \mathbf{r}_\perp(0) - \frac{c\hbar}{eB} \mathbf{B}_0 \times [\mathbf{k}(t) - \mathbf{k}(0)], \quad e \equiv |e|, \quad (10.28)$$

where $\mathbf{B}_0 = \mathbf{B}/B$ is the unit vector along the direction of $\mathbf{B}$, $\mathbf{r}_\perp(t)$ is the component of $\mathbf{r}(t)$ perpendicular to $\mathbf{B}_0$, and $\mathbf{B}_0(\mathbf{r}(t) \cdot \mathbf{B}_0)$ is the component of $\mathbf{r}(t)$ parallel to $\mathbf{B}_0$. Notice that the motion along the direction of $\mathbf{B}_0$ is of constant $\mathbf{k}_\parallel = \mathbf{B}_0(\mathbf{k}(t) \cdot \mathbf{B}_0)$ (since the force along the direction of $\mathbf{B}_0$ is zero) but not of constant $v_\parallel$; the latter is given by $v_\parallel = \partial E_n(\mathbf{k})/\hbar \partial k_{11}$, which depends not only on $k_\parallel$ but also on $\mathbf{k}_\perp(t)$ (which is not constant). To prove (10.28) multiply $\mathbf{v}_k \times \mathbf{B}$ in (10.26) by $\mathbf{B}_0$ to obtain

$$\begin{aligned} \mathbf{B}_0 \times (\mathbf{v}_k \times \mathbf{B}) &= \mathbf{v}_k(\mathbf{B}_0 \cdot \mathbf{B}) - \mathbf{B}(\mathbf{B}_0 \cdot \mathbf{v}_k) \\ &= \mathbf{v}_k B - B \mathbf{B}_0(\mathbf{B}_0 \cdot \mathbf{v}_k) \\ &= B[\mathbf{v}_k - (\mathbf{B}_0 \cdot \mathbf{v}_k) \mathbf{B}_0] \\ &= B \mathbf{v}_{k\perp} = B(d\mathbf{r}_\perp/dt). \end{aligned} \quad (10.29)$$

Hence, (10.29) combined with (10.26) gives

$$\mathbf{B}_0 \times \dot{\mathbf{k}} = -\frac{eB}{c\hbar} \frac{d\mathbf{r}_\perp}{dt}. \quad (10.30)$$

By integrating (10.30) with respect to time, we end up with (10.28). As we shall see in the next section, the wavevector $\mathbf{k}$ in (10.28) and (10.30) must

⁴ In SI c must be deleted.

be taken in the repeated-zone scheme. Since $\mathbf{k}(t) - \mathbf{k}(0)$ is perpendicular to the unit vector $\mathbf{B}_0$, the product $\mathbf{B}_0 \times [\mathbf{k}(t) - \mathbf{k}(0)]$ is a vector of magnitude equal to $|\mathbf{k}(t) - \mathbf{k}(0)|$ and normal to both $\mathbf{B}_0$ and $[\mathbf{k}(t) - \mathbf{k}(0)]$. Hence, the cross multiplication by $-\mathbf{B}_0$ rotates the vector $\mathbf{k}(t) - \mathbf{k}(0)$ by -90° . Thus, *the projection on a plane perpendicular to $\mathbf{B}$ of the trajectory of the semiclassical particle in real space is obtained by rotating the projection of the trajectory in $\mathbf{k}$ -space by -90° and rescaling it by a factor $\hbar c/eB$ (or $\hbar/eB$ in SI).* In the free-electron model, the projections of both trajectories (in $\mathbf{k}$ -space and in real space) are circles. In a periodic case, we have many different trajectories that can be grouped in three different categories, as we shall see in the next section, where some simple but instructive tight binding (TB) models will be examined.

10.5 Two Simple but Elucidating TB Models

The first model is a 2D periodic square lattice with one s -orbital per site; its Hamiltonian in the Dirac notation is

$$\hat{H} = \varepsilon \sum_n |n\rangle\langle n| + V_2 \sum_n \sum_m' |n\rangle\langle m|, \quad (10.31)$$

where the $\mathbf{n}$ -summation is over all the N orbitals (in this case $N = N_{pc}$) and the prime in the summation over $\mathbf{m}$ signifies that $\mathbf{m}$ is restricted to the nearest neighbors of $\mathbf{n}$. V_2 is negative. The eigensolutions to (10.31) have the form

$$\psi_{\mathbf{k}} = \frac{1}{\sqrt{N}} \sum_l e^{i\mathbf{k} \cdot \mathbf{R}_l} |l\rangle, \quad (10.32)$$

and the corresponding eigenenergies are

$$E(\mathbf{k}) = \varepsilon + V_2 \sum_m' e^{i\mathbf{k} \cdot \mathbf{R}_m}, \quad (10.33)$$

where $\mathbf{R}_m$ takes the four values $\pm a\mathbf{x}_0$ and $\pm a\mathbf{y}_0$; a is the lattice constant. Hence,

$$E(\mathbf{k}) = \varepsilon + 2V_2(\cos k_x a + \cos k_y a). \quad (10.34)$$

Problem 10.2t. Show that $\psi_{\mathbf{k}}$ as given by (10.32) and $E(\mathbf{k})$ as given by (10.33) or (10.34) satisfy the relation $\hat{H}\psi_{\mathbf{k}} = E(\mathbf{k})\psi_{\mathbf{k}}$, where $\hat{H}$ is as in (10.31).

In Fig. 10.2, we plot $E(\mathbf{k})$ as $\mathbf{k}$ moves along the straight line segments ΓX , XM , $\text{M}\Gamma$ of the first BZ.

Problem 10.3t. Show that the only nonidentical points at which the group velocity, $\mathbf{v}_{\mathbf{k}} = \partial E(\mathbf{k})/\hbar \partial \mathbf{k}$, vanishes are the following: Γ , M , X , X' .

Problem 10.4t. Show by symmetry considerations only that the group velocity vanishes at the points Γ , M , X , X' .

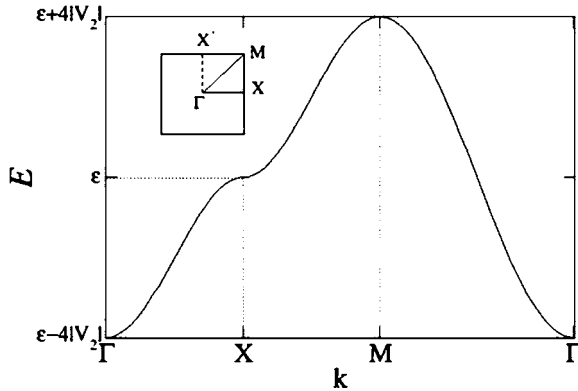


Fig. 10.2. For the band structure of (10.34) we plot $E(\mathbf{k})$ vs. $\mathbf{k}$, as $\mathbf{k}$ moves along the straight line segments ΓX , XM , $M\Gamma$ of the first BZ (shown in the insert). This is a standard way of plotting $E_n(\mathbf{k})$ vs. $\mathbf{k}$; $\mathbf{k}$ is varying along high symmetry straight line segments of the first BZ

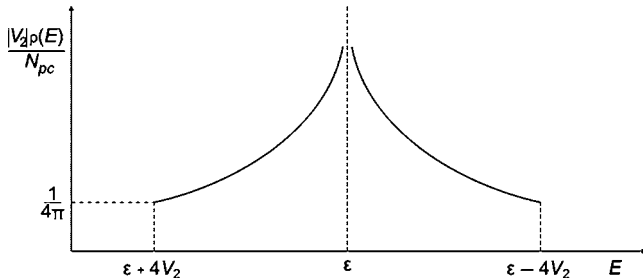


Fig. 10.3. Sketch of the DOS for the 2-D model of (10.31). The site energy ε can be chosen equal to zero without loss of generality

Having the dispersion relation $E(\mathbf{k})$ ((10.34) in the present case), we can obtain the DOS, either by (10.3), or by (10.6), or by (10.8), or by other means (see Problem 10.2s). We can also have a reasonable sketch of the DOS vs. E by taking into account that the integral of the $\rho_n(E)$ over the band is $N_{pc} = N$, and by identifying the van Hove singularities (i.e., the energies corresponding to the $\mathbf{k}$ -points at which the group velocity vanishes) and determining the behavior of the DOS at such singular energies. In the present case, there are two extremal points, Γ and M , corresponding to the lower and the upper band edges respectively; there, the DOS exhibits a discontinuity equal to $N/4\pi|V_2|$. There are also two equivalent but not identical saddle points, X and X' , at which the DOS exhibits a logarithmic singularity of the form $|\ln|E - \varepsilon||$ with a prefactor equal to $2N/4\pi^2|V_2|$ (see Problem 9.17). Furthermore, the integral from the lower to the upper band edge of $|V_2|\rho(E)/N$ over $E/|V_2|$ is equal to 1. With these information we obtain for the model of (10.31) the sketch of the DOS shown in Fig. 10.3

Besides plotting $E_n(\mathbf{k})$, as shown in Fig. 10.2 (and in Figs. 7.7), there is another way of presenting graphically the band structure $E_n(\mathbf{k})$. According to this second way, we draw lines in $\mathbf{k}$ -space of constant energy, $E_n(\mathbf{k}) = E$, (for 2-D systems), or surfaces in $\mathbf{k}$ -space of constant energy (for 3-D systems). Of particular interest is the line (for a 2-D case) or surface (for a 3-D case) for which the constant energy is taken to be the Fermi energy. This line or surface is known as Fermi line or Fermi surface respectively. As we shall see, this way of presenting graphically the dispersion relation $E_n(\mathbf{k})$ is indispensable for analyzing the semiclassical trajectories in the presence of a magnetic field $\mathbf{B}$.

In Fig. 10.4 we plot lines of constant energy for the 2-D dispersion relation (10.34). In Fig. 10.4a the lines of constant energy are plotted in the first Brillouin zone (reduced zone scheme), while in Fig. 10.4b the equivalent repeated-zone scheme is chosen.

If a magnetic field normal to the $\mathbf{k}$ -plane and pointing out of it is applied, each electron with an initial wavevector $\mathbf{k}_0$ will follow a semiclassical trajectory in $\mathbf{k}$ -space that will coincide with a line of constant energy (since the magnetic field does not do any work; see also (10.26)). The *arrows* in Fig. 10.4a show the direction followed by the electron. For the lower half of the band, $E < \varepsilon$, the trajectories in $\mathbf{k}$ -space are closed contours run counter-clockwise by the electron. For the upper half of the band, $E > \varepsilon$, each trajectory consists of four disjoint pieces in the first BZ (e.g., the one numbered 4, consists of the four pieces 4a, 4b, 4c, and 4d and it is run from A_1 to A_2 (which is the same as A'_2), from A'_2 to A_3 (which is the same as A'_3), from A'_3 to A_4 (which is the same as A'_4), and from A'_4 to A_1 (which is the same as the initial point A_1)). This artificially complicated picture simplifies drastically in the repeated-zone scheme (Fig. 10.4b) where now the same trajectory appears as follows: From A_1 to A_2 , from A_2 to A'_3 (which is the same as A_3 and A'_3), from A'_3 to A'_4 (which is the same as A'_4 and A_4), and from A'_4 back to A_1 . Thus, the trajectory is a closed contour but it is run by the electron clockwise and not counter-clockwise as the contours with $E < \varepsilon$. All the contours with $E > \varepsilon$ are run by the electrons clockwise as if the electrons had a positive charge. For this reason, the contours run clockwise are called **hole contours** or **hole trajectories**. Finally, let us examine how the trajectory corresponding to $E = \varepsilon$ is run, both in the reduced-zone scheme (Fig. 10.4a) and in the repeated-zone scheme (Fig. 10.4b). If the initial $\mathbf{k}_0$ is in the interior of the segment X_1X_2 , the electron in the first BZ will follow the trajectory in $\mathbf{k}$ -space from X_1 to X_2 (which is the same as X'_2 and X''_2) and from X_2 to X'_1 (which is the same as X_1) and from X'_1 to X'_2 and from X'_2 to X_1 completing thus the square contour $X_1X_2X'_1X'_2X_1$. Again within the first BZ the electron of energy $E = \varepsilon$ can run several other trajectories, e.g., $X_1X_2X'_2X_1$ or $X_1X_2X'_1X_1$, etc. In the repeated zone scheme there many more possibilities such as *open* zig-zag trajectories, e.g. $X'_2X_1X_2X'_1X''_2 \dots$, or open zig-zag trajectories in other directions including or not including loops. It must be stressed that in general the repeated-zone scheme not only simplifies drastically the appearance of the trajectories in $\mathbf{k}$ -space, but also becomes obligatory if (10.28), connecting the trajectory in real space to the trajectory in $\mathbf{k}$ -space, is to be valid. Indeed,

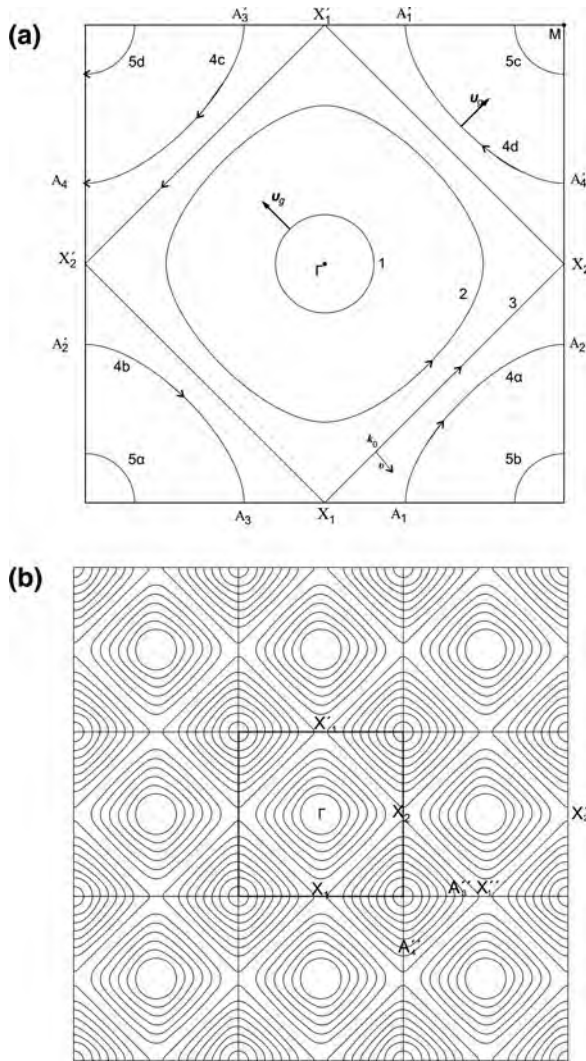


Fig. 10.4. Lines of constant energy for the 2-D band structure of (10.34) plotted either in the 1st BZ (reduced-zone scheme, (a)) or in the repeated-zone scheme (b). Energy is increasing as we go from contour 1 to the disjoint pieces denoted by 5a, 5b, 5c, 5d (a). The square $X_1X_2X_1'X_2'$ (numbered 3) corresponds to $E(\mathbf{k}) = \varepsilon$ (center of the band) and includes the two nonidentical but equivalent points X_2 and X_1' at which the group velocity vanishes giving rise to a logarithmic van-Hove singularity. The group velocity $\mathbf{v} = \partial E(\mathbf{k})/\hbar\partial\mathbf{k}$ is perpendicular to the lines of constant energy and always points towards the line of higher energy. In the repeated-zone scheme (b) the contour of the first BZ is denoted by the thick line. The disjoint equal energy pieces for $E > \varepsilon$ in the 1st BZ become closed contours in the repeated-zone scheme and the square with $E = \varepsilon$ may become open zig-zag lines in various directions with or without closed loops

the trajectory in real space is necessarily continuous⁵; hence, so must be the corresponding one in $\mathbf{k}$ -space. However, in general, only in the repeated-zone scheme are all trajectories in $\mathbf{k}$ -space continuous and uniquely determined by their initial point $\mathbf{k}_0$. (The $E = \varepsilon$ in the present model is an exception in the sense that it allows infinitely many continuous paths).

Concluding the study of this simple 2-D TB model, we point out that this model allowed us to introduce and examine some of the basic generic aspects of electronic motion in periodic systems, such as the three categories of electronic semiclassical trajectories in $\mathbf{k}$ -space (in the repeated-zone scheme) under the action of a magnetic field:

- (a) Closed trajectories enclosing in their interior states of lower energy and run by the electron counter-clockwise as in the free electron case. These trajectories are called *electron-like*.
- (b) Closed trajectories enclosing in their interior states of higher energy and run by the electron clock-wise, as if the electron were a hole. For this reason, these trajectories, which are absent in the free-electron case, are called *hole-like*.
- (c) Open trajectories, which in the repeated-zone scheme continue indefinitely. These open trajectories can be periodic in $\mathbf{k}$ -space (in the sense that, if $\mathbf{k}$ belongs to a finite section of the trajectory, the vector $\mathbf{k} + n\mathbf{G}$ belongs to the trajectory) as the one $X'_2 X_1 X_2 X'_1 \dots$ in Fig. 10.4b, or aperiodic. Such open trajectories do not exist in the free-electron case. They are expected to offer conductivity channels and thus provide an explanation for the observed magnetoresistance.

As the $\mathbf{k}$ -space repeated-zone scheme trajectories are directly related to the real space trajectories, through (10.28), there are three categories of trajectories in real space as well: electron-like, hole-like, and open ones.

We shall conclude this section by examining a 3-D extension of the 2-D model studied up to now. The model consist of only one s -orbital per atom with diagonal matrix elements equal to ε and nearest neighbor off-diagonal matrix elements V_2 . The atoms now are arranged in a 3-D simple cubic lattice.

Problem 10.5t. Show that the dispersion relation for this model is as follows:

$$E(\mathbf{k}) = \varepsilon + 2V_2(\cos k_x a + \cos k_y a + \cos k_z a) \quad (10.35)$$

Plot $E(\mathbf{k})$ as $\mathbf{k}$ runs over the segments ΓX , XR , RF , ΓM , MX of the first BZ (for these segments see Fig. 3.20).

Problem 10.6t. Show that, for the band structure (10.35), the points of zero group velocity are:

$$\begin{aligned} \Gamma(0, 0, 0); \quad E(\Gamma) &= \varepsilon - 6|V_2|, \quad \text{minimum,} \\ R(\pi/a, \pi/a, \pi/a); \quad E(R) &= \varepsilon + 6|V_2|, \quad \text{maximum,} \end{aligned}$$

⁵ A discontinuity requires an infinite force.

$$\left. \begin{array}{l} X(\pi/a, 0, 0) \\ X'(0, \pi/a, 0) \\ X''(0, \pi/a, 0) \end{array} \right\} E(X) = E(X') = E(X'') = \varepsilon - 2|V_2|, \quad \text{saddle points,}$$

$$\left. \begin{array}{l} M(\pi/a, \pi/a, 0) \\ M'(0, \pi/a, \pi/a) \\ M''(\pi/a, 0, \pi/a) \end{array} \right\} E(M) = E(M') = E(M'') = \varepsilon + 2|V_2|, \quad \text{saddle points,}$$

According to the results of Fig. 9.7 (see also Problem 9.17), we have the following expressions for the DOS near the van Hove singularities:

$$\rho(E) = N \frac{1}{4\pi^2 |V_2|^{3/2}} (E - E_{\min})^{1/2} \quad (10.36)$$

$$\rho(E) = N \frac{1}{4\pi^2 |V_2|^{3/2}} (E_{\max} - E)^{1/2}, \quad (10.37)$$

$$\rho(E) = \rho(E_X) - N \frac{3}{4\pi^2 |V_2|^{3/2}} (E_X - E)^{1/2}, \quad E \rightarrow E_X^-, \quad (10.38)$$

$$\rho(E) = \rho(E_M) - N \frac{3}{4\pi^2 |V_2|^{3/2}} (E - E_M)^{1/2}, \quad E \rightarrow E_M^+. \quad (10.39)$$

On the basis of these relations and the overall integral of $\rho(E)$ from E_Γ to E_R , we obtain the following sketch of the DOS. (Fig. 10.5)

In Fig. 10.6, we show three characteristic surfaces (in $\mathbf{k}$ -space) of constant energy of the 3-D band structure of (10.35). In Fig. 10.6(b) three lines are shown resulting by the intersection of the constant energy surface by planes perpendicular to various directions of the magnetic field. These lines, as was mentioned before, are electronic semiclassical trajectories in $\mathbf{k}$ -space. Trajectory a is electron-like, trajectory b is hole-like, and trajectory c is an open one.

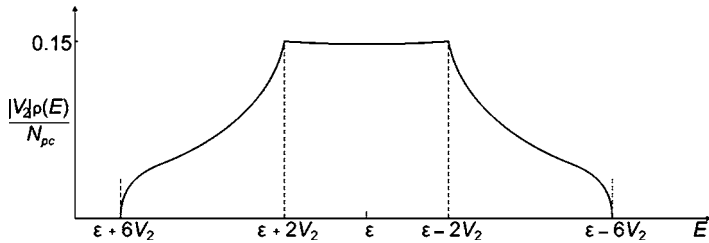


Fig. 10.5. Sketch of the DOS $\rho(E)$ vs. E for the dispersion relation shown in (10.35). The site energy ε can be taken as zero

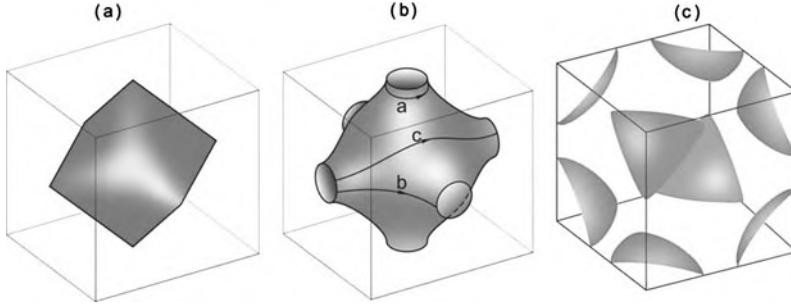


Fig. 10.6. Three different surfaces of constant energy plotted within the 1st BZ for the band structure of (10.35). The eight disjoint pieces in case (c) form a closed almost spherical surface in the repeated-zone scheme. The lines a, b, c in case (b) are representing semiclassical trajectories of electrons in the presence of a static magnetic field. Trajectories a, b, c, are electron-like, hole-like, and open respectively

10.6 Cyclotron Resonance and the de Haas–van Alphen Effect

The time, $t_{12} \equiv t_2 - t_1$, required for the electron to go from point 1 to point 2 in its trajectory $\mathbf{k}_\perp(t)$ (see Fig. 10.7) in the presence of a magnetic field, B , pointing along the z -axis is given by the following formula:

$$t_{12} = \lim_{\delta E \rightarrow 0} \frac{\hbar^2}{eB} \frac{\delta A_{12}}{\delta E} = \frac{\hbar^2}{eB} \frac{\partial A_{12}}{\partial E}, \quad (10.40)$$

where δA_{12} is the area in the plane of the trajectory bounded by the segment 1, 2, of the trajectory $\mathbf{k}_\perp(t)$ corresponding to the initial energy, E , and the segment 1', 2' corresponding to the energy $E + \delta E$ as shown in Fig. 10.7.

Problem 10.7t. Prove (10.40).

Hint: From (10.26), we have $dt = (\hbar/eB)(dk/|v_{k\perp}|)$, where $|v_{k\perp}| = |\mathbf{v}_k| \cos \phi$; ϕ is the angle between $\mathbf{v}_k$ and the plane of the trajectories. However, $|\mathbf{v}_k| = \delta E / \hbar \delta k_\perp$ and $\delta k_\perp = \delta k \cos \phi$, where $\delta k_\perp$ is the distance between the two surfaces ($E_n(\mathbf{k}) = E$ and $E_n(\mathbf{k}) = E + \delta E$) in $\mathbf{k}$ -space along the normal direction to the surfaces.

Equation (10.40) applied to a closed trajectory gives its period $T(E, k_z)$:

$$T(E, k_z) = \frac{\hbar^2 c}{eB} \left| \frac{\partial A(E, k_z)}{\partial E} \right|, \quad (10.41)$$

where $A(E, k_z)$ is the area enclosed by the trajectory; the latter is uniquely determined by the energy E and the component, k_z , of $\mathbf{k}$ parallel to $\mathbf{B}$. Notice that E and k_z are conserved along the trajectory. Equation (10.41) can have the same appearance as the free-electron formula if one introduces the cyclotron effective mass

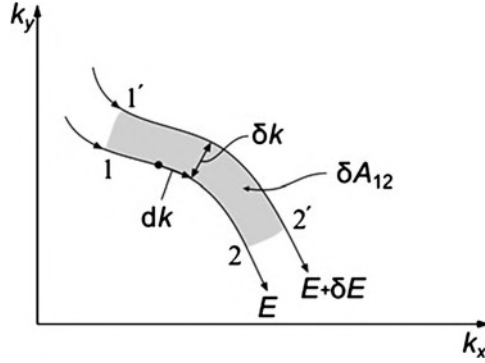


Fig. 10.7. The semiclassical electron trajectory in $\mathbf{k}$ -space passing through the points 1 and 2 is defined as the intersection of the surface $E_n(\mathbf{k}) = E$ with a plane normal to the magnetic field; the trajectory passing through the points 1' and 2' is the intersection of the same plane with the surface $E_n(\mathbf{k}) = E + \delta E$. The shaded area is δA_{12}

$$m_c^* = m_c^*(E, k_z) = \frac{\hbar^2}{2\pi} \left| \frac{\partial A(E, k_z)}{\partial E} \right|. \quad (10.42)$$

We have then

$$T(E, k_z) = \frac{2\pi}{\omega_c(E, k_z)} = \frac{2\pi m_c^* c}{eB}. \quad (10.43)$$

The cyclotron effective mass does not coincide in general with the effective mass, m^* , appearing in the DOS. In terms of the mass tensor, m_{ij} , where $(m^{-1})_{ij} = \partial^2 E_n(\mathbf{k}) / \hbar^2 \partial k_i \partial k_j$, we have for the DOS effective mass, m^* , and the cyclotron effective mass, m_c^* , the following formulae:

$$m^* = |\det(m_{ij})|^{1/3}, \quad (10.44)$$

$$m_c^* = |\det(m_{ij}) / m_{zz}|^{1/2}. \quad (10.45)$$

In Problem 5.14 we have shown, in the framework of the JM, that the DOS at E_F , ρ_F , exhibits sharp peaks vs. $1/B$ with a period equal to $2\pi e / \hbar A_F c$ (in G-CGS; in SI set $c = 1$) where $A_F \equiv \pi k_F^2$ is the maximum cross-section of the Fermi surface. The periodic peaks in ρ_F translates to a periodic oscillation as a function of $1/B$ of various quantities that depend on ρ_F , such as the magnetic susceptibility (*de Haas-van Alphen effect*), the electrical conductivity (*Shubnikov-de Haas effect*), etc in crystalline metals. The origin of these phenomena can be traced back to the quantized Landau energy levels for the motion perpendicular to the magnetic field (see (5.67)). To examine the de Haas-van Alphen effect for crystalline solids, we must generalize the concept of the quantized Landau levels for electrons moving in a periodic potential. This can be achieved through the correspondence principle of Bohr

$$E_{n+1}(k_z) - E_n(k_z) = \hbar \omega_c, \quad (10.46)$$

valid for very high quantum numbers⁶ n . That n is a large integer follows from the fact that $\hbar\omega_c$ is of the order of 10^{-4} eV for $B \simeq 1$ T, while the Fermi energy is of the order of 6 eV. Hence, for the Landau levels to reach energies around the Fermi level, n must be of the order of 10^5 . The cyclotron frequency ω_c is equal to $2\pi/T(E, k_z)$ where $T(E, k_z)$ is given by (10.41). Thus, (10.46) becomes

$$E_{n+1}(k_z) - E_n(k_z) = \frac{2\pi eB}{\hbar c} \frac{\delta E}{A(E + \delta E; k_z) - A(E, k_z)}. \quad (10.47)$$

Choosing $E = E_n(k_z)$ and $E + \delta E = E_{n+1}(k_z)$ we obtain

$$A(E_{n+1}, k_z) - A(E_n, k_z) = A_0 \equiv \frac{2\pi eB}{\hbar c}. \quad (10.48)$$

Thus, the quantization of energy has been translated to the quantization of the area enclosed by the orbit of the electron in $\mathbf{k}$ -space. Equation (10.48) is equivalent to the following relation

$$A(E_n(k_z), k_z) = (n + \gamma)A_0, \quad (10.49)$$

where γ does not depend on n . For the free-electron model, (10.49) reduces to $E_n(k_z) = \hbar\omega_c(n + 1/2) + \hbar^2 k_z^2/2m$, if γ is taken as $1/2$. Equation (10.49) can be expanded in powers of $\delta k_z \equiv k_z - k_{z0}$ around a chosen value k_{z0} in order to express $\delta E_n \equiv E_n(k_z) - E_n(k_{z0})$ in terms of δk_z . We have then

$$\frac{\partial A}{\partial E_n} \delta E_n + \frac{\partial A}{\partial k_z} \delta k_z + \frac{1}{2} \frac{\partial^2 A}{\partial k_z^2} \delta k_z^2 = 0,$$

or

$$E_n(k_z) = E_n(k_{z0}) - \frac{(\partial A / \partial k_z)}{(\partial A / \partial E_n)} \delta k_z - \frac{1}{2} \frac{\partial^2 A / \partial k_z^2}{(\partial A / \partial E_n)} \delta k_z^2. \quad (10.50)$$

Now if k_{z0} is such that A is an extremal area (either maximum or minimum), i.e., if $(\partial A / \partial k_z)_{k_z=k_{z0}} = 0$, then (10.50) is of the form of (5.67) (with δk_z instead of k_z and $-(\partial^2 A / \partial k_z^2) / (\partial A / \partial E_n)$ instead of $\hbar^2/m$). Hence, the DOS around $E_n(k_{z0})$ will exhibit a peak of the same form as in Fig. 5.6b. Thus, if E_F coincides with $E_n(k_{z0})$, ρ_F will develop a peak. Substituting $E_F = E_n(k_{z0})$ and $k_z = k_{z0}$ in (10.49) and taking into account (10.48), we obtain the following relation giving the peaks of ρ_F :

$$A(E_F, k_{z0}) = (n + \gamma) \frac{2\pi eB}{\hbar c}, \quad (10.51)$$

which implies that these peaks appear at values of $1/B$ with a separation, $\Delta(1/B)$, between consecutive values given by:

⁶ The integer number n characterizes the quantized energy level n and it should not be confused with the band index, which is not shown in this section.

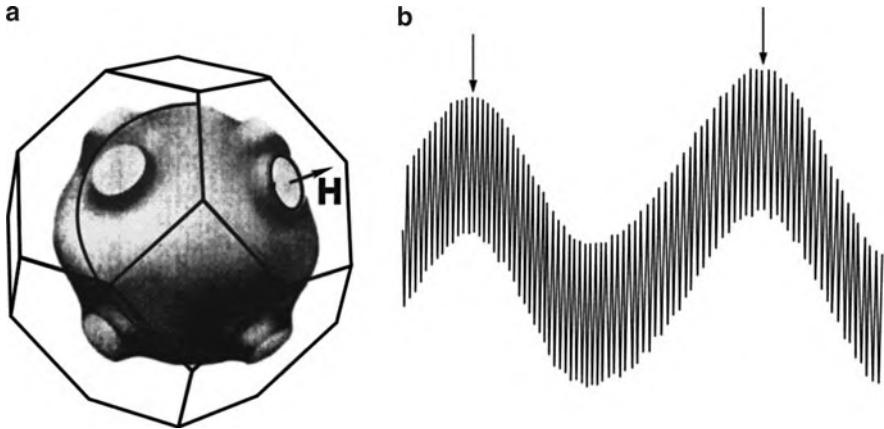


Fig. 10.8. (a) The Fermi surface of silver for the indicated $[111]$ direction of the magnetic field exhibits two extremal cross-sections marked with the corresponding closed trajectories. (b) The de Haas-van Alphen oscillations exhibit two periods, $\Delta(1/B)$, the large one, which corresponds to the small cross-section at the neck, and the small one, which corresponds to the large cross-section at the belly. From the ratio of the two periods, which is 51, one determines immediately the ratio of the large to the small cross-section

$$\Delta\left(\frac{1}{B}\right) = \frac{2\pi e}{\hbar A_F(E_F, k_{z0})c}, \quad \text{G-CGS}, \quad (10.52)$$

(in SI omit c). The values of the DOS, $\rho(E)$, between peaks are associated with nonextremal areas A at which $\partial A/\partial k_z \neq 0$. For a pictorial argument supporting this last statement, the readers are referred to the book by Ashcroft and Mermin [SS75], p. 273. Equation (10.52) is extremely important, because it permits, by measuring the periods $\Delta(1/B)$, to determine the extremal cross-sections of the Fermi surface, for each orientation of $\mathbf{B}$. This information usually allows us to reconstruct experimentally (by measuring, e.g., the magnetic susceptibility in monocrystals of metals) the shape of the Fermi surface (often with the help of theoretical calculations as well). Notice that the Fermi surface is in general rather complicated with more than one extremal cross sections perpendicular to each chosen direction. In Fig. 10.8 we show the de Haas-van Alphen oscillations for silver and for the indicated direction of the magnetic field.

10.7 Hall Effect and Magnetoresistance

In Problem 5.15 it was shown that a static electric field, $\mathbf{E}_\perp$, perpendicular to the magnetic field $\mathbf{B}$ adds to the equation for the velocity a term equal to $\mathbf{v}_0$. Hence, a term $\mathbf{v}_0 t$ proportional to t will be added to the trajectory $\mathbf{r}_\perp(t)$, where

$$\mathbf{v}_0 = c \frac{E_\perp}{B} (\mathbf{E}_0 \times \mathbf{B}_0), \quad \text{G - CGS}, \quad (10.53)$$

and $\mathbf{E}_0 = \mathbf{E}_\perp / |\mathbf{E}_\perp|$, $\mathbf{B}_0 = \mathbf{B} / |\mathbf{B}|$. This is true for the case of electrons moving in a periodic potential as well.⁷ Thus, the semiclassical trajectory in real space is given by the following equation:

$$\mathbf{r}_\perp(t) - \mathbf{r}_\perp(0) = -\frac{c\hbar}{eB} \mathbf{B}_0 \times [\mathbf{k}(t) - \mathbf{k}(0)] + \mathbf{v}_0 \cdot t. \quad (10.54)$$

To go back from the trajectory in real space to the trajectory in $\mathbf{k}$ -space, we differentiate (10.54) with respect to t , we take into account that $\dot{\mathbf{r}}(t) = \mathbf{v}_\mathbf{k} = \partial E(\mathbf{k}) / \hbar \partial \mathbf{k}$, and we write $\mathbf{v}_0$ as $\partial(\hbar \mathbf{v}_0 \cdot \mathbf{k}) / \hbar \partial \mathbf{k}$. We have then by solving with respect to $\dot{\mathbf{k}}$

$$\dot{\mathbf{k}} = -\frac{e}{c} \frac{\partial \tilde{E}_n(\mathbf{k})}{\hbar \partial \mathbf{k}} \times \mathbf{B}, \quad (10.55)$$

where

$$\tilde{E}_n(\mathbf{k}) = E_n(\mathbf{k}) - \hbar \mathbf{v}_0 \cdot \mathbf{k}, \quad (10.56)$$

In (10.55) and (10.56), we have restored the band index n to remind the readers that each semiclassical trajectory is specified by the band index, n , the initial $\mathbf{k}$ -point, and the force acting on it. Hence, the trajectory in $\mathbf{k}$ -space in the presence of both $\mathbf{B}$ and $\mathbf{E}_\perp$ is determined by the intersection of a plane normal to $\mathbf{B}$ (and passing through the initial point $\mathbf{k}_0$) with the surface $\tilde{E}_n(\mathbf{k}) = \text{const.}$, where the modified dispersion relation $\tilde{E}_n(\mathbf{k})$ is given by (10.56). The modification $\hbar \mathbf{v}_0 \cdot \mathbf{k}$ due to the electric field is very small⁸ in comparison with the typical values of $E_n(\mathbf{k})$ in metals. Hence, the trajectories in $\mathbf{k}$ -space are very slightly modified by the presence of the electric field $\mathbf{E}_\perp$.

Let us consider now a closed trajectory in the limit of very large magnetic field and in a monocrystalline metal as pure as possible, so that $\omega_c \tau \gg 1$. This inequality means that the electron goes around its closed trajectory many times before it undergoes a scattering event. During the time τ between two consecutive scattering events the average electron velocity $\mathbf{v}_\perp$ perpendicular to the magnetic field will be (according to (10.54))

$$\mathbf{v}_\perp \equiv \frac{\mathbf{r}_\perp(\tau) - \mathbf{r}_\perp(0)}{\tau} = \mathbf{v}_0 - \frac{c\hbar}{eB} \mathbf{B}_0 \times \frac{\mathbf{k}(\tau) - \mathbf{k}(0)}{\tau}. \quad (10.57)$$

⁷ In a reference system moving with velocity $\mathbf{v}_0$ with respect to the initial system, the electric field is zero (see Griffiths [E14].) As a result, in this system, the trajectory is given by (10.28). Hence, to return to the initial system, we have to add simply $\mathbf{v}_0 t$ to the rhs of (10.28).

⁸ Typical values of $E(\mathbf{k})$ are of the order of $E_F \simeq 6 \text{ eV}$. To estimate $\hbar \mathbf{v}_0 \cdot \mathbf{k}$, we assume that the current-density j is of the order of 10^2 A/cm^2 or less, the resistivity, ρ_e , in a metal is of the order of $100 \mu\Omega \times \text{cm}$ or less and the magnetic field is of the order of 1 T . Then $\hbar \mathbf{v}_0 \cdot \mathbf{k}$ is of the order of 10^{-5} eV or less.

Let us assume that all occupied trajectories of a given band n are closed and let us average (10.57) over them. We have then that

$$\langle \mathbf{v}_\perp \rangle_n = \mathbf{v}_0 - \frac{c\hbar}{eB} \mathbf{B}_0 \times \left\langle \frac{\mathbf{k}(\tau) - \mathbf{k}(0)}{\tau} \right\rangle_n. \quad (10.58)$$

Now $|\mathbf{k}(\tau) - \mathbf{k}(0)|$ is no larger than the size of the 1st BZ, π/a . The averaging procedure over all occupied trajectories reduces the value of $|\mathbf{k}(\tau) - \mathbf{k}(0)|$ by a factor of the order of $|\hbar \mathbf{v}_0 \cdot \mathbf{k}|/E_n(\mathbf{k}) \simeq v_0/(\hbar/ma)$. To prove this statement, we notice first that in the absence of electric field the average, $\langle \mathbf{k}(\tau) - \mathbf{k}(0) \rangle_n$ is zero; the reason is that for every occupied $\mathbf{k}$ there is an occupied $-\mathbf{k}$, since $E_n(\mathbf{k}) = E_n(-\mathbf{k})$; furthermore, since $\mathbf{v}_{-\mathbf{k}} = -\mathbf{v}_\mathbf{k}$, for each trajectory $\mathbf{k}(\tau) - \mathbf{k}(0)$ there is a trajectory given by $-\mathbf{k}(\tau) + \mathbf{k}(0)$. In the presence of the electric field the band structure $E_n(\mathbf{k})$ is replaced by $\tilde{E}_n(\mathbf{k}) = E_n(\mathbf{k}) - \hbar \mathbf{v}_0 \cdot \mathbf{k}$, for which the reflection symmetry is violated: $\tilde{E}_n(\mathbf{k}) \neq \tilde{E}_n(-\mathbf{k})$. It is the breaking of the reflection symmetry that makes the average $\langle \mathbf{k}(\tau) - \mathbf{k}(0) \rangle_n$ different from zero. Thus, $\langle \mathbf{k}(\tau) - \mathbf{k}(0) \rangle_n$ is expected to be equal to a typical value of $\mathbf{k}(\tau) - \mathbf{k}(0)$ multiplied by the ratio of the symmetry-breaking term, $\hbar \mathbf{v}_0 \cdot \mathbf{k}$, over the symmetry-preserving term, $E_n(\mathbf{k})$. Substituting in (10.58) the maximum value of $|\mathbf{k}(\tau) - \mathbf{k}(0)|$ times the factor $|\hbar \mathbf{v}_0 \cdot \mathbf{k}|/E_n(k)$ (due to averaging), we obtain

$$\langle \mathbf{v}_\perp \rangle = \mathbf{v}_0 \left(1 + \frac{A \cos \theta}{\omega_c \tau} \right) + |\mathbf{v}_0| \mathbf{E}_0 \frac{A \sin \theta}{\omega_c \tau}, \quad (10.59)$$

where θ is the angle between $\langle \mathbf{k}(\tau) - \mathbf{k}(0) \rangle$ and $\mathbf{E}$ and A is a number of the order of one or less. The term $\mathbf{v}_0$ is of order of $1/B$ as $B \rightarrow \infty$ and it is normal to the electric field, while the second one is of order of $1/B^2$ as $B \rightarrow \infty$; finally the third term is parallel to the electric field and of order $1/B^2$. Thus, under the said conditions of all occupied orbits to be closed and $\omega_c \tau \gg 1$, we have the simple relation

$$\langle \mathbf{v}_\perp \rangle_n = \mathbf{v}_0 + \mathcal{O}(1/B^2), \quad B \rightarrow \infty \quad (10.60)$$

which means that all the information about the particulars of the material incorporated in the second term of the rhs of (10.58) disappear. Equation (10.60) implies that the current density due to the n th band, $\mathbf{j}_n$, is given by

$$\mathbf{j}_n = -en_{en} \langle \mathbf{v}_\perp \rangle \simeq -en_{en} \mathbf{v}_0, \quad (10.61)$$

where n_{en} is the concentration of electrons populating the n th band. If there are open trajectories among the occupied ones in the n th band, the simple equation (10.61) fails. This difficulty may be overcome by considering the unoccupied states of the n th band; these states, if they were occupied, would make a contribution to the current density $\tilde{\mathbf{j}}_n$, which satisfies the relation $\mathbf{j}_n + \tilde{\mathbf{j}}_n = 0$ (because a completely full band cannot produce any current). Thus, $\mathbf{j}_n = -\tilde{\mathbf{j}}_n$. If there are no open trajectories among the unoccupied ones

(and if $\omega_c\tau \gg 1$), $\tilde{\mathbf{j}}_n$ can be calculated as before and the final result will be similar to (10.60): $\mathbf{j}_n \simeq -en_{hn}\mathbf{v}_0$; this implies that the current density due to the n th band, $\mathbf{j}_n$, is given by the following equation

$$\mathbf{j}_n \simeq en_{hn}\mathbf{v}_0, \quad (10.62)$$

where n_{hn} is the concentration of holes in the n th band. We remind the readers that (10.61) holds only when there are no open trajectories among the occupied states of the n th band, while (10.62) is valid only when there are no open trajectories among the unoccupied states of the n th band. Since there are always open trajectories in any band, it is not possible for both (10.61) and (10.62) to be valid simultaneously. Actually, either (10.61) or (10.62) will be valid or none of them; the last case corresponds to the situation where there are open trajectories in the band n among both the occupied and the unoccupied states. For the time being, we shall ignore the last case and we shall return to it a little later. Taking into account (10.61) and (10.62), we have for the total current $\mathbf{j}$

$$\mathbf{j} = \sum_n \mathbf{j}_n = e(n_h - n_e)\mathbf{v}_0 + \mathcal{O}(1/B^2), \quad (10.63)$$

where the summation is over all bands that are neither completely empty nor fully occupied; n_h is the concentration of holes resulting by summing n_{hn} over the subset⁹ of these bands that possess no open trajectories among the unoccupied states; n_e is the electron concentration resulting by summing n_{en} over the subset of these bands that possess no open trajectories among the occupied states. By multiplying (10.63) by $\mathbf{B}_0$ and taking into account (10.53) for $\mathbf{v}_0$, we find¹⁰

$$\mathbf{E}_\perp = \frac{1}{ce(n_h - n_e)} \mathbf{B} \times \mathbf{j} + \mathcal{O}(1/B). \quad (10.64)$$

Equation (10.64) implies that the off-diagonal resistivity ρ_{yx} equals to $[ce(n_h - n_e)]^{-1}B$. Since by definition the Hall coefficient, R , equals ρ_{yx}/B , we have

$$R \simeq \frac{1}{ce(n_h - n_e)} + \mathcal{O}(1/B^2), \quad \text{G - CGS}^{11}. \quad (10.65)$$

Equation (10.65) is valid under the conditions of $\omega_c\tau \gg 1$ (which implies that $B\tau \gg c\langle m_c^* \rangle/e$) and of only closed trajectories in either the occupied or the unoccupied states in every one of the bands contributing to the total current. The quantity $\langle m_c^* \rangle$ is a properly averaged cyclotron resonance effective mass.

If for all bands contributing to $\mathbf{j}$ in (10.63), the occupied states contain no open trajectories, then, $n_h = 0$, and the Hall coefficient is the same as in the

⁹ This subset may coincide for some metals with the full set.

¹⁰ We used also the identity $\mathbf{B}_0 \times (\mathbf{E}_0 \times \mathbf{B}_0) = \mathbf{E}_0 - \mathbf{B}_0(\mathbf{B}_0 \cdot \mathbf{E}_0) = \mathbf{E}_0$.

¹¹ In SI c must be deleted.

free-electron case. On the other hand, if for all these bands the unoccupied states contain no open trajectories, then $n_e = 0$, and the Hall coefficient becomes positive, $R = 1/cen_h$; R is also positive when $n_h > n_e$, as in the case of Al. Thus, the mystery of positive values of R has been solved.

To understand the unexpectedly simple and universal result (10.65), we must go back to (10.58), which shows that there are two contributions to the average drift velocity: one is independent of any property of the solid and it is equal to the velocity of a reference frame at which the electric field vanishes; the other depends on the properties of each solid through the average $\langle \mathbf{k}(\tau) - \mathbf{k}(0) \rangle$ and through the collision time τ in addition to its dependence on the fields B and E . However, at very high magnetic fields and clean specimens such that $\omega_c \tau \gg 1$, and under the condition that the open trajectories can be sidestepped for all bands contributing to the total current density, the second term is much smaller than the first one, and hence, it can be omitted without appreciable error.

What happens when the aforementioned conditions are not satisfied? More specifically, what happens if there are open trajectories in both the occupied and the unoccupied states in at least one of the bands contributing to the current density $\mathbf{j}$? Then, it is impossible to ignore the existence of open trajectories. To be specific, we consider the open trajectories among the occupied states in the n th band and we assume that all of them are parallel to each other and in direction in real space determined by the unit vector $\mathbf{d}_0$. For each one of these open trajectories, $|\mathbf{k}(\tau) - \mathbf{k}(0)|$ grows without limit as $\tau \rightarrow \infty$. Actually, $|\mathbf{k}(\tau) - \mathbf{k}(0)| = A(\tau, 0)/\delta k$, where $A(\tau, 0)$ is as in Fig. 10.7 with $t_2 = \tau$ and $t_1 = 0$. It follows from (10.40) that $A(\tau, 0)$, and hence, $|\mathbf{k}(\tau) - \mathbf{k}(0)|$ is proportional to τ and proportional to B . Then, the first term in the rhs of (10.54) divided by t is independent of B and independent of t ; its magnitude in the absence of electric field is $|\mathbf{r}_\perp(t) - \mathbf{r}_\perp(0)|/t \simeq |\mathbf{v}_\mathbf{k}|$ and its direction is along the direction $\mathbf{d}_0$, of the open trajectory in real space. As we have mentioned before, the electric field, $\mathbf{E}_\perp$, hardly influences the trajectory; its main role is in the averaging procedure over the open trajectories: instead of being zero as in the absence of $\mathbf{E}_\perp$, the average is now $|\mathbf{r}_\perp(t) - \mathbf{r}_\perp(0)|/t$ multiplied by $|\hbar \mathbf{v}_0 \cdot \mathbf{k}(\tau)|/|E_n(\mathbf{k})|$, where $\mathbf{k}(\tau) \simeq \mathbf{k}(\tau) - \mathbf{k}(0)$ as $\tau \rightarrow \infty$. Substituting the expressions for $\mathbf{v}_0$ (from (10.53)) and $|\mathbf{k}(\tau) - \mathbf{k}(0)| = \tau e B |\mathbf{v}_{k\perp}|/\hbar c$, we obtain

$$\frac{|\hbar \mathbf{v}_0 \cdot \mathbf{k}(\tau)|}{|E(\mathbf{k})|} = \frac{|(\mathbf{E}_\perp \times \mathbf{B}_0) \cdot \mathbf{k}_0| \tau e |\mathbf{v}_{k\perp}|}{|E(\mathbf{k})|}, \quad (10.66)$$

where $\mathbf{k}_0$ is the unit vector along the trajectory in $\mathbf{k}$ -space. The triple product $(\mathbf{E}_\perp \times \mathbf{B}_0) \cdot \mathbf{k}_0$ is equal to $\mathbf{E}_\perp \cdot (\mathbf{B}_0 \times \mathbf{k}_0) = \mathbf{E}_\perp \cdot \mathbf{d}_0$. Hence, the contribution to the current of open trajectories parallel to $\mathbf{d}_0$ in real space is of the form $en_{e0} \mathbf{v}_0 + e^2 n_{e0} (v_k^2/E_k) \tau (\mathbf{E}_\perp \cdot \mathbf{d}_0) \mathbf{d}_0$, where n_{e0} is the concentration of electrons occupying the open trajectories. Thus, in the presence of unavoidable open

trajectories parallel in real space to the unit vector $\mathbf{d}_0$, the current density has the following form¹² in the limit $B \rightarrow \infty$:

$$\mathbf{j} = \sigma_a(\mathbf{E}_\perp \times \mathbf{B}_0) + \sigma_b(\mathbf{E}_\perp \cdot \mathbf{d}_0)\mathbf{d}_0 + \mathcal{O}(1/B^2), \quad (10.67)$$

where $\sigma_a \sim 1/B$, and $\sigma_b \rightarrow \text{const} \neq 0$ as $B \rightarrow \infty$.

Let us summarize the results of the electrical conductivity tensor in the presence of a very large static uniform magnetic field B (such that $\omega_c\tau \gg 1$) perpendicular to the static uniform electric field $\mathbf{E}_\perp$. The z -axis has been chosen along the direction of $\mathbf{B}$ and the x -axis along the direction, $\mathbf{d}_0$, of the open trajectories in real space. Notice that the components of the tensor σ_{ij} must satisfy the general relation $\sigma_{ij}(\mathbf{B}) = \sigma_{ji}(-\mathbf{B})$

Case 1. In every band contributing to $\mathbf{j}$ there are only closed trajectories in either the occupied or the unoccupied states. There are no open trajectories in both occupied and unoccupied states in any of these bands. For metals, since only states in the immediate vicinity of the Fermi energy matter, Case 1 corresponds to no open trajectories at the Fermi surface in the repeated-zone scheme.

Case 1a. Uncompensated solids, $n_h \neq n_e$. The result for σ_{ij} is as follows:

$$\sigma = \begin{vmatrix} \frac{A_{xx}}{B^2} & \frac{A_{xy}}{B} & \frac{A_{xz}}{B} \\ -\frac{A_{xy}}{B} & \frac{A_{yy}}{B^2} & \frac{A_{yz}}{B} \\ -\frac{A_{xz}}{B} & -\frac{A_{yz}}{B} & A_{zz} \end{vmatrix}, \quad B \rightarrow \infty, \quad \omega_c\tau \rightarrow \infty, \quad (10.68)$$

where A_{ij} ($ij = x, y, z$) are independent of B in the limit $B \rightarrow \infty$, and $A_{xy} = ce(n_h - n_e)$. The diagonal elements σ_{xx} and σ_{yy} are of the order $1/B^2$ as $B \rightarrow \infty$ because, according to (10.59), they are proportional to $|v_0|/\omega_c\tau$. The nondiagonal elements σ_{zx} and σ_{zy} are proportional to $\langle v_{\mathbf{k},z} \rangle$. The velocity $v_{\mathbf{k},z}$ is equal to $\langle \hbar k_z/m^* \rangle$ where m^* depends on the mass tensor at $\mathbf{k}(t)$ and the average is over the closed trajectory. In general, $\langle \hbar k_z/m^* \rangle$ is different from zero. Averaging over the occupied (or unoccupied) trajectories introduces the by-now-familiar factor of $\hbar \mathbf{v}_0 \cdot \mathbf{k}/E_n(\mathbf{k})$ for each band that produces the $1/B$ dependence, unless there is such a symmetry that makes $A_{zx} = A_{zy} = 0$ (e.g., if the magnetic field is perpendicular to a plane of mirror symmetry of $E_n(\mathbf{k})$, then $v_{\mathbf{k},z} = -v_{-\mathbf{k},z}$ and the averaging over the occupied (or unoccupied) trajectories is zero. For the JM, the A_{ij} are as follows: $A_{xx} = A_{yy} = c^2 n_e m/\tau$, $A_{xy} = -cen_e$, $A_{zx} = A_{zy} = 0$, and $A_{zz} = e^2 \tau n_e/m$.

Case 1b. Compensated solids, $n_h = n_e$. Then, according to (10.63), the quantities $A_{xy} = -A_{yx}$ are equal to zero and we should keep the next power of $1/B$. Thus,

¹² For compensated solids (i.e., for $n_e = n_h$) and in the absence of unavoidable open orbits $\sigma_a \sim 1/B^2$ as $B \rightarrow \infty$ (See (10.63)).

$$\boldsymbol{\sigma} = \begin{vmatrix} \frac{C_{xx}}{B^2} & \frac{C_{xy}}{B^2} & \frac{C_{xz}}{B} \\ \frac{C_{xy}}{B^2} & \frac{C_{yy}}{B^2} & \frac{C_{yz}}{B} \\ -\frac{C_{xz}}{B} & -\frac{C_{yz}}{B} & C_{zz} \end{vmatrix}, \quad B \rightarrow \infty, \quad \omega_c \tau \rightarrow \infty, \quad (10.69)$$

Case 2. At least in one band contributing to $\mathbf{j}$, there are open trajectories in both the occupied and in the unoccupied states. This is the case of unavoidable open trajectories. Then, the conductivity tensor, according to (10.67), has the form

$$\boldsymbol{\sigma} = \begin{vmatrix} D_{xx} & \frac{D_{xy}}{B} & D_{xz} \\ -\frac{D_{xy}}{B} & \frac{D_{yy}}{B^2} & \frac{D_{yz}}{B} \\ D_{xz} & -\frac{D_{yz}}{B} & D_{zz} \end{vmatrix}, \quad B \rightarrow \infty, \quad \omega_c \tau \rightarrow \infty, \quad (10.70)$$

where the D_{ij} s are independent of B in the limit of $B \rightarrow \infty$ and $\mathbf{d}_0$, the direction of open orbit in real space, is along the x -axis. The quantity σ_{xz} is independent of B (in the limit $B \rightarrow \infty$), because $|\mathbf{k}(\tau) - \mathbf{k}(0)| \sim B$, and as a result, it cancels the $1/B$ of $|\mathbf{v}_0|$ in the expression $\hbar \mathbf{v}_0 \cdot \mathbf{k}$. To obtain the resistivity tensor ρ_{ij} , we have to take the inverse of σ_{ij} . For simplicity we shall assume that σ_{xz} and σ_{yz} are zero. Then

$$\boldsymbol{\rho} = \begin{vmatrix} \rho_{xx} & \rho_{xy} & 0 \\ \rho_{yx} & \rho_{yy} & 0 \\ 0 & 0 & \rho_{zz} \end{vmatrix}, \quad (10.71)$$

where

$$\rho_{xx} = \frac{\sigma_{yy}}{\Delta}, \quad \rho_{yy} = \frac{\sigma_{xx}}{\Delta}, \quad \rho_{xy} = -\frac{\sigma_{xy}}{\Delta}, \quad \rho_{yx} = -\frac{\sigma_{yx}}{\Delta}, \quad (10.72)$$

and

$$\Delta = \sigma_{xx}\sigma_{yy} - \sigma_{xy}\sigma_{yx}. \quad (10.73)$$

Problem 10.8t. Prove that the diagonal element of $\boldsymbol{\rho}$ along an axis making an angle θ with the x -axis is given by the following expression

$$\rho_{\theta\theta} = \rho_{xx} \cos^2 \theta + \rho_{yy} \sin^2 \theta + (\rho_{xy} + \rho_{yx}) \cos \theta \sin \theta \quad (10.74)$$

Hint: Any 2×2 tensor in an orthogonal system rotated by an angle θ with respect to the original orthogonal system is given by the following expression:

$$\boldsymbol{\rho}' = M(\theta) \boldsymbol{\rho} M^T(\theta),$$

$$\text{where } M(\theta) = \begin{vmatrix} \cos \theta & \sin \theta \\ -\sin \theta & \cos \theta \end{vmatrix} \text{ and } M^T(\theta) = \begin{vmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{vmatrix}.$$

Problem 10.9t. Show that $\rho_{\theta\theta}$ is given by the following expressions in the limit $B \rightarrow \infty$ and $\omega_c \tau \rightarrow \infty$

$$\rho_{\theta\theta} = \frac{A_{xx} \sin^2 \theta + A_{yy} \cos^2 \theta}{A_{xy}^2}, \quad \text{case 1.a,} \quad (10.75)$$

$$\rho_{\theta\theta} = \frac{C_{xx} \sin^2 \theta + C_{yy} \cos^2 \theta - C_{xy} \sin 2\theta}{C_{xx} C_{yy} - C_{xy}^2} B^2, \quad \text{case 1.b,} \quad (10.76)$$

$$\rho_{\theta\theta} = \frac{D_{xx} \sin^2 \theta}{D_{xx} D_{yy} + D_{xy}^2} B^2, \quad \text{case 2.} \quad (10.77)$$

Equation (10.75) shows that for Case 1a (uncompensated solid and “absence” of open trajectories), the resistivity tends to a constant value as $\omega_c \tau \rightarrow \infty$; when $A_{xx} = A_{yy}$, this constant value is the same for all direction. This result is qualitatively similar to the free-electron formula. The latter is recaptured by setting $A_{xx} = A_{yy} = n_e m c^2 / \tau$ and $A_{xy} = -n_e e c$; we have then $\rho_{\theta\theta} = m / e^2 n_e \tau$, which coincides with (5.86). Equations (10.76) and (10.77) show a behavior radically different from that of the JM. Indeed, for Case 1b (compensated solid and “absence” of open trajectories), the magnetoresistance increases without limit as $B \rightarrow \infty$ being proportional to B^2 in this limit. The angular dependence of the coefficient of B^2 is rather weak, and in the special case $C_{xx} = C_{yy}$ and $C_{xy} = 0$ disappears altogether. Finally, in Case 2 (presence of unavoidable open trajectories), the magnetoresistance grows again as B^2 (in the limit $B \rightarrow \infty$) with a coefficient that depends strongly on the direction in the plane normal to $\mathbf{B}$; it is maximum for the current density normal to the direction of open orbits in real space and disappears for the current density parallel to the direction of open orbits.

Concluding this section, we shall write a formula for the calculation of the conductivity tensor in the presence of magnetic field. This formula is based on Boltzmann’s equation (see Appendix G) and its known as *Shockley’s tube-integral formula*:

$$\sigma_{ij}^{(n)} = 2e^2 \int \frac{d^3 k}{(2\pi)^3} \tau v_i^{(n)} \tilde{v}_j^{(n)}(\mathbf{k}) \left(-\frac{\partial f}{\partial E} \right)_{E=E_n(\mathbf{k})}, \quad (10.78)$$

where

$$\tilde{\mathbf{v}}^{(n)}(\mathbf{k}) = \int_{-\infty}^0 \frac{dt}{\tau} e^{t/\tau} \mathbf{v}^{(n)}(\mathbf{k}(t)). \quad (10.79)$$

Equation (10.78) gives the contribution to σ_{ij} ($\sigma_{ij} = \sum_n \sigma_{ij}^{(n)}$) from a particular band of index n . The collision time τ depends in general on both the band index n and on the band structure $E_n(\mathbf{k})$; the end point of the vector $\mathbf{k}(t)$ follows the electron semiclassical trajectory in $\mathbf{k}$ -space as t varies; the initial value $\mathbf{k}$ is integrated over in (10.78).

10.8 Key Points

- A wavepacket made out of n -band Bloch functions belonging to a small neighborhood of the 1st BZ centered at $\mathbf{k}$ and of radius δk under the action of an additional nonperiodic force, $\mathbf{F}_{\text{add}}$ (due usually to external fields) follows a trajectory in $\mathbf{k}$ and in real space determined by the relations

$$\begin{aligned}\hbar \frac{d\mathbf{k}}{dt} &= \mathbf{F}_{\text{add}}, \\ \frac{d\mathbf{r}}{dt} &\equiv v_{n\mathbf{k}} = \frac{\partial E_n}{\hbar \partial \mathbf{k}},\end{aligned}$$

The conditions for the validity of these equations were presented.

- In the presence of a static constant magnetic field $\mathbf{B} = B\mathbf{B}_0$, the $\mathbf{k}$ -space trajectory is determined by the intersection of a plane normal to $\mathbf{B}$ and passing through the initial point $\mathbf{k}_0$ and the surface $E_n(\mathbf{k}) = E_n(\mathbf{k}_0)$. The real space trajectory has a component parallel to $\mathbf{B}$ and one normal to $\mathbf{B}$. The latter is given by

$$\mathbf{r}_{\perp}(t) = \mathbf{r}_{\perp}(0) - \frac{c\hbar}{|e|B} \mathbf{B}_0 \times [\mathbf{k}(t) - \mathbf{k}(0)].$$

There are three types of trajectories in $\mathbf{k}$ -space:

Closed trajectories run by the electron counterclockwise as in the free-electron case. They are called electron-like.

Closed trajectories run by the electron clockwise as if the electron were a hole. They are called hole-like.

Open trajectories which in the repeated-zone scheme continue indefinitely.

- The period of a closed trajectory in $\mathbf{k}$ -space is given by the following expression

$$T(E, k_z) = \frac{c\hbar^2}{|e|B} \left| \frac{\partial A(E, k_z)}{\partial E} \right|,$$

where $A(E, k_z)$ is the area in $\mathbf{k}$ -space enclosed by the trajectory (the z -axis is chosen parallel to $\mathbf{B}$)

- The quantization of energy is transferred to the quantization of the $\mathbf{k}$ -space area A defined by the closed trajectory as follows

$$A(E_n(k_z), k_z) = (n + \gamma)(2\pi|e|B/\hbar c), \quad n = 0, 1, 2, \dots$$

- The “period” in the de Haas–Van Alphen effect is

$$\Delta\left(\frac{1}{B}\right) = \frac{2\pi|e|}{c\hbar A_F(E_F, k_{z0})},$$

where k_{z0} has such a value (if any) that $A_F(E_F, k_{z0})$ is extremal (for the given orientation of the z -axis with respect to the principal axes).

- If only closed trajectories exist in either the occupied or the unoccupied states, the Hall coefficient is given by

$$R = \frac{1}{ce(n_h - n_e)} + O\left(\frac{1}{B^2}\right), \quad \omega_c\tau \gg 1.$$

- The resistivity in the direction θ and in the presence of a magnetic field is given by the following expressions in the limit $\omega_c\tau \gg 1$

$$\rho_{\theta\theta} = [A_{xx} \sin^2 \theta + A_{yy} \cos^2 \theta] / A_{xy}^2, \quad \text{case 1}$$

$$\rho_{\theta\theta} = [C_{xx} \sin^2 \theta + C_{yy} \cos^2 \theta - C_{xy} \sin 2\theta] B^2 / [C_{xx} C_{yy} - C_{xy}^2], \quad \text{case 2}$$

$$\rho_{\theta\theta} = D_{xx} B^2 \sin^2 \theta / [D_{xx} D_{yy} + D_{xy}^2], \quad \text{case 3}$$

Case 1 is for uncompensated solids ($n_h \neq n_e$) and absence of relevant open orbits. Case 2 is for compensated solids and absence of relevant open orbits. Case 3 is for unavoidable open orbits in the x -direction in real space.

10.9 Problems

10.1 Prove (10.23).

Hint: Consider the operator $\hat{E}_n(-i\frac{\partial}{\partial \mathbf{r}}) = \sum_{\mathbf{R}} E_{n\mathbf{R}} e^{\mathbf{R} \cdot (\partial/\partial \mathbf{r})}$ acting on $\mathbf{r}\psi_{n\mathbf{k}}(\mathbf{r})$ and take into account that $\hat{\mathbf{v}} = (i/\hbar)[\hat{H}, \mathbf{r}]$, where $[\hat{H}, \mathbf{r}]$ is the commutator.

10.2s Show that the DOS can be obtained by the following formula

$$\rho_n(E) = -\frac{V}{\pi} \text{Im} \frac{1}{(2\pi)^3} \int_{BZ} \frac{d^3 k}{E + is - E_n(\mathbf{k})},$$

where Im signifies the imaginary part of the integral and $s \rightarrow 0^+$.

10.3 Using the formula of Problem 10.2s adapted for a 2-D case, show that the DOS for the model of (10.31) (the band structure of which is given by (10.34)) is as follows

$$\rho(E) = \frac{2N}{4\pi^2 |V_2|} \mathbb{K}(\sqrt{x}),$$

where

$$x \equiv 1 - (E - \varepsilon)^2 / 16V_2^2,$$

and $\mathbb{K}$ is the complete elliptic integral of first kind. Find the limiting values of $\rho(E)$ as $E \rightarrow \varepsilon$ and verify that they coincide with the ones used in obtaining Fig. 10.3

10.4s Consider a 3-D LCAO model with only one s -orbital per atom; the atoms form an fcc or bcc lattice. The only nonzero matrix element is

among nearest neighbor atoms and is denoted by V_2 ($V_2 < 0$). Show that the dispersion relations for these models are:

$$E(\mathbf{k}) = -4|V_2|(\cos \phi_1 \cdot \cos \phi_2 + \cos \phi_2 \cdot \cos \phi_3 + \cos \phi_3 \cdot \cos \phi_1), \quad \text{fcc},$$

$$E(\mathbf{k}) = -8|V_2| \cos \phi_1 \cdot \cos \phi_2 \cdot \cos \phi_3, \quad \text{bcc},$$

where $\phi_i = k_i a/2$, $i = x, y, z$, and a is the lattice constant. Plot $E(\mathbf{k})$ vs. $\mathbf{k}$ as $\mathbf{k}$ moves along straight line segments of the 1st BZ. Identify the singular points or lines at which $\partial E(\mathbf{k})/\partial \mathbf{k} = 0$ and the corresponding van Hove singularities; then, produce a sketch of the DOS for both the **fcc** and the **bcc** lattice.

10.5s Prove (10.45).

10.6 Prove (10.74).

10.7 Starting from (10.78) and (10.79), prove that σ has the form $\tau \mathbf{F}(B\tau)$; then prove Kohler's rule, according to which $[\rho_{xx}(B) - \rho_{xx}(0)]/\rho_{xx}(0)$ is a function only of the product $B\tau$.

Further Reading

- See Ashcroft and Mermin, [SS75], pp. 229–239 and 262–281.

Methods for Calculating the Band Structure

Summary. The concept of pseudopotential is presented. It is almost equivalent to the actual potential but without its strong singularity. The absence of singularity allows the solution to Schrödinger's equation as a weighted sum of plane waves. Degenerate perturbation theory simplifies further the problem. Other methods for solving Schrödinger's equation in periodic media, such as the APW, KKR, and the $\mathbf{k} \cdot \mathbf{p}$ methods are briefly presented.

11.1 Introductory Remarks

The readers should be convinced by now that the band structure $E_n(\mathbf{k})$ is “sine qua non” for the qualitative understanding and the quantitative determination of the properties of crystalline solids. For certain phenomena, as, e.g., the magnetoresistance, band structure is necessary not only for the quantitative details but also for explaining their very existence. Thus, it is not pointless to review the various theoretical/calculational methods to obtain $E_n(\mathbf{k})$. In Fig. 11.1 some of these methods are mentioned and their degree of applicability to various types of solids is indicated. Among these methods, two, the LCAO and the plane wave/pseudopotential stand out.

The LCAO, in its simplest version, has already been presented in Chap. 6, in Chap. 10, Sect. 10.5, and in Appendix F; more realistic results and data based on LCAO were given in Chap. 7. If really accurate results are sought, this method has to be extended in various directions: (a) At least nine atomic orbitals must be included (one s, three p's, and five d's); (b) The atomic orbitals belonging to different atoms are not orthogonal; so their overlap integrals have to be taken into account; (c) Matrix elements and overlap integrals up to second- and even third-nearest neighbors must be included; (d) The matrix elements do not depend only on the orientation of the orbitals relative to the vector joining the two neighboring atoms but on the local environment as well; and (e) Finally – and this is the main disadvantage of the LCAO method – ab initio reliable calculation of the required matrix elements of

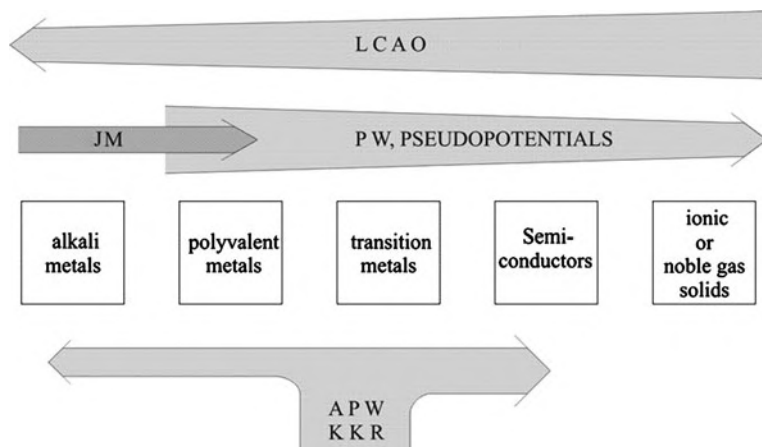


Fig. 11.1. In alkali metals the valence electrons spread themselves almost uniformly over the volume of the solid. This spreading becomes less and less uniform as we move to polyvalent metals, to transition metals, to semiconductors and finally, to closed shell solids (ionic solids, or noble gas solids) where the electrons stay within the ions or the parent atoms respectively. The LCAO, which is based on atomic (or atomic-like) orbitals, is naturally adapted to the right end of the figure, although with fitted matrix elements it can treat all kind of solids. The JM, which assumes uniform eigenstates (i.e., plane waves) can be extended, through linear combination of plane waves (PW) and the concept of pseudopotential, to all types of crystalline solids. More complicated methods, such as the *augmented plane waves* (APWs) or the Green's Function approach, known as the *Korringa-Kohn-Rostoker* (KKR) method, are better adapted to the middle category of transition metals, although they work quite well for other types of crystalline solids. The method called $\mathbf{k} \cdot \mathbf{p}$ is used for semiconductors near the band edges

the Hamiltonian is not feasible. Usually, if accurate results are sought, these matrix elements are obtained by fitting the outcome of the LCAO calculations to results obtained by other methods such as augmented plane wave (APW), or korringa-kohn-rostoker (KKR), or plane wave/pseudopotentials. Even then, the transferability of those fitted matrix elements from one to another local environment requires special care.

Do not forget though that this disadvantage of the LCAO method has to be balanced against its several significant advantages:

1. It offers easy physical interpretation, since it connects directly the band structure with the energy levels and the orbitals of the atoms or the molecules making up the solid.
2. It allows easy qualitative estimates and semiquantitative calculations.
3. It is appropriate for handling complicated solids with many atoms per primitive cell (of the order of thousands), or more generally, for calculating properties that involve a large number of atoms.
4. It can handle better than any other method amorphous solids, noncrystalline solids, or solids with high degree of disorder.

In this chapter, we shall proceed with the presentation of the plane wave/pseudopotential method. We shall also describe briefly the APW, KKR, and the $\mathbf{k} \cdot \mathbf{p}$ methods. All these first principle methods are variations of the scheme presented in Sect. 8.4; their main difference is in step 8 (page 220) concerning the solution to Schrödinger's equation, and in step 4 for the determination of the ionic potential.

11.2 Ionic and Total Pseudopotentials

The ionic contribution, $\mathcal{V}_i(\mathbf{r})$, to the total effective potential $\mathcal{V}(\mathbf{r})$, inside and in the immediate vicinity of the ionic core located at $\mathbf{R}_n$ is of the form $Z^*e^2/4\pi\epsilon_0|\mathbf{r} - \mathbf{R}_n|$, where Z^* depend on the distance $|\mathbf{r} - \mathbf{R}_n|$, approaching the atomic number Z as $|\mathbf{r} - \mathbf{R}_n| \rightarrow 0$ and the valence¹ number ζ when $|\mathbf{r} - \mathbf{R}_n|$ is much larger than the ionic radius r_c . The singular behavior of $\mathcal{V}_i(\mathbf{r})$ as $|\mathbf{r} - \mathbf{R}_n| \rightarrow 0$ and hence, of $\mathcal{V}(\mathbf{r})$ (see (8.32)), makes the solution to Schrödinger's equation in terms of plane waves impractical. On the other hand, the regions within each ion core play a negligible (or, at best, minor) role in the formation of solids; the latter depends mainly on the ζ “valence” electrons (i.e., on their atomic eigenenergies and on the behavior of the corresponding atomic orbitals in the region beyond the ionic radius r_c . This situation is rather peculiar: Regions of no physical relevance, as the interiors of the ionic cores create mathematical difficulties in the sense that they reduce inapplicable the very convenient plane wave expansion approach. To overcome this problem the idea of pseudopotential has been developed: For each ion we introduce a pseudopotential that has the following properties:

- (a) Its eigenenergies for the valence electrons are the same as those in the parent atom.
- (b) However, for $r < r_c$ the corresponding eigenstates are smooth without nodes, whereas for $r > r_c$ they are the same as those in the parent atom.
- (c) The pseudopotential is finite everywhere and usually smooth.

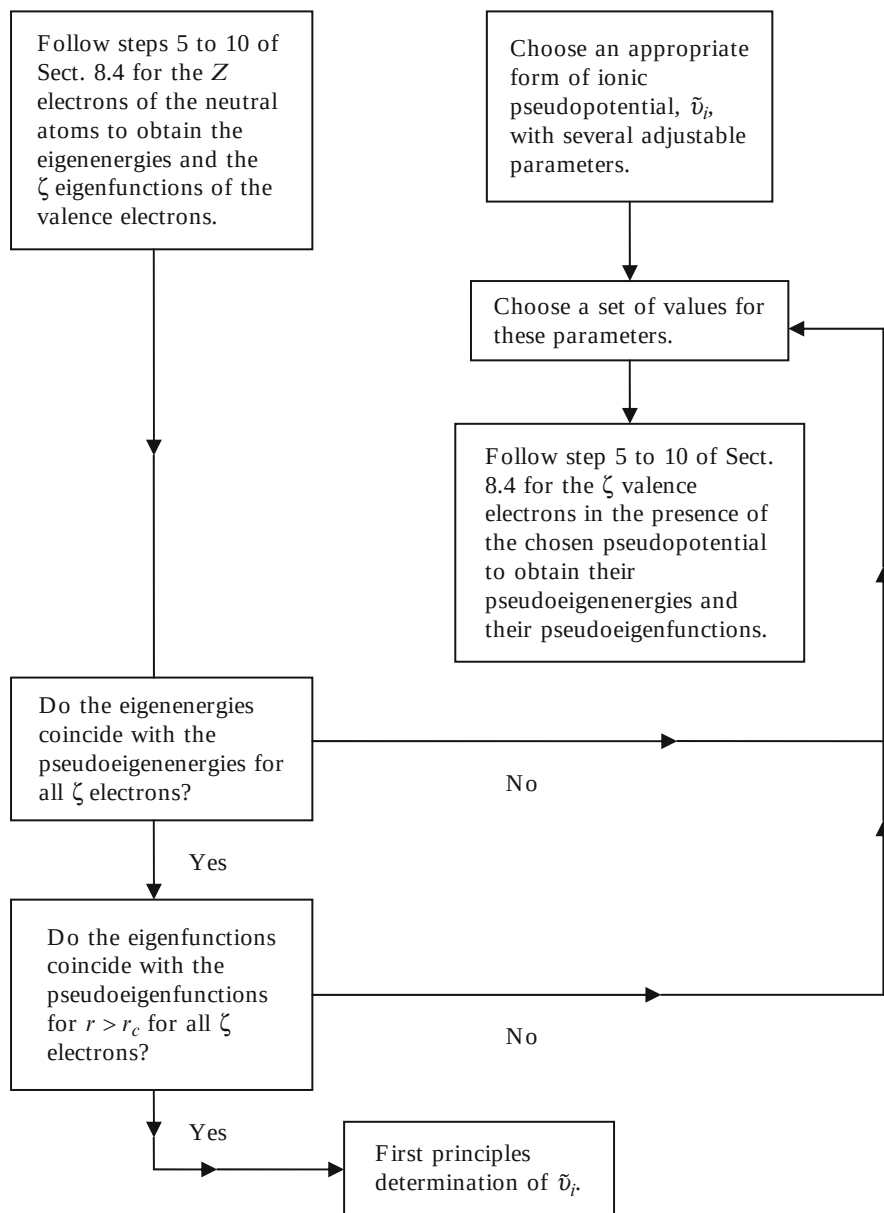
Thus, an ionic pseudopotential, as far as solid formation and solid state properties are concerned, is almost² equivalent to the actual ionic potential, while at the same time, it is smooth and finite as to allow the employment of plane wave expansions.

In Table 11.1 we outline the procedure by which an ionic pseudopotential is calculated from first principles.

¹ As it was mentioned in Chap. 8, the atom is separated to an ionic core containing $Z - \zeta$ electrons and ζ potentially detached electrons. The ionic core contains only those electrons that are expected to remain practically unaffected by the formation of the solid.

² There is a question of whether the pseudopotential is transferable, i.e., to what extent is modified by the different solid state environments in which the ion finds

Table 11.1. Ab initio calculation of the ionic pseudopotential for an ion of $Z-\zeta$ core electron where Z is the atomic number (i.e. the number of protons in the nucleus) and ζ is the number of “valence” electrons (“valence” electrons are the ones not belonging to the core; in the core we include those expected to remain practically unaffected by the formation of the solid)



In Fig. 11.2 we plot schematically the actual ionic potential as well as one of the actual valence electrons eigenfunctions and we compare them with the pseudopotential $\tilde{v}_i$ and the corresponding pseudoeigenfunction.³

If one is willing to sacrifice accuracy for the sake of convenience and physical clarity, one can use a simple model pseudopotential that is everywhere finite and that almost coincides with the actual ionic potential for $r > r_c$. Such a simple model is the so-called *empty-core pseudopotential* proposed by Ashcroft, pictured in Fig. 11.3, and given by the following expressions:

$$\tilde{v}_{iA}(r) = 0, \quad r < r_c, \quad (11.1)$$

$$\tilde{v}_{iA}(r) = -\zeta e^2/4\pi\epsilon_0 r, \quad r > r_c. \quad (11.2)$$

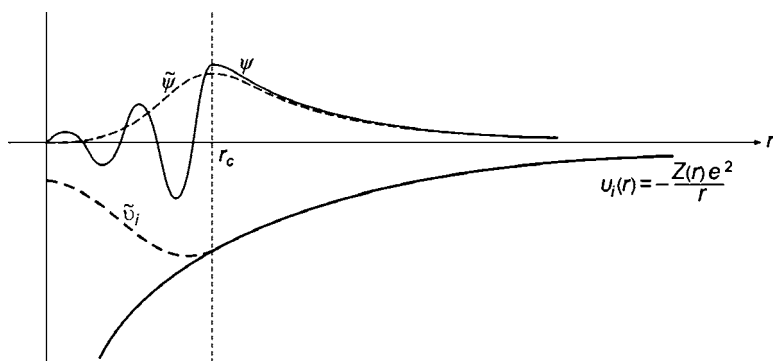


Fig. 11.2. Schematic plot of the actual ionic potential (v_i solid line) and the corresponding pseudopotential ($\tilde{v}_i$, dashed line); actual typical valence eigenfunction (ψ , solid line) and the corresponding pseudoeigenfunction ($\tilde{\psi}$, dashed line)

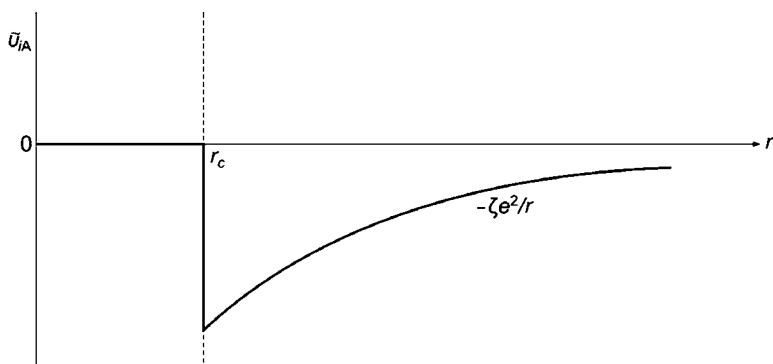


Fig. 11.3. Plot of the simple, approximate, empty-core pseudopotential

itself. It turns out that such undesirable modifications do appear, although of second order in the difference among various environments.

³ For realistic examples see Fig. 10.2, p. 232 in the book by Marder.

As we shall see shortly, it is convenient to introduce the Fourier transform, $\tilde{v}_i(\mathbf{q})$, of the pseudopotential, $\tilde{v}_i(\mathbf{r})$, (multiplied by the concentration of atoms, n_a):

$$\tilde{v}_i(\mathbf{q}) = n_a \int d^3r e^{-i\mathbf{q}\cdot\mathbf{r}} \tilde{v}_i(\mathbf{r}). \quad (11.3)$$

For the empty-core ionic pseudopotential we obtain, by substituting (11.1) and (11.2) in (11.3) and performing the 3D integration, the following simple formula (see Problem 11.1):

$$\tilde{v}_{iA}(\mathbf{q}) = -\frac{4\pi\zeta e^2 n_a}{4\pi\epsilon_0 q^2} \cos q r_c. \quad (11.4)$$

Having $\tilde{v}_i(\mathbf{q})$ we can obtain $\tilde{v}_i(\mathbf{r})$ by the inverse Fourier transform:

$$\tilde{v}_i(\mathbf{r}) = \frac{1}{N_a} \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} \tilde{v}_i(\mathbf{q}). \quad (11.5)$$

Furthermore, the total ionic potential $\mathcal{V}_i(\mathbf{r}) = \sum_{\mathbf{n}} \sum_{v=1}^p \tilde{v}_{iv}(|\mathbf{r} - \mathbf{R}_n - \mathbf{r}_v|)$ can be expressed in terms⁴ of $\tilde{v}_{iv}(\mathbf{q})$ as follows:

$$\mathcal{V}_i(\mathbf{r}) = \frac{1}{N_{pc}} \frac{1}{p} \sum_{\mathbf{q}} \sum_{\mathbf{n}} e^{-i\mathbf{q}\cdot\mathbf{R}_n} \sum_{v=1}^p e^{-i\mathbf{q}\cdot\mathbf{r}_v} \tilde{v}_{iv}(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{r}} = \sum_{\mathbf{G}} \tilde{v}_i(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}. \quad (11.6)$$

To arrive at the last expression, we have used the following relations: $N_a = N_{pc}p$ where N_{pc} is the total number of primitive cells; $\sum_{\mathbf{n}} \exp(-i\mathbf{q}\cdot\mathbf{R}_n) = N_{pc}$, if $\mathbf{q}$ is equal to a lattice vector $\mathbf{G}$ of the reciprocal lattice, and zero otherwise; hence, the “summation” over $\mathbf{q}$ is reduced to a genuine summation over all vectors of the reciprocal lattice; finally, by definition

$$\tilde{v}_i(\mathbf{q}) \equiv \frac{1}{p} \sum_{v=1}^p e^{-i\mathbf{q}\cdot\mathbf{r}_v} \tilde{v}_{iv}(\mathbf{q}). \quad (11.7)$$

Notice that (11.6) implies that, for a crystal, the ionic potential $\mathcal{V}_i(\mathbf{r})$ does not depend on all $\mathbf{q}$ s but only on the discrete set of the vectors of the reciprocal lattice; this is a consequence of the periodicity. For a nonperiodic solid where the atoms occupy positions $\mathbf{r}_\ell$ ($\ell = 1, \dots, N_a$), the ionic potential depends on the continuous variable $\mathbf{q}$ as follows

$$\mathcal{V}_i(\mathbf{r}) = \sum_{\mathbf{q}} \tilde{v}_i(\mathbf{q}) S_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}}, \quad (11.8)$$

⁴ We assume that within each primitive cell characterized by the lattice vector $\mathbf{R}_n$ there are p atoms the positions of which are given by $\mathbf{R}_n + \mathbf{r}_v$ ($v = 1, \dots, p$); these p atoms may be different from each other; hence, the subscript v in $\tilde{v}_{iv}$.

where, by definition,

$$\tilde{v}_i(\mathbf{q})S_{\mathbf{q}} \equiv \frac{1}{N_a} \sum_{\mathbf{r}_\ell} \tilde{v}_{i\ell}(\mathbf{q})e^{-i\mathbf{q} \cdot \mathbf{r}_\ell}. \quad (11.9)$$

There is a point about (11.6) and (11.8) worth of attention: The ionic pseudopotential in $\mathbf{q}$ -space, $\tilde{v}_i(\mathbf{q})$, screened by the valence electrons, would give the total pseudopotential in $\mathbf{q}$ -space. However, the screening can be simply expressed in terms of the dielectric function $\varepsilon(\mathbf{q})$ (see (5.7)). Thus,

$$\tilde{v}(\mathbf{q}) = \frac{v_i(\mathbf{q})}{\varepsilon(\mathbf{q})}. \quad (11.10)$$

The quantity $\tilde{v}(\mathbf{q})$ is called **pseudopotential form factor**.

Hence, by combining (11.6) and (11.10), we are in a position to write down the full periodic pseudopotential in $\mathbf{r}$ -space without following the computationally demanding procedure of Steps 5–10 of Sect. 8.4:

$$\mathcal{V}(\mathbf{r}) = \sum_{\mathbf{G}} \tilde{v}(\mathbf{G})e^{i\mathbf{G} \cdot \mathbf{r}}, \quad \tilde{v}(\mathbf{G}) = \frac{\tilde{v}_i(\mathbf{G})}{\varepsilon(\mathbf{G})}, \quad (11.11)$$

where $\tilde{v}_i(\mathbf{G})$ is given by (11.7); there is a corresponding expression for the general nonperiodic case of (11.8). To avoid any misunderstanding, we point out that the calculation of the dielectric function from first principles in realistic solids is a more difficult problem than the implementation of the procedure outlined in Sect. 8.4. Hence, if our goal is band structure calculations of the highest possible accuracy, then (11.10) and (11.11) ought to be avoided. On the other hand, if we are willing to sacrifice accuracy and possibly consistency for the sake of simplicity and transparency, then (11.10) and (11.11) offer a very convenient path for obtaining $\mathcal{V}(\mathbf{r})$. Indeed, if we employ the JM dielectric function

$$\varepsilon(q) = 1 + \frac{k_s^2}{q^2} f(q/k_F), \quad (11.12)$$

where $k_s^2 = k_{\text{TF}}^2 = 4k_F/\pi a_B$ and $f(q/k_F)$ is given by (D.26), together with a model ionic pseudopotential, e.g., the one in (11.4), we have

$$\tilde{v}_A(q) = -\frac{4\pi e^2 n_e}{4\pi \varepsilon_0 (q^2 + k_{\text{TF}}^2 f)} \cos qr_c. \quad (11.13)$$

Taking into account that $f(0) = 1$ and that $n_e = k_F^3/3\pi^2$, we find that $-\tilde{v}_A(q)$ at $q = 0$ is equal to $2E_F/3$ (see Problem 11.6 and compare with (5.50):

$$v(0) = -\frac{2}{3}E_F = -E_s. \quad (11.14)$$

In Fig. 11.4 we compare the pseudopotential form factor $\tilde{v}(q)$ as obtained from the first principle calculation outlined in Table 11.1 with the pseudopotential given in (11.13) for a metal (Al). In obtaining $\tilde{v}_A(q)$ we have

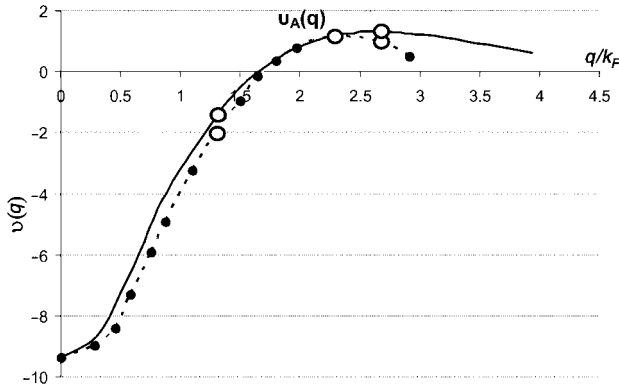


Fig. 11.4. Pseudopotential form factor for Al. The points are the result of a first principle calculation, while the *solid line* is based on (11.13) and the RJM with $\zeta = 2.76$ and $r_c = 0.5$ Å (see Table 4.3 in p. 95). The *open dots* on the curves of $\tilde{v}(q)$ and $\tilde{v}_A(q)$ give the values of $\tilde{v}(|\mathbf{G}_n|)$ and $\tilde{v}_A(|\mathbf{G}_n|)$ for the reciprocal lattice vectors, $\mathbf{G}_n$, which give the main contributions in (11.11)

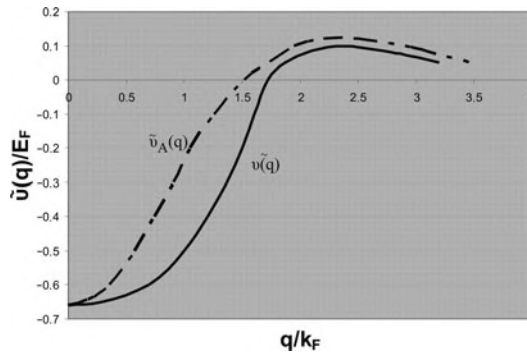


Fig. 11.5. The pseudopotential form factors for Si ($\zeta = 4$). The *solid line* is the result of an accurate first principle calculation, while the *dashed line* is based on (11.13) and the experimental values for $\bar{r}_s = 2.0$, and $\bar{r}_c = 1.06$

used $\zeta = 2.76$, $r_c = 0.5$ Å and the RJM to calculate $\bar{r}_s = 1.90$, and $\bar{k}_F = 1,919/\bar{r}_s = 1.01$.

In Fig. 11.5 we compare an accurate pseudopotential for Si with that based on (11.13). We see that the overall shape of $\tilde{v}_A(q)$, as determined by the simple equation (11.13), is similar to that obtained by the procedures of Table 11.1 and that of Sect. 8.4.

There are of course quantitative differences, which are more pronounced in the semiconductor case as expected, since the JM dielectric function (11.12) is not appropriate for semiconductors and tends to overscreen the ionic poten-

tial producing smaller values of $|\tilde{v}_A(q)|$ than the actual ones, mainly for $q/k_F \leq 1.6$.

We shall conclude this section by reminding the readers that for a periodic solid we need the pseudopotential form factor $\tilde{v}(q)$ only for $\mathbf{q} = \mathbf{G}_n$, where $\mathbf{G}_n$ are vectors of the reciprocal lattice; furthermore since $\tilde{v}(q)$ for $q \gtrsim 3.5 k_F$ is practically zero, only a few values of $\tilde{v}(|\mathbf{G}_n|)$ matter. We shall see that for diamond lattice elemental semiconductors three values of $\tilde{v}(|\mathbf{G}_n|)$ corresponding to $\mathbf{G}_1 = (2\pi/a)(1, 1, 1)$, $\mathbf{G}_2 = (2\pi/a)(2, 2, 0)$ and $\mathbf{G}_3 = (2\pi/a)(3, 1, 1)$ suffice for the solution to Schrödinger's equation.⁵ Based on this observation the *empirical pseudopotential method (EPM)* has been developed. EPM determines the three or four required values of $\tilde{v}(|\mathbf{G}_n|)$ by fitting the resulting theoretical calculations to experimental data for reflectivity and photoemission in the optical and ultraviolet parts of the EM spectrum.

11.3 Schrödinger Equation, Plane Wave Expansion, and Bloch's Theorem

Having a smooth and finite pseudopotential for a periodic solid, it is only natural to express the solution as a superposition of plane waves

$$\psi(\mathbf{r}) = \sum_{\mathbf{k}} c_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{r}}. \quad (11.15)$$

We shall not make use of Bloch's theorem at this point so that (11.15) can be viewed as a Fourier representation of $\psi(\mathbf{r})$ (in which all $\mathbf{k}$'s participate). Substituting (11.11) and (11.15) in Schrödinger's equation

$$\left[-\frac{\hbar^2 \nabla^2}{2m} + \mathcal{V}(\mathbf{r}) \right] \psi(\mathbf{r}) = E \psi(\mathbf{r}). \quad (11.16)$$

We obtain (see Problem 11.2)

$$\left(\frac{\hbar^2 k^2}{2m} - E \right) c_{\mathbf{k}} + \sum_{\mathbf{G}} \tilde{v}(\mathbf{G}) c_{\mathbf{k}-\mathbf{G}}. \quad (11.17)$$

In (11.17) $c_{\mathbf{k}}$ is connected not to every other $c_{\mathbf{k}'}$ but only to those $\mathbf{k}'$ that are equal to $\mathbf{k} - \mathbf{G}$. Hence, the sum in (11.15) can be restricted to $\mathbf{k}$'s differing by any vector of reciprocal lattice (One and only one of those $\mathbf{k}$'s is in the 1st BZ). Thus we have

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} e^{i(\mathbf{k}-\mathbf{G}) \cdot \mathbf{r}} = e^{i\mathbf{k} \cdot \mathbf{r}} w_{\mathbf{k}}(\mathbf{r}), \quad (11.18)$$

where

⁵ For compound semiconductors, $\tilde{v}(|\mathbf{G}_n|)$, $\mathbf{G} = (2\pi/a)(2, 0, 0)$, is also needed.

$$w_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} e^{-i\mathbf{G}\cdot\mathbf{r}} = \sum_{\mathbf{G}} c_{\mathbf{k}+\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}. \quad (11.19)$$

Equations (11.18) and (11.19) constitute a proof of Bloch's theorem, since the function $w_{\mathbf{k}}(\mathbf{r})$ is periodic, i.e., $w_{\mathbf{k}}(\mathbf{r}) = w_{\mathbf{k}}(\mathbf{r} + \mathbf{R}_n)$, as a consequence of the relation $\mathbf{G} \cdot \mathbf{R}_n = 2\pi$ times an integer.

To proceed with the solution to (11.17) we truncate the sum by setting $c_{\mathbf{k}-\mathbf{G}} = 0$ for $|\mathbf{G}| > G_{\max}$. Thus, (11.17) becomes a system of M equations with M unknowns (the coefficients, $c_{\mathbf{k}}, c_{\mathbf{k}-\mathbf{G}_1}, c_{\mathbf{k}-\mathbf{G}_2}, \dots, c_{\mathbf{k}-\mathbf{G}_{M-1}}$). Owing to the smoothness of $\tilde{v}(q)$, we have acceptable results for relatively small values of M . Even for calculations of high accuracy, there is no need for M to exceed a few hundreds. For the linear homogeneous system of M equations with M unknowns to have a solution, its determinant (which is a polynomial of M degree with respect to the energy E) must be set equal to zero. Thus, for each value of $\mathbf{k}$ there would be M roots, denoted by $E_n(\mathbf{k})$, $n = 1, 2, \dots, M$. To each $E_n(\mathbf{k})$ corresponds one eigenfunction $\psi_{\mathbf{k}n}(\mathbf{r})$. As $\mathbf{k}$ varies within the first BZ, each $E_n(\mathbf{k})$ gives rise to the energy band n .

11.4 Plane Waves and Perturbation Theory

We consider a normalized plane wave

$$\psi_{\mathbf{q}}^{(0)}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{q}\cdot\mathbf{r}}, \quad (11.20)$$

with energy $E_{\mathbf{q}}^{(0)} = \hbar^2 q^2 / 2m$, where $\mathbf{q}$ is not necessarily in the first BZ. The question is to find how this wave (11.20) and the corresponding energy $E_{\mathbf{q}}^{(0)}$ are modified in the presence of a *weak* periodic pseudopotential of the form of (11.11). Since the pseudopotential is weak, we apply perturbation theory. We have to distinguish two cases:

- (a) *Nondegenerate case*, which means that $|\tilde{v}(\mathbf{G})| \ll |E_{\mathbf{q}}^{(0)} - E_{\mathbf{q}+\mathbf{G}}^{(0)}|$ for every $\mathbf{G} \neq 0$. Under those conditions the correction to $\psi_{\mathbf{q}}^{(0)}$ up to first order in $\mathcal{V}(\mathbf{r})$ can be obtained by applying (B.53) with the following replacements:

$$\begin{aligned} \langle \mathbf{r} | \chi_n \rangle &\rightarrow \psi_{\mathbf{q}}^{(0)}(\mathbf{r}) \\ \langle \mathbf{r} | \chi_m \rangle &\rightarrow \psi_{\mathbf{q}+\mathbf{G}}^{(0)}(\mathbf{r}), \\ \hat{H}_1 &\rightarrow \sum_{\mathbf{G}'} \tilde{v}(\mathbf{G}') e^{i\mathbf{G}'\cdot\mathbf{r}} \\ \langle \chi_m | \hat{H}_1 | \chi_n \rangle &\rightarrow \frac{1}{V} \sum_{\mathbf{G}'} v(\mathbf{G}') \int d^3r e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} e^{i\mathbf{G}'\cdot\mathbf{r}} e^{i\mathbf{q}\cdot\mathbf{r}} \\ &= \sum_{\mathbf{G}'} \tilde{v}(\mathbf{G}') \delta_{\mathbf{G}, \mathbf{G}'} = \tilde{v}(\mathbf{G}) \end{aligned} \quad (11.21)$$

Thus we have

$$\psi_{\mathbf{q}}^{(0)} + \psi_{\mathbf{q}}^{(1)} = \frac{1}{\sqrt{V}} e^{i\mathbf{q} \cdot \mathbf{r}} \left[1 + \sum_{\mathbf{G} \neq 0} \frac{\tilde{v}(\mathbf{G})}{E_{\mathbf{q}}^{(0)} - E_{\mathbf{q}+\mathbf{G}}^{(0)}} e^{i\mathbf{G} \cdot \mathbf{r}} \right], \quad (11.22)$$

which means that the initial plane wave acquires as a result of the scattering by the weak periodic potential other plane waves of the form $\exp[i(\mathbf{q} + \mathbf{G}) \cdot \mathbf{r}]$; this is expected, since the momentum, which a periodic potential can transfer to the particle, is of the form $\hbar \mathbf{G}$, where $\mathbf{G}$ is any vector of the reciprocal lattice.

To find the corrections to $E_{\mathbf{q}}^{(0)}$ up to second order in $\mathcal{V}(\mathbf{r})$ we are using (B.54) and the replacements (11.21). The result is

$$E_{\mathbf{q}}^{(0)} + E_{\mathbf{q}}^{(1)} + E_{\mathbf{q}}^{(2)} = \frac{\hbar^2 q^2}{2m} + \tilde{v}(0) + \sum_{\mathbf{G} \neq 0} \frac{|\tilde{v}(\mathbf{G})|^2}{E_{\mathbf{q}}^{(0)} - E_{\mathbf{q}+\mathbf{G}}^{(0)}}. \quad (11.23)$$

- (b) **The degenerate (or almost degenerate) case** appears when for the given, $\mathbf{q}$, there is one or more $\mathbf{G}$ s ($\neq 0$) such that $|E_{\mathbf{q}}^{(0)} - E_{\mathbf{q}+\mathbf{G}}^{(0)}| \lesssim |\tilde{v}(\mathbf{G})|$. If this is the case, it is clear that (11.22) and (11.23) would fail, since there would be one or more terms in the sum larger than the unperturbed one. Such terms would appear in the higher order corrections as well. Hence, it is unjustified to stop the expansion at any finite order. As it was pointed out in Appendix B the way out of this problem is to make the corresponding numerator equal to zero by a proper reselection of the basis. To be more specific, let us assume that there are no more than m $\mathbf{G}$ s such that for the chosen $\mathbf{q}$ we have the inequalities $|E_{\mathbf{q}}^{(0)} - E_{\mathbf{q}+\mathbf{G}_i}^{(0)}| \lesssim |\tilde{v}(\mathbf{G}_i)|$ ($i = 1, 2, \dots, m$). Then we try to find $m + 1$

different linear combination $\phi_{\mathbf{q},\ell}^{(0)} = \sum_{\mathbf{G}_i=0}^{\mathbf{G}_m} c_i^{(\ell)} \psi_{\mathbf{q}+\mathbf{G}_i}^{(0)}$ ($\ell = 1, 2, \dots, m + 1$)

such that in the new basis, $\{\phi_{\mathbf{q},\ell}^{(0)}\}$, the full Hamiltonian $\hat{H}_0 + \hat{H}_1$ to have the off-diagonal matrix elements equal to zero. This is equivalent to the exact diagonalization of $\hat{H} = \hat{H}_0 + \hat{H}_1 = -\hbar^2 \nabla^2 / 2m + \mathcal{V}(\mathbf{r})$ within the *subspace* spanned by the functions $\psi_{\mathbf{q}+\mathbf{G}_i}^{(0)}$ ($\mathbf{G}_i = 0, \mathbf{G}_1, \dots, \mathbf{G}_m$). The diagonal matrix elements $\langle \psi_{\mathbf{q}+\mathbf{G}_i}^{(0)} | \hat{H} | \psi_{\mathbf{q}+\mathbf{G}_i}^{(0)} \rangle$ are equal to $E_{\mathbf{q}+\mathbf{G}_i}^{(0)} + \tilde{v}(0)$ and the off-diagonal matrix elements $H_{ij} \equiv \langle \psi_{\mathbf{q}+\mathbf{G}_i}^{(0)} | \hat{H} | \psi_{\mathbf{q}+\mathbf{G}_j}^{(0)} \rangle = \langle \psi_{\mathbf{q}+\mathbf{G}_i}^{(0)} | \mathcal{V} | \psi_{\mathbf{q}+\mathbf{G}_j}^{(0)} \rangle = \tilde{v}(\mathbf{G}_i - \mathbf{G}_j) = \tilde{v}^*(\mathbf{G}_j - \mathbf{G}_i)$, $i \neq j$.

If $m = 1$, the matrix to be diagonalized is a 2×2 of the following form:

$$\begin{pmatrix} E_{\mathbf{q}}^{(0)} + \tilde{v}(0) & \tilde{v}^*(\mathbf{G}_1) \\ \tilde{v}(\mathbf{G}_1) & E_{\mathbf{q}+\mathbf{G}_1}^{(0)} + \tilde{v}(0) \end{pmatrix}. \quad (11.24)$$

The eigenenergies within this subspace are:

$$E_{q,\pm} = \tilde{v}(0) + (E_q^{(0)} + E_{q+G_1}^{(0)})/2 \pm \sqrt{\Delta^2 + |\tilde{v}(G_1)|^2}, \quad (11.25)$$

where Δ is half the difference of the diagonal matrix elements

$$\Delta = (E_q^{(0)} - E_{q+G_1}^{(0)}) / 2. \quad (11.26)$$

The corresponding eigenfunctions within this subspace $\phi_{q,\pm}^{(0)} = c_q^\pm \psi_q^{(0)} + c_{q+G_1}^\pm \psi_{q+G_1}^{(0)}$ are determined by the ratio

$$\frac{c_q^\pm}{c_{q+G_1}^\pm} = \frac{\tilde{v}^*(G_1)}{-\Delta \pm \sqrt{\Delta^2 + |\tilde{v}(G_1)|^2}}, \quad (11.27)$$

and the normalization condition $\langle \phi_\pm^{(0)} | \phi_\pm^{(0)} \rangle = 1$. Notice that the correction to $\psi_q^{(0)}$ in the degenerate case is not of first or higher order in the small parameter, $|\tilde{v}(G_i - G_j)|$, but it is of the same order as the unperturbed one. For example, if $\Delta = 0$, $|c_q^\pm / c_{q+G}^\pm| = 1$. This feature holds not only in the special case of $m = 1$ but also for any m : In the degenerate case, the corrections to the unperturbed wavefunctions are of the *order of unity* and the corrections to the unperturbed eigenenergies are of *first order* in the small parameter $|\tilde{v}(G_i - G_j)|$ and not of second order as in the nondegenerate case (ignoring the trivial term $\tilde{v}(0)$).

Now, if we wish to obtain the next order corrections (first order in $|\tilde{v}(G_i - G_n)|$ for the eigenfunctions, and second order for the eigenenergies) we have to take into account the coupling of the degenerate subspace with the rest of the Hilbert space, $\psi_{q+G_s}^{(0)}$, where $G_s \neq 0, G_1, \dots, G_m$. Then, we can apply (B.53) and (B.54) to find the following (assuming that $|\langle \psi_{q+G_s} | \mathcal{V}(\mathbf{r}) | \phi_{q,\ell}^{(0)} \rangle| \ll |E_{q,\ell} - E_{q,G_s}^{(0)}|$)

$$\phi_{q,\ell}^{(0)} + \phi_{q,\ell}^{(1)} = \phi_{q,\ell}^{(0)} + \sum_{G_s} \frac{\langle \psi_{q+G_s}^{(0)} | \mathcal{V}(\mathbf{r}) | \phi_{q,\ell} \rangle}{E_{q,\ell} - E_{q+G_s}^{(0)}} \psi_{q+G_s}^{(0)}, \quad (11.28)$$

and

$$E_{q,\ell} + E_{q,\ell}^{(2)} = E_{q,\ell} + \sum_{G_s}' \frac{\left| \langle \psi_{q+G_s}^{(0)} | \mathcal{V}(\mathbf{r}) | \phi_{q,\ell}^{(0)} \rangle \right|^2}{E_{q,\ell} - E_{q+G_s}^{(0)}}, \quad (11.29)$$

where the prime in the summation indicates that G_s must be different from all G_i ($0, G_1, \dots, G_m$). Remember that $\phi_{q,\ell}^{(0)}$ and $E_{q,\ell}$ are exact eigenfunctions and eigenenergies if the coupling of the subspace, $\psi_{q+G_i}^{(0)}$, $G_i = 0, G_1, \dots, G_m$ to the rest of the Hilbert space is omitted.

In the next Chaps. 12 and 13, we shall present how pseudopotentials and degenerate perturbation theory can be employed to determine the band structure of not only model systems but also real metallic and semiconducting solids.

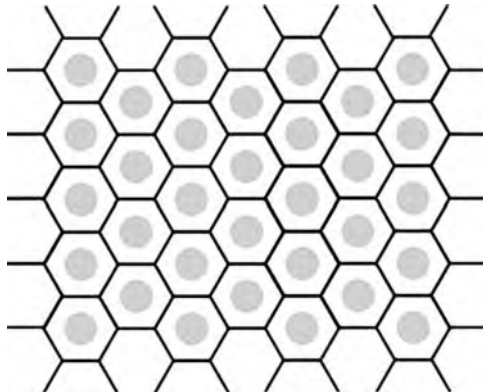


Fig. 11.6. Schematic 2D plot of the muffin-tin potential. The *shaded areas* denote the regions where the potential is not constant

11.5 Muffin–Tin Potential

The APW and KKR methods can be implemented by employing the actual one-electron potential $\mathcal{V}(\mathbf{r})$ as determined by following Steps 1–10 of Sect. 8.4 in Chap. 8. However, in practice the so-called muffin–tin approximation (MTA) is used (Fig. 11.6). According to this approximation, the potential is assumed to be spherically symmetric within every sphere of radius⁶ r_0 , centered at each atomic site; in what follows the radius r_0 is chosen so as to assure that the spheres do not overlap. In the region outside these spheres, the potential is taken as a constant, $\mathcal{V}_c$:

$$\mathcal{V}(\mathbf{r}) = \mathcal{V}_c = \text{const.}, \quad \text{when, for all } \mathbf{R}_n, |\mathbf{r} - \mathbf{R}_n| > r_0, \quad (11.30)$$

$$\mathcal{V}(\mathbf{r}) = \sum_n v(|\mathbf{r} - \mathbf{R}_n|), \quad \text{for } |\mathbf{r} - \mathbf{R}_n| < r_0, \quad (11.31)$$

where

$$v(|\mathbf{r} - \mathbf{R}_n|) = 0, \quad \text{for } |\mathbf{r} - \mathbf{R}_n| > r_0. \quad (11.32)$$

11.6 Schrödinger Equation and the Augmented Plane Wave (APW) Method

Although the APW method can be formulated without the MTA, we shall adopt this approximation in what follows. The APW seeks the solution to Schrödinger’s equation in the presence of the periodic potential $\mathcal{V}(\mathbf{r})$ (given by (11.30)–(11.32)) as a linear superposition similar in form to (11.18):

⁶ For simplicity we assume that we are dealing with an elemental solid for which all atoms are identical, and hence, r_0 is the same for every atomic site. Usually the muffin–tin spheres do not overlap, i.e., $2r_0 \leq d$, where d is the nearest neighbor distance.

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}+\mathbf{G}} \phi_{\mathbf{k}+\mathbf{G}, E}(\mathbf{r}). \quad (11.33)$$

However, since in the regions $|\mathbf{r} - \mathbf{R}_n| < r_0$ the actual potential strongly varies and goes to minus infinity as $|\mathbf{r} - \mathbf{R}_n| \rightarrow 0$, it is advisable to choose a basis $\{\phi_{\mathbf{k}+\mathbf{G}, E}\}$, other than plane waves and capable of handling these inconvenient regions. One choice, suggested originally by Slater, is to have $\phi_{\mathbf{k}, E}(\mathbf{r})$ to satisfy Schrödinger's equation in each region $|\mathbf{r} - \mathbf{R}_n| < r_0$ (by expanding it in spherical harmonics, $Y_{\ell m}$) and to be plane wave in the interstitial region, $|\mathbf{r} - \mathbf{R}_n| > r_0$ (for all $\mathbf{R}_n$); furthermore, the two types of solution must be matched at the interfaces $|\mathbf{r} - \mathbf{R}_n| = r_0$. More explicitly this choice for $\phi_{\mathbf{k}, E}(\mathbf{r})$ is as follows⁷

$$\phi_{\mathbf{k}, E} = \sum_n \delta_n \sum_{\ell m} A_{\ell m} Y_{\ell m}(\rho_0 n) R_{\ell}(\rho_n), \quad \rho_n \equiv |\mathbf{r} - \mathbf{R}_n| \leq r_0, \quad (11.34)$$

$$\phi_{\mathbf{k}, E} = e^{i\mathbf{k} \cdot \mathbf{r}}, \quad \rho_n \geq r_0, \quad \text{for all } \mathbf{R}_n, \quad (11.35)$$

where (see Problem 11.3s)

$$A_{\ell m} = 4\pi e^{i\mathbf{k} \cdot \mathbf{R}_n} i^{\ell} Y_{\ell m}^*(\mathbf{k}_0) \frac{j_{\ell}(kr_0)}{R_{\ell}(r_0; E)}. \quad (11.36)$$

$\delta_n = 1$ for $|\mathbf{r} - \mathbf{R}_n| < r_0$ and zero for $|\mathbf{r} - \mathbf{R}_n| > r_0$; $R_{\ell}(\rho, E)$ satisfies the radial Schrödinger's equation (see Appendix B.)

$$-\frac{\hbar^2}{2m} \frac{1}{\rho^2} \frac{d}{d\rho} \left(\rho^2 \frac{dR_{\ell}}{d\rho} \right) + \left[\frac{\hbar^2}{2m} \frac{\ell(\ell+1)}{\rho^2} + v(\rho) \right] R_{\ell} = E R_{\ell}. \quad (11.37)$$

In these equations, $\rho_0 n$ is the unit vector along the direction of $\mathbf{r} - \mathbf{R}_n$; $\mathbf{k}_0$ is the unit vector along the direction of $\mathbf{k}$; j_{ℓ} is the spherical Bessel function of first kind, and $v(\rho)$ is as in (11.31). Notice that the part of the solution inside the muffin-tins satisfies Schrödinger's equation with the energy E (and hence, involves E explicitly), while the part of the solution in the interstitial region does not depend on E , but it does depend on $\mathbf{k}$. The choice for $A_{\ell m}$ in (11.36) is such as to make $\phi_{\mathbf{k}, E}(\mathbf{r})$ continuous at each interface, $|\mathbf{r} - \mathbf{R}_n| = r_0$.

It is worthwhile to point out the following:

- (a) There is no relation in each $\phi_{\mathbf{k}, E}$ between $\mathbf{k}$ and E . Simply each $\phi_{\mathbf{k}, E}$ depends on four independent parameters, the three components of $\mathbf{k}$ (through (11.35) and E (through (11.37)). The coefficients $A_{\ell m}$ as given by (11.36) involve both $\mathbf{k}$ and E in order to guarantee the continuity of $\phi_{\mathbf{k}, E}$ at the interfaces.
- (b) Each individual $\phi_{\mathbf{k}, E}$ does not satisfy Schrödinger's equation for two reasons: First, the derivative, $\nabla_{\mathbf{r}} \phi_{\mathbf{k}, E}(\mathbf{r})$, of $\phi_{\mathbf{k}, E}(\mathbf{r})$ at the interfaces is not

⁷ The sum over ℓ is truncated in practice by keeping at least up to $\ell = 8$ and often up to $\ell = 13$.

continuous, as required by any acceptable solution; second Schrödinger's equation, $\hat{H}\phi_{\mathbf{k},E} = E\phi_{\mathbf{k},E}$, is not satisfied in the interstitial region, where $\phi_{\mathbf{k},E} = \exp(i\mathbf{k} \cdot \mathbf{r})$, since there $\hat{H}\phi_{\mathbf{k},E} = [\hbar^2 k^2 / 2m + \mathcal{V}_c]\phi_{\mathbf{k},E}$ and $E \neq \hbar^2 k^2 / 2m + \mathcal{V}_c$.

- (c) Each $\phi_{\mathbf{k},E}(\mathbf{r})$ satisfies Bloch's theorem: $\phi_{\mathbf{k},E}(\mathbf{r} + \mathbf{R}_n) = \exp(i\mathbf{k} \cdot \mathbf{R}_n)\phi_{\mathbf{k},E}(\mathbf{r})$, because both the plane wave part, $\exp(i\mathbf{k} \cdot \mathbf{r})$, and the part in (11.34) satisfy it; the latter because of (11.36).

The discontinuity of the derivative of $\phi_{\mathbf{k},E}(\mathbf{r})$ will produce a δ – function singularity in the second derivative of $\phi_{\mathbf{k},E}(\mathbf{r})$ appearing in Schrödinger's equation. To avoid this singularity we shall employ a variational approach that is equivalent to Schrödinger's equation. This approach is based on the minimization of the energy functional

$$E[\psi] = N / D, \quad (11.38)$$

where

$$N \equiv \int d^3r \left[(\hbar^2 / 2m) |\nabla_r \psi|^2 + \mathcal{V}(\mathbf{r}) |\psi(\mathbf{r})|^2 \right], \quad (11.39)$$

$$D = \int d^3r |\psi(\mathbf{r})|^2. \quad (11.40)$$

The minimization leads to the following equation

$$\frac{\delta E}{\delta \psi} = \frac{1}{D} \frac{\delta N}{\delta \psi} - \frac{N}{D^2} \frac{\delta D}{\delta \psi} = \frac{1}{D} \left(\frac{\delta N}{\delta \psi} - E \frac{\delta D}{\delta \psi} \right) = 0. \quad (11.41)$$

Substituting (11.33) in N and D , we see that both of them become quadratic functions of the coefficients $c_{\mathbf{k}+\mathbf{G}}$. In practice we truncate the sum in (11.33) by keeping a finite number, M , of terms of the order of one hundred or so. Minimizing $E(\psi)$ with respect to each of the M coefficients $c_{\mathbf{k}+\mathbf{G}}$, (11.41) becomes a linear homogeneous system of M equations with M unknowns. By setting the determinant equal to zero we obtain an implicit relation between E and $\mathbf{k}$, which for a given $\mathbf{k}$ is satisfied for M different values⁸ of E .

11.7 Schrödinger Equation and the Korringa–Kohn–Rostoker (KKR) Method

The starting point of this method is to express Schrödinger's equation in an integral form using (B.59) in the $\mathbf{r}$ -representation

$$\psi(\mathbf{r}) = \int d^3r' G_0(\mathbf{r} - \mathbf{r}'; E) \mathcal{V}(\mathbf{r}') \psi(\mathbf{r}'), \quad (11.42)$$

⁸ The energy E enters implicitly in both $\delta N / \delta \psi$ and $\delta D / \delta \psi$, since $\phi_{\mathbf{k}+\mathbf{G},E}$ depend on E . Thus, it is easier to choose a value of E and find all $\mathbf{k}$'s that make the determinant equal to zero. This way, one finds the surface in $\mathbf{k}$ -space corresponding to energy E .

where in the present case G_0 corresponds to the Hamiltonian $\hat{H}_0 = -\hbar^2 \nabla^2 / 2m$ and the unperturbed solution appearing in (B.59) is necessarily equal to zero in the present case, since the energy E is negative. The unperturbed Green's function G_0 satisfies the relation $(E - \hat{H}_0)\hat{G}_0 = 1$, which in the $\mathbf{r}$ -representation becomes

$$(E + \hbar^2 \nabla^2 / 2m)G_0(\mathbf{r} - \mathbf{r}'; E) = \delta(\mathbf{r} - \mathbf{r}'). \quad (11.43)$$

The most general solution to (11.43) that gives an outgoing spherical wave at infinity, if $E > 0$, and a decaying solution, if $E < 0$, is (see Problem 11.4)

$$G_0(\mathbf{r} - \mathbf{r}'; E) = -\frac{m}{2\pi\hbar^2} \frac{e^{ik_0|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|}, \quad (11.44)$$

where

$$\begin{aligned} k_0 &= \sqrt{2mE / \hbar^2}, & E &\geq 0 \\ k_0 &= i\sqrt{2m|E| / \hbar^2}, & E &\leq 0 \end{aligned} \quad (11.45)$$

It is easy to show that ψ as given by (11.42) and in view of (11.43), satisfies Schrödinger's equation, $[-\hbar^2 \nabla^2 / 2m + \mathcal{V}(\mathbf{r}) - E]\psi(\mathbf{r}) = 0$. The next step is to replace in (11.42) $\mathcal{V}(\mathbf{r})$ by its expression in (11.30) and (11.31) (choosing for simplicity $\mathcal{V}_c = 0$), $\psi(\mathbf{r}')$ by $\exp(i\mathbf{k} \cdot \mathbf{R}_n)\psi_{\mathbf{k}}(\mathbf{r}' - \mathbf{R}_n)$, in accordance with Bloch's theorem, and $\mathbf{r}' - \mathbf{R}_n$ by ρ . We have then

$$\psi_{\mathbf{k}}(\mathbf{r}) = \int d^3\rho \mathcal{G}_0(\mathbf{r} - \rho; E, \mathbf{k})v(\rho)\psi_{\mathbf{k}}(\rho), \quad (11.46)$$

where

$$\mathcal{G}_0(\mathbf{r} - \rho; E, \mathbf{k}) = \sum_{\mathbf{R}_n} G_0(\mathbf{r} - \rho - \mathbf{R}_n)e^{i\mathbf{k} \cdot \mathbf{R}_n}. \quad (11.47)$$

Notice that the function $\mathcal{G}_0$ depends on the lattice structure, on $\mathbf{k}$, and on E but it does not depend on the atomic potential. All the information about the nature of the atoms making up the solid has been concentrated in the function $v(\rho)$, which is different from zero only in the interior of the muffin-tin sphere and does not depend on $\mathbf{k}$, on E or on the crystal structure. Since $v(\rho) = 0$, for $\rho > r_0$, the integration in (11.46) is limited to the interior of one muffin-tin sphere. There, the solution $\psi_{\mathbf{k}}(\rho)$ can be written as in (11.34):

$$\psi_{\mathbf{k}}(\rho) = \sum_{\ell m} c_{\ell m} Y_{\ell m}(\theta, \phi) R_{\ell}(\rho), \quad \rho \leq r_0, \quad (11.48)$$

where $R_{\ell}(\rho)$ satisfies (11.37) for $\rho \leq r_0$. For a given energy E and a given potential $v(\rho)$, there is a unique solution for $R_{\ell}(\rho)$, which behaves properly at $\rho = 0$. Hence, to obtain the solution $\psi_{\mathbf{k}}(\rho)$ for $\rho \leq r_0$ only the coefficients

$c_{\ell m}$ remain to be determined. However, if the solution inside the muffin-tin sphere has been obtained, the solution outside the muffin-tin spheres can be found too from (11.46) by choosing $\mathbf{r}$ to be in the interstitial region. Thus, the solution both inside and outside the muffin-tin spheres has been expressed in terms of the still undetermined coefficients $c_{\ell n}$. However, the two solutions (the one obtained by (11.37) and (11.48), and the other obtained by (11.46)) must be the same at $r = r_0$. From this self-consistency requirement we get as many equations as the number of unknown coefficients, $c_{\ell m}$, kept in (11.48).

The coincidence of the two solutions at $\rho = r_0$ can be brought to the following form (see Problem 11.5s)

$$\begin{aligned} & \int d\Omega \mathcal{G}_0(r_0, \theta', \phi', r_0, \theta, \phi; E, \mathbf{k}) \frac{\partial}{\partial \rho} \psi(\rho, \theta, \phi) \Big|_{\rho=r_0} \\ &= \int d\Omega \psi(r_0, \theta, \phi) \frac{\partial}{\partial \rho} \mathcal{G}_0(r_0, \theta', \phi', \rho, \theta, \phi; E, \mathbf{k}) \Big|_{\rho=r_0}. \end{aligned} \quad (11.49)$$

The integration in (11.49) is over the solid angle $d\Omega = \sin \theta d\theta d\phi$. We can substitute ψ in (11.49) by (11.48), multiply both sides of (11.49) by $Y_{\ell' m'}^*(\theta', \phi')$, and integrate over the solid angle $d\Omega' = \sin \theta' d\theta' d\phi'$. We then obtain the following linear, homogeneous system of N equations for the N unknown coefficients $c_{\ell m}$:

$$\sum_{\ell, m} A_{\ell m, \ell' m'}(\mathbf{k}, E) \frac{dR_\ell}{d\rho} \Big|_{\rho=r_0} \times c_{\ell m} = \sum_{\ell, m} B_{\ell m, \ell' m'}(\mathbf{k}, E) R_\ell(r_0) c_{\ell m}. \quad (11.50)$$

Problem 11.1t. Express the quantities $A_{\ell m, \ell' m'}(\mathbf{k}, E)$ and $B_{\ell m, \ell' m'}(\mathbf{k}, E)$ as double integrals over the solid angles $d\Omega$ and $d\Omega'$ of the product $Y_{\ell' m'}^* \mathcal{G}_0 Y_{\ell m}$ and $Y_{\ell' m'}^* (\partial \mathcal{G}_0 / \partial \rho) Y_{\ell m}$ respectively (for $\rho = r_0$).

11.8 The $\mathbf{k} \cdot \mathbf{p}$ Method of Band Structure Calculations

The $\mathbf{k} \cdot \mathbf{p}$ method allows us to determine the eigenenergy and the eigenfunction at the wavevector $\mathbf{k} + \mathbf{q}$ of the band n , if the corresponding quantities at $\mathbf{q}$ and n' are known, assuming that $|\mathbf{k}|$ is small enough to allow the use of second-order perturbation theory.

The difference $\hat{H}_{\mathbf{q}+\mathbf{k}} - \hat{H}_{\mathbf{q}}$ between the Hamiltonians corresponding to the points $\mathbf{q} + \mathbf{k}$ and $\mathbf{q}$ and acting on the periodic amplitudes $w_{n, \mathbf{q}+\mathbf{k}}$ and $w_{n', \mathbf{q}}$ of the Bloch functions respectively is according to (3.22) of Problem 3.11

$$\delta \hat{H} = \frac{\hbar^2}{2m} [2\mathbf{k} \cdot (\mathbf{q} - i\nabla) + k^2]. \quad (11.51)$$

The Hamiltonian $\delta \hat{H}$ is the perturbation acting on the unperturbed states $w_{n' \mathbf{k}'}$. It is easy to show that

$$\langle \psi' | \hat{\mathbf{p}} | \psi \rangle = \hbar \mathbf{k} \langle \psi' | \psi \rangle + \left\langle w' \left| e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}} \hat{\mathbf{p}} \right| w \right\rangle, \quad (11.52)$$

where $\psi = w \exp(i\mathbf{k} \cdot \mathbf{r})$ and $\psi' = w' \exp(i\mathbf{k}' \cdot \mathbf{r})$ and $\mathbf{p} = -i\hbar \nabla$. Since both $\langle \psi' | \hat{\mathbf{p}} | \psi \rangle$ and $\langle \psi' | \psi \rangle$ are zero when $\mathbf{k}' \neq \mathbf{k}$, the last term in (11.52) is zero as well. Hence, only the diagonal terms $\mathbf{k}' = \mathbf{k}$ are nonzero and (11.52) become

$$\langle \psi'_{n'\mathbf{k}} | \hat{\mathbf{p}} | \psi_{n\mathbf{k}} \rangle = \hbar \mathbf{k} \delta_{nn'} + \langle w'_{n'\mathbf{k}} | \hat{\mathbf{p}} | w_{n\mathbf{k}} \rangle, \quad (11.53)$$

where the band indices are explicitly displayed.

The next step is to apply second-order nondegenerate perturbation theory according to (B.54) with $\delta \hat{H}$ in the place of $\hat{H}_1$ and $w_{n\mathbf{q}}$ in the place of χ_n . This is valid if there are no other states with the same unperturbed energy at the same $\mathbf{q}$.

$$\begin{aligned} \varepsilon_{n, \mathbf{q}+\mathbf{k}} &= \varepsilon_{n, \mathbf{q}} + \frac{\hbar}{m} \mathbf{k} \cdot \langle w_{n\mathbf{q}} | (\hbar \mathbf{q} + \hat{\mathbf{p}}) | w_{n\mathbf{q}} \rangle + \frac{\hbar^2 k^2}{2m} \\ &+ \frac{\hbar^2}{m^2} \sum_{n' \neq n} \frac{|\mathbf{k} \cdot \langle w_{n, \mathbf{q}} | (\hbar \mathbf{q} + \hat{\mathbf{p}}) | w_{n', \mathbf{q}} \rangle|^2}{\varepsilon_{n, \mathbf{q}} - \varepsilon_{n', \mathbf{q}}} + \mathcal{O}(k^3), \end{aligned} \quad (11.54)$$

or by taking into account (11.53),

$$\varepsilon_{n, \mathbf{q}+\mathbf{k}} = \varepsilon_{n, \mathbf{q}} + \frac{\hbar}{m} \mathbf{k} \cdot \langle \psi_{n\mathbf{q}} | \hat{\mathbf{p}} | \psi_{n\mathbf{q}} \rangle + \frac{\hbar^2 k^2}{2m} + \frac{\hbar^2}{m^2} \sum_{n' \neq n} \frac{|\mathbf{k} \cdot \langle \psi_{n, \mathbf{q}} | \hat{\mathbf{p}} | \psi_{n', \mathbf{q}} \rangle|^2}{\varepsilon_{n, \mathbf{q}} - \varepsilon_{n', \mathbf{q}}} + \mathcal{O}(k^3). \quad (11.55)$$

By differentiating (11.55) once with respect to $\mathbf{k}$ and then setting $\mathbf{k} = 0$, we have

$$\lim_{\mathbf{k} \rightarrow 0} \sum_{j=1}^3 \frac{\varepsilon_{n, \mathbf{q}+\mathbf{k}} - \varepsilon_{n, \mathbf{q}}}{\hbar k_j} \mathbf{j}_0 \equiv \frac{\partial \varepsilon_{n, \mathbf{q}}}{\hbar \partial \mathbf{q}} = \left\langle \psi_{n, \mathbf{q}} \left| \frac{\hat{\mathbf{p}}}{m} \right| \psi_{n, \mathbf{q}} \right\rangle = v_{n, \mathbf{q}}, \quad (11.56)$$

where $\mathbf{j}_0$ is the unit vector along the direction j of the Cartesian coordinate system. Equation (11.56) is identical to (10.21) and (10.23), which have been proved in Chap. 10 by a different method. By differentiating (11.55) twice with respect to $\mathbf{k}$, setting then $\mathbf{k} = 0$ and recalling the definition (7.38) of the effective mass tensor, we have

$$\left(\frac{1}{m_{n, \mathbf{q}}^*} \right)_{ij} = \frac{1}{m} \delta_{ij} + \frac{1}{m^2} \sum_{n' \neq n} \frac{p_{nn', i} p_{n', n, j} + p_{nn', j} p_{n', n, i}}{\varepsilon_{n, \mathbf{q}} - \varepsilon_{n', \mathbf{q}}}, \quad (11.57)$$

where $p_{nn', i} \equiv \langle \psi_{n\mathbf{q}} | p_i | \psi_{n'\mathbf{q}} \rangle$

In the principal axes the mass tensor becomes diagonal. Thus,

$$\frac{1}{m_{n, \mathbf{q}, i}^*} = \frac{1}{m} + \frac{2}{m^2} \sum_{n' \neq n} \frac{p_{nn', i} p_{n', n, i}}{\varepsilon_{n, \mathbf{q}} - \varepsilon_{n', \mathbf{q}}}. \quad (11.58)$$

Equation (11.58) finds application for the calculation of the effective electronic mass at the bottom of the CB of direct-gap tetrahedral semiconductors. In this case the main contribution to the sum in (11.58) is coming from the three p_x , p_y , p_z eigenstates at the top of the VB. Then, taking into account that $\psi_{n\mathbf{q}} \equiv \psi_{CB,s}$ is s-like we have: $\langle \psi_{VB,x} | p_x | \psi_{CV,s} \rangle = \langle \psi_{VB,y} | p_y | \psi_{CV,s} \rangle = \langle \psi_{VB,z} | p_z | \psi_{CV,s} \rangle \equiv p$. Hence,

$$\frac{m}{m_e^*} \simeq 1 + \frac{2p^2}{mE_g}. \quad (11.59)$$

It follows from (11.59) that m_e^* at the bottom of the CB is smaller than the bare electronic mass. Numerical estimates can be obtained by choosing for $2p^2/m$ its typical value, which is about 20 eV. We have then:

Semiconductors	GaAs	InSb	GaSb	GaN	InAs	ZnSe
m_e^* / m (11.59)	0.071	0.012	0.039	0.15	0.021	0.124
$m_e / m(\text{exp})$	0.067	0.014	0.0412	0.2	0.0239	0.13

The most common and important case of the degenerate $\mathbf{k} \cdot \mathbf{p}$ method is at the top of the valence band of tetrahedral semiconductors, where the three degenerate states of p-character at $\mathbf{k} = 0$ will be denoted by $|X\rangle$, $|Y\rangle$ and $|Z\rangle$. Their degeneracy is lifted even at $\mathbf{k} = 0$ ($\mathbf{q}$ has already been taken as zero) because of the spin-orbit coupling, which adds a term to the unperturbed Hamiltonian at $\mathbf{k} = \mathbf{q} = 0$ of the form

$$\hat{H}_{s-o} = \frac{\hbar}{4m^2c^2}(\boldsymbol{\sigma} \times \nabla\mathcal{V}) \cdot \hat{\mathbf{p}}, \quad (11.60)$$

where the Cartesian components of $\boldsymbol{\sigma} = 2\mathbf{s}$ are the Pauli matrices:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (11.61)$$

The inclusion of the spin variable doubles the number of degeneracy to 6. If the potential $\mathcal{V}$ were spherically symmetric, the quantity $(\boldsymbol{\sigma} \times \nabla\mathcal{V}) \cdot \hat{\mathbf{p}}$ would become

$$(\boldsymbol{\sigma} \times \nabla\mathcal{V}) \cdot \hat{\mathbf{p}} = \frac{\hbar}{r} \frac{d\mathcal{V}}{dr} \boldsymbol{\sigma} \cdot \hat{\boldsymbol{\ell}}, \quad (11.62)$$

where $\hat{\boldsymbol{\ell}} \equiv \mathbf{r} \times \hat{\mathbf{p}}/\hbar$ is the angular momentum operator (over $\hbar$). The total angular momentum (over $\hbar$) $\hat{\mathbf{j}} \equiv \hat{\boldsymbol{\ell}} + \hat{\mathbf{s}}$, which is conserved, can take the value $j = 3/2$ (with four states $j_z = \pm 3/2$ and $j_z = \pm 1/2$) or $j = 1/2$ (with two states $j_z = \pm 1/2$). The quantity $\boldsymbol{\sigma} \cdot \hat{\boldsymbol{\ell}}$ in (11.62) can be written as

$$\begin{aligned} \boldsymbol{\sigma} \cdot \hat{\boldsymbol{\ell}} = j(j+1) - \ell(\ell+1) - s(s+1) &= 1 \quad \text{for } j = 3/2 \\ &= -2 \quad \text{for } j = 1/2. \end{aligned} \quad (11.63)$$

Thus, in view of (11.60)–(11.63) we have at $\mathbf{k} = \mathbf{q} = 0$

$$\left\langle \hat{H}_{s-o} \right\rangle_{3/2} = \frac{\hbar^2}{4m^2c^2} \left\langle \frac{1}{r} \frac{dV}{dr} \right\rangle, \quad (11.64)$$

$$\left\langle \hat{H}_{s-o} \right\rangle_{1/2} = -\frac{2\hbar^2}{4m^2c^2} \left\langle \frac{1}{r} \frac{dV}{dr} \right\rangle. \quad (11.65)$$

Hence, the states with total angular momentum $j = 1/2$ ($j_z = \pm 1/2$) are split-off from the rest at $\mathbf{k} = \mathbf{q} = 0$ by an amount Δ approximately equal to

$$\Delta \simeq \frac{3\hbar^2}{4m^2c^2} \left\langle \frac{1}{r} \frac{dV}{dr} \right\rangle. \quad (11.66)$$

For $\mathbf{k} \neq 0$ (and $\mathbf{q} = 0$) the total perturbation is

$$\delta \hat{H} = \hat{H}_{s-o} + \frac{\hbar^2}{2m} k^2 + \frac{\hbar}{m} \mathbf{k} \cdot \left(\hat{\mathbf{p}} + \frac{\hbar}{4mc^2} \boldsymbol{\sigma} \times \nabla V \right). \quad (11.67)$$

The name $\mathbf{k}$ dot $\mathbf{p}$ for the corresponding perturbation theory is usually kept, in spite of the fact that what multiplies $\mathbf{k}$ is not $\mathbf{p}$ but the vector-operator in the final bracket in (11.67). The readers are referred to the book by Yu and Cardona ([Se119], pp. 71–79) for the treatment of this perturbation within the six degenerate states (including spin) at the top of the valence band and another eight states (including spin) at the conduction band; the latter are connected to the six degenerate states at the top of the VB by strong matrix elements. This 14×14 Hamiltonian matrix can be reduced (by treating the 8 states of the CB through second-order perturbation theory) to a 6×6 Hamiltonian matrix involving the six states of the VB. Next the 6×6 can be split approximately to 4×4 and 2×2 matrices, because of the spin-orbit coupling. The 2×2 Hamiltonian matrix is associated with the two states $j_z = \pm 1/2$ of the $j = 1/2$ split-off branches, while the 4×4 involves the four states of the $j = 3/2$.

The end results of this series of approximations are the following dispersion relations for the six hole branches of the top of the VB for tetrahedral semiconductors:

$$E_{hh}(\mathbf{k}) = \frac{\hbar^2}{2m} \left\{ \gamma_1 k^2 - 2 [\gamma_2^2 k^4 + 3 (\gamma_3^2 - \gamma_2^2) (k_x^2 k_y^2 + k_y^2 k_z^2 + k_z^2 k_x^2)]^{1/2} \right\}, \quad (11.68)$$

$$E_{lh}(\mathbf{k}) = \frac{\hbar^2}{2m} \left\{ \gamma_1 k^2 + 2 [\gamma_2^2 k^4 + 3 (\gamma_3^2 - \gamma_2^2) (k_x^2 k_y^2 + k_y^2 k_z^2 + k_z^2 k_x^2)]^{1/2} \right\}, \quad (11.69)$$

$$E_{soh}(k) = \Delta + \frac{\hbar^2 k^2}{2m_{soh}}. \quad (11.70)$$

Each of these branches is doubly degenerate⁹ because of the inclusion of the spin degrees of freedom; the first two relations ((11.68) and (11.69)) correspond to the $j = 3/2$ subspace, while the third one, (11.70), is associated with the $j = 1/2$ subspace. The last subscript, h , denotes hole branches for which $E_{nh}(\mathbf{k}) = -E_{ne}(\mathbf{k})$, where $E_{ne}(\mathbf{k})$ are the electron branches; the subscript hh denotes the heavy hole branch of the $j = 3/2$ subspace, while lh denotes the light hole. The parameters $\gamma_1, \gamma_2, \gamma_3$, known as the **Kohn-Luttinger parameters**¹⁰ are related to momentum matrix elements between the VB states and the CB states and the corresponding energy gaps (see Yu and Cardona book [Se119], eqns. (2.63) till (2.71c)). The split-off hole branch involves in addition the quantity Δ . Notice that the $j = 3/2$ branches are not isotropic; as a result the effective masses in the k_x direction (i.e., the (100)) are different from those in the direction (110) or the (111).

Problem 11.2t. Show that the effective masses for the heavy and the light hole in the (100), (110), and (111) directions are as follows:

$$m_{hh}^{(100)} = \frac{m}{\gamma_1 - 2\gamma_2}, \quad m_{lh}^{(100)} = \frac{m}{\gamma_1 + 2\gamma_2}, \quad (11.71)$$

$$m_{hh}^{(110)} = \frac{m}{\gamma_1 - \sqrt{\gamma_2^2 + 3\gamma_3^2}}, \quad m_{lh}^{(110)} = \frac{m}{\gamma_1 + \sqrt{\gamma_2^2 + 3\gamma_3^2}}, \quad (11.72)$$

$$m_{hh}^{(111)} = \frac{m}{\gamma_1 - 2\gamma_3}, \quad m_{lh}^{(111)} = \frac{m}{\gamma_1 + 2\gamma_3}. \quad (11.73)$$

11.9 Key Points

- The main weakness of the LCAO method, to be balanced against its many advantages, is its inability to obtain from first principles the required matrix elements.
- The pseudopotential is designed to be smooth and practically equivalent to the actual potential as far as the valence electrons are concerned. This smoothness allows us to obtain solutions to Schrödinger's equation as linear combination of plane waves.
- For weak pseudopotential, perturbation theory, especially degenerate perturbation theory, captures the essential features of the solutions.
- The Augmented plane wave (APW) method of solving Schrödinger's equation seek its solutions as a linear combination of modified plane waves satisfying Bloch's condition. The modification consists in using the

⁹ This degeneracy is sometimes called “Kramers degeneracy”. It is based on time-inversion symmetry which is obeyed by the spin-orbit interaction, but violated by magnetic impurities.

¹⁰ For GaAs the accepted values are $\gamma_1 = 6.9$, $\gamma_2 = 2.2$, $\gamma_3 = 2.9$; for other semiconductors see Table 2.24 of the book by Yu and Cardona [Se119] in connection with their equations (2.71a)–(2.71c).

actual solution in the difficult regions inside the ionic cores and matching it to the plane wave in the interstitial regions; in the latter the potential is taken usually as a constant (this is the so-called muffin-tin approximation (MTA)).

- The Korringa–kohn–rostocker (KKR) method of solving Schrödinger’s equation transforms the latter into an integral equation with the help of the free electron Green’s function. By employing Bloch’s theorem, the integral equation takes the form

$$\psi_{\mathbf{k}}(\mathbf{r}) = \int d^3\rho \mathcal{G}_0(\mathbf{r} - \boldsymbol{\rho}; E, \mathbf{k}) v(\rho) \psi_{\mathbf{k}}(\boldsymbol{\rho}),$$

where $\mathcal{G}_0$ depends on E , $\mathbf{k}$ and the lattice structure but not on the type of atom (or atoms) involved. All this material specific information is concentrated exclusively on the potential $v(\rho)$. The solution to the integral equation inside the ionic core is expressed as a linear combination of spherical harmonics times the radial function. The coefficients in this expansion are determined by matching the solutions inside and outside the ionic core.

- The $\mathbf{k} \cdot \mathbf{p}$ method allows us to determine the energy at the wavevector $\mathbf{q} + \mathbf{k}$ in terms of the energy at $|\mathbf{q}|$ assuming that $\mathbf{k}$ is small so that nondegenerate or degenerate perturbation theory can be employed. By taking the second derivative of $\varepsilon_{\mathbf{q}+\mathbf{k}}$ with respect to $\mathbf{k}$ we obtain the effective mass at the bottom of the CB,

$$m / m^* = 1 + (2p^2 / mE_g).$$

We obtain also the dispersions $E_{\text{hh}}(\mathbf{k})$, $E_{\text{lk}}(\mathbf{k})$ and $E_{\text{soh}}(k) = \Delta + (\hbar^2 k^2 / m_{\text{soh}})$ for the heavy hole (hh), for the light hole (lh), and for the split-off hole (soh) respectively in terms of the parameters $\gamma_1, \gamma_2, \gamma_3, \Delta$, and m_{soh} .

11.10 Problems

- 11.1. Prove (11.4) for the Fourier transform of the empty-core ionic pseudopotential.
- 11.2. Prove (11.17), which shows that only $\mathbf{k}$ ’s differing by vectors of the reciprocal lattice need to enter in the Fourier expansion of the eigenfunctions $\psi(\mathbf{r})$.
- 11.3s. By employing the continuity of $\phi_{\mathbf{k},E}(\mathbf{r})$ and the expansion of a plane wave in spherical harmonics

$$e^{i\mathbf{k} \cdot \mathbf{r}} = 4\pi \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} i^{\ell} Y_{\ell m}^*(\mathbf{k}_0) Y_{\ell m}(\mathbf{r}_0) j_{\ell}(kr), \quad (11.74)$$

prove (11.36). [$\mathbf{k}_0$, $\mathbf{r}_0$ are unit vectors in the direction of $\mathbf{k}$ and $\mathbf{r}$ respectively].

- 11.4. Prove that (11.44) satisfies the unperturbed equation (11.43).
 11.5s. Prove (11.49), starting from the following relation

$$\int_{r' < r_0} d^3r' \nabla' \cdot [\mathcal{G}_0(\mathbf{r} - \mathbf{r}') \nabla' \psi(\mathbf{r}') - \psi(\mathbf{r}') \nabla' \mathcal{G}_0(\mathbf{r} - \mathbf{r}')] = 0, \quad (11.75)$$

where, for both $|\mathbf{r}|$ and $|\mathbf{r}'|$ smaller than $|\mathbf{r}_0|$,

$$(E + (\hbar^2 / 2m) \nabla'^2) \mathcal{G}_0(\mathbf{r} - \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}'). \quad (11.76)$$

- 11.6. Prove that $\tilde{v}_A(0) = -(2/3)E_F$.
 11.7. Calculate the value of q / k_F for which the empty-core pseudopotential form factor $\tilde{v}_A(q)$ vanishes for Al. Take $\zeta = 2,76$, $r_c = 0.582$ Å. The corresponding empirical value is $q / k_F = 1.47$.
 11.8. Calculate the values of $\tilde{v}_v(\mathbf{G}_i)$ for $\mathbf{G}_i = (2\pi/a)(1, 1, 1)$, $\mathbf{G}_i = (2\pi/a)(2, 2, 0)$, $\mathbf{G}_i = (2\pi/a)(3, 1, 1)$ for individual atoms of Si. The $\tilde{v}(\mathbf{G}_i) = \frac{1}{2} \sum_{v=1}^2 \exp(-i\mathbf{G} \cdot \mathbf{r}_v) \tilde{v}_v(\mathbf{G}_i)$. (See (11.7)). Employ the empty-core pseudopotential with $r_c = 0.56$ Å. Compare the values with the corresponding empirical values as given in the book by Yu and Cardona (p. 63).
 11.9s. Show that the interaction energy U_{ie} between ions and electrons, $\int \mathcal{V}_I(\mathbf{r}) n(\mathbf{r}) d^3r$ can be expressed in terms of the Fourier transforms $\mathcal{V}_{Iq}$ and $n_{\mathbf{k}}$, where

$$\mathcal{V}_I(\mathbf{r}) \equiv \frac{1}{\sqrt{V}} \sum_{\mathbf{q}} \mathcal{V}_{Iq} e^{i\mathbf{q} \cdot \mathbf{r}}, \quad (11.77)$$

$$n(\mathbf{r}) \equiv \frac{1}{\sqrt{V}} \sum_{\mathbf{k}} n(\mathbf{r}) e^{i\mathbf{q} \cdot \mathbf{r}}, \quad (11.78)$$

as follows:

$$U_{ie} = \sum_{\mathbf{q}} \mathcal{V}_{Iq} n_{-\mathbf{q}} = \sum_{\mathbf{q}} \frac{4\pi}{4\pi\epsilon_0 q^2} \rho_{Iq} \rho_{-\mathbf{q}}. \quad (11.79)$$

The quantities ρ_{Iq} and $\rho_{\mathbf{k}}$ are the Fourier transforms of the ionic and the electronic charge density respectively.

Further Reading

- N. W. Ashcroft & N. D. Mermin [SS75], pp. 193–210. (For methods of band structure calculations).
- P. Y. Yu & M. Cardona [Se119], pp. 68–82. (For the $\mathbf{k} \cdot \mathbf{p}$ method).
- W. A. Harrison [SS76], pp. 360–363. (For pseudopotentials).
- M. P. Marder [SS82], pp. 230–236. (For pseudopotentials).

Pseudopotentials in Action

Summary. In this chapter we shall illustrate how the plane wave/pseudopotential degenerate case can be used to produce the band structure $E_n(\mathbf{k})$ from the unperturbed free-electron relation $E_k^{(0)} = \hbar^2 k^2 / 2m$. We shall present first the simplest 1D case, and then we shall examine a model 2D case that incorporates the basic concepts and the main graphical constructions without burdening, at this stage, the presentations with plots pertinent to 3-D systems. These plots will be examined in connection with real 3D solids in the next chapter after the readers become familiar with the general features of the plane wave/pseudopotential approach. The latter also provides corrections to the ground state energy and to the electron-phonon interactions; it also allows realistic calculations of the phononic dispersion relations ω_{qs} at least for simple metals.

12.1 The One-Dimensional Case

In Fig. 12.1, we show how the free-electron parabola $E_k^{(0)} = \hbar^2 k^2 / 2m$ is transformed into a band structure either in the reduced-zone scheme (Fig. 12.1c) or the extended-zone scheme (Fig. 12.1d). Notice in Fig. 12.1a that for k far away from the end points, $n\pi/a$, of the Brillouin zones, all the energies $E_{k+G}^{(0)}$ are quite different from $E_k^{(0)}$, where $G = 2n\pi/a$, $n = \pm 1, \pm 2, \pm 3, \dots$. Hence, for a not-so-large $\tilde{v}(G)$, the nondegenerate perturbation theory is applicable and the correction to $E_k^{(0)}$ is of second order and small (the constant $\tilde{v}(0)$ appearing in (11.23) has been omitted in order to facilitate the comparison of Fig. 12.1b–d with 12.1a).

On the contrary, for k in the vicinity of the end points of the BZs, $k = (n\pi/a) - \delta k$ (the $n = 2$ case is shown in Fig. 12.1a–c there is always one $G = -2n\pi/a$ such that the difference $E_k^{(0)} - E_{k+G}^{(0)}$ is small, and equal to $-2\hbar^2 n\pi\delta k / ma$ as $\delta k \rightarrow 0$. Thus, degenerate perturbation theory is applicable giving a result as in (11.25); the latter in the limit, $\delta k \rightarrow 0$, reduces to

$$E_{k,\pm} \simeq \tilde{v}_0 + \frac{\hbar^2(k_{0n}^2 + \delta k^2)}{2m} \pm |\tilde{v}(G_n)| \pm \frac{\hbar^4 k_{0n}^2 \delta k^2}{2m^2 |\tilde{v}(G_n)|}, \quad (12.1)$$

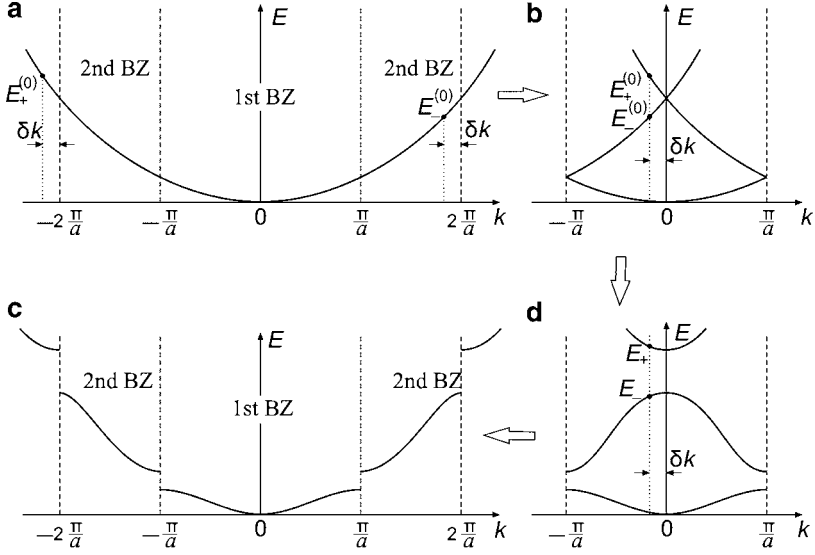


Fig. 12.1. (a) The free-electron parabola, $E^{(0)} = \hbar^2 k^2 / 2m$; the vertical dash lines denote the end points, $n\pi/a$, of the BZs, where a is the period of the periodic potential, and n is any nonzero integer. (b) The same parabola plotted in the reduced-zone scheme; this was obtained by transferring horizontally the pieces of the parabola belonging to the n th BZ by “vectors” of the reciprocal lattice $\pm G_{n-1} = \pm 2(n-1)\pi/a$ as to be brought to the 1st BZ, $-\pi/a < k \leq \pi/a$. (c) By applying (11.23), Fig. 12.1b is transformed to 12.1(c). (d) By reversing the transformation (a) to (b), the reduced-zone scheme of Fig. 12.1(c) becomes the extended zone representation, Fig. 12.1(d), where the n th branch is plotted in the n th BZ ($n = 1, 2, 3, \dots$)

where $k_{0n} = n\pi/a$ and $G_n = -2n\pi/a$. Hence, the gap, E_g , at k_{0n} is

$$E_g = 2|\tilde{v}(G_n)|, \quad |\tilde{v}(G_n)| \ll \hbar^2 k_{0n}^2 / mn \quad (12.2)$$

and the effective mass m_+ , m_- of upper (electron) and the lower (hole) branch at $k = k_{0n}$ is respectively

$$\frac{1}{m_{\pm}} = \frac{1}{m} \left| 1 \pm \frac{\hbar^2 k_{0n}^2}{m |\tilde{v}(G_n)|} \right|. \quad (12.3)$$

According to (12.3), the electron effective mass is smaller than that of the hole.

From (12.2) we can conclude that in the 1D case, a periodic potential possessing in general an infinite number of Fourier components, no matter how small, always creates an infinite number of gaps and bands. The gaps appear in general at $k = n\pi/a$, which in the reduced-zone scheme correspond to $k = 0$ and $k = \pm\pi/a$; these values are those satisfying Bragg’s condition, $k = G/2 = n\pi/a$. The unperturbed energies corresponding to these values of k are $E^{(0)} = \hbar^2 n^2 \pi^2 / 2ma^2$. As $|n|$ increases, the bands become wider and

the gaps narrower (because $|\tilde{v}(G_n)|$ in general goes to zero as $G_n \rightarrow \infty$). The readers may check these features by studying the Kronig–Penney model (Problem 12.1).

Since every band can accept up to two electrons per primitive cell, it follows that, when the number of electrons per primitive cell is even, i.e., equal to $2p$, then, for $T = 0$, the p lower bands are fully occupied and the rest are completely empty. Hence, in this case, the one-dimensional “solid” would be an insulator or a semiconductor.¹ On the other hand, if the number of electrons per primitive cell is odd, then the highest occupied band would be exactly half full, the 1D “solid” would exhibit conducting behavior with the Fermi wavenumber k_F being equal to $\pi/2a$ in the reduced-zone scheme.

12.2 The Two-Dimensional Square Lattice

12.2.1 Spaghetti Diagrams

One way to present graphically $E_n(\mathbf{k})$ for the 2D square lattice is to plot it in the reduced-zone scheme as $\mathbf{k}$ varies along the straight line segments ΓX , XM , $M\Gamma$ forming a triangle ΓXM in the first Brillouin zone $MM^{(1)}M^{(2)}M^{(3)}$, shown in Fig. 12.2. To obtain the 2D analog of the 1D plot shown in Fig. 12.1b we have to find the values of the unperturbed energy $E^0(\mathbf{k}) = \hbar^2(k_x^2 + k_y^2)/2m$ as $\mathbf{k}$ moves along the perimeter of the triangle ΓXM as well as along the perimeter of all the other equivalent triangles. For example, as $\mathbf{k}$ moves along XM $E^{(0)}(\mathbf{k}) = (\hbar^2/2m)(\pi^2/a^2 + \pi^2 y^2/a^2) = (\hbar^2\pi^2/2ma^2)(1 + y^2)$, $0 \leq y \leq 1$. The function $1 + y^2$ for $0 \leq y \leq 1$ corresponds to the lowest-energy branch in units of $\hbar^2\pi^2/2ma^2$ between X and M in Fig. 12.3. The index 2 on this curved segment in Fig. 12.3 indicates that there are 2 (and only 2) identical straight segments in Fig. 12.2 (the XM and the $X^{(1)}M^{(1)}$) that produce the same curve in Fig. 12.3. The next branch between X and M in Fig. 12.3 is obtained as $\mathbf{k}$ moves along the $X^{(4)}M^{(2)}$ straight line segment or along the $X^{(5)}M^{(3)}$ segment of Fig. 12.2. The analytical representation of this branch is $1 + y^2$, $1 \leq |y| \leq 2$ (in units of $\hbar^2\pi^2/2ma^2$). Another example is the third branch between M and Γ , which is given analytically by $x^2 + y^2$ with $x = y$ and $-2 \leq x \leq -1$ and corresponds to the $M^{(2)}\Gamma^{(7)}$ straight line segment (and only this).

In a similar way, the four or five lowest branches between the points Γ and X , X and M , and M and Γ have been plotted in Fig. 12.3. The readers may spend some time to make the correspondence between the curves in Fig. 12.3

¹ Accidentally, this 1D “solid” can be a conductor, if $\tilde{v}(G) = 0$, when $G = 2p\pi/a$. In this case, the p^{th} band joins smoothly with the $(p+1)^{\text{th}}$ band and the Fermi level is at the seamless joining point of the two consecutive bands. In general, $\tilde{v}(G) \neq 0$, and for weak potentials, $|\tilde{v}(G_n)| \ll \hbar^2 k_{0n}^2/2m$; thus, each simple band is followed by a gap as shown in Fig. 12.1(c).

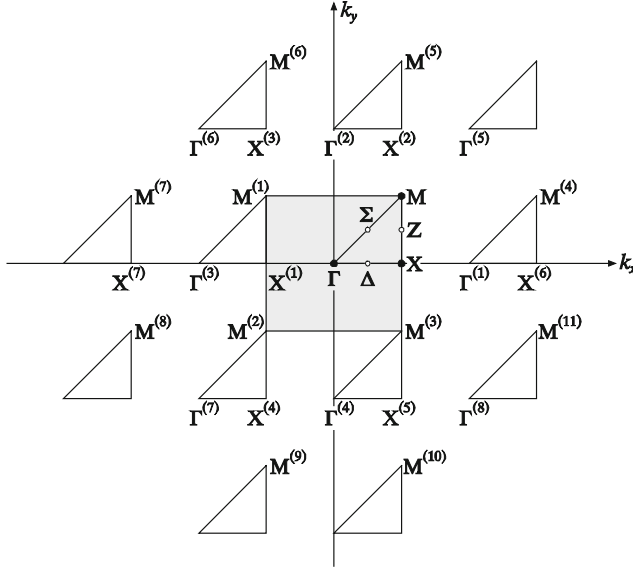


Fig. 12.2. The 1st BZ $MM^{(1)}M^{(2)}M^{(3)}$ for a 2D square lattice with lattice constant a . The points $\Gamma(0, 0)$, $X(1, 0)(\pi/a)$, and $M(1, 1)(\pi/a)$ form a triangle along the perimeter of which the $E_n(\mathbf{k})$ shall be plotted. Several other identical triangles are shown, each of which coincides with ΓXM through a translation by a proper vector $\mathbf{G}$ of the reciprocal lattice

and the line segments in Fig. 12.2. The end result of this exercise is the plotting of the unperturbed energy $E^0(\mathbf{k}) = \hbar^2(k_x^2 + k_y^2)/2m$ in the reduced-zone scheme (i.e., in the 1st BZ) of a square lattice. This considerable investment in time and effort in reaching the rather complicated plot of Fig. 12.3 pays back when we introduce a weak periodic pseudopotential. Essentially what we have to do is to diagonalize each subspace corresponding to the degenerate or almost-degenerate eigenstates, which are the ones around the points of intersection of the curves in Fig. 12.3. For example, the degenerate point of lowest energy is doubly degenerate (X and $X^{(1)}$), while the next two points in energy are fourfold degenerate (M , $M^{(1)}$, $M^{(2)}$, $M^{(3)}$) and ($\Gamma^{(1)}$, $\Gamma^{(2)}$, $\Gamma^{(3)}$, $\Gamma^{(4)}$).

Problem 12.1t. Diagonalize the 4×4 matrix at the degenerate point M . The matrix element between any nearest neighbor pairs (e.g., $MM^{(1)}$, or $MM^{(3)}$, or $M^{(2)}M^{(3)}$, etc) is $\tilde{v}$ and the matrix element between diagonally located points in the 1st BZ ($MM^{(2)}$ and $M^{(1)}M^{(3)}$) is $\tilde{v}'$. Show that the eigenenergies are

$$E_1 = E_M^{(0)} + \tilde{v}(0) + 2\tilde{v} + \tilde{v}', \quad (12.4)$$

$$E_2 = E_M^{(0)} + \tilde{v}(0) - 2\tilde{v} + \tilde{v}', \quad (12.5)$$

$$E_{3,4} = E_M^{(0)} + \tilde{v}(0) - \tilde{v}', \quad (12.6)$$

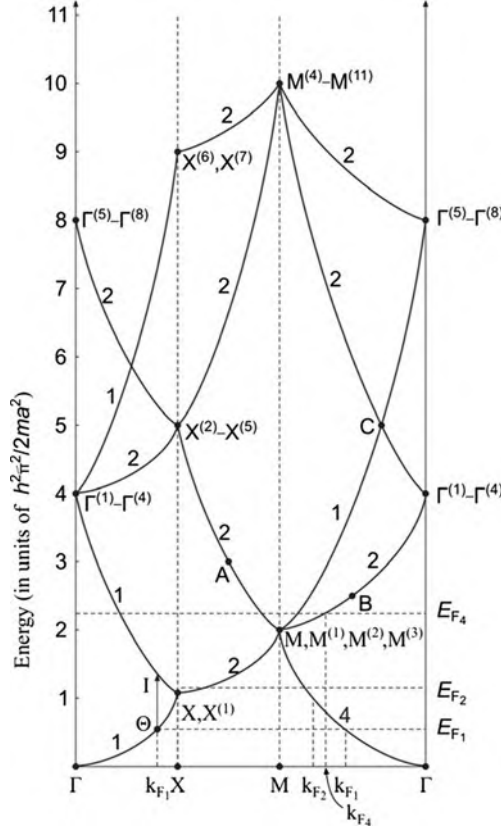


Fig. 12.3. The first four or five branches of the *unperturbed* energy $E^0(\mathbf{k}) = \hbar^2 (k_x^2 + k_y^2) / 2m$ for a square lattice of lattice constant a plotted in the first BZ (reduced-zone scheme) as $\mathbf{k}$ varies along the straight line segments ΓX , XM , $M\Gamma$ and their identical segments. The number on each curve indicates how many straight line segments produce this curve. The *horizontal dashed lines* denoted by $E_{F,n}$ ($n = 1, 2, 4$) show the position of the Fermi energy if there are n electrons per primitive cell

where $E_M^{(0)} = \hbar^2 \pi^2 / ma^2$. The levels E_3 and E_4 are degenerate. Determine the eigenstates corresponding to these eigenenergies. Similar are the results at the points $\Gamma^{(1)}$ to $\Gamma^{(4)}$. Obtain numerical values for E_1 to E_4 by taking $a = 4.5 \text{ \AA}$. Use the 3D empty core pseudopotential, with $r_c = 0.9 \text{ \AA}$, $n_e = (1/37) \text{ \AA}^{-3}$, $k_{TF} = 1.5 \text{ \AA}^{-1}$ and take f in (11.12) to be equal to 0.8.

Thus, on the basis of these results and taking into account the vanishing of the group velocity at the perturbed degenerate points, the unperturbed reduced-zone scheme plot of the $E^0(\mathbf{k})$ vs. $\mathbf{k}$ (Fig. 12.3) becomes a genuine band structure, $E_n(\mathbf{k})$. In Fig. 12.4 a qualitative sketch of this band structure is presented. Notice that, in spite of the opened gaps at points X and M , the

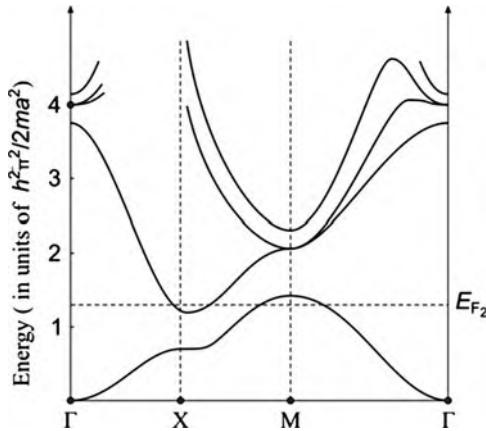


Fig. 12.4. The modification of the unperturbed branches, shown in Fig. 12.3, as a consequence of the application, of the periodic pseudopotential, and the resulting partial, or total removal of the degeneracies (The question of the lifting or not of degeneracies is treated in the book by Burns [SS77], p.289–308). This is a qualitative sketch. The *dashed line* denotes the Fermi energy for two electrons per primitive cell

lowest band still overlaps with the next one. Thus, according to Fig. 12.4, this periodic “solid” with 2 electrons per primitive cell would still exhibit metallic or semimetallic behavior.

12.2.2 Fermi Lines

A periodic pseudopotential, if strong enough, can, under certain additional conditions, transform a free-electron metal into a semiconductor or insulator. This transition can be studied in a more illuminating way by following how the Fermi line (a circle in the unperturbed case) is deformed and eventually may disappear in the semiconducting state, as the strength of the periodic potential increases.

To determine the Fermi wavenumber k_F for the free-electron 2D case, we shall use the relation

$$2 \frac{SS_{k_F}}{(2\pi)^2} = N_e = N_{pc}N_{ep}, \quad (12.7)$$

where S is the total area in real space of our 2D system, $S_{k_F} = \pi k_F^2$ is the area in k -space inside the free-electron Fermi circle, and N_e is the total number of electrons, which is equal the number of primitive cells, N_{pc} , times the number of electrons, N_{ep} , per primitive cell. The lhs of (12.7) gives the total number of states (including the two orientations of spin) inside the area S_{k_F} of k -space (see (4.11) adapted to 2D). For a square lattice of lattice constant a , we have that $S = N_{pc}a^2$. Hence, the unperturbed Fermi wavevector is given by

$$k_F = \frac{\sqrt{2\pi N_{ep}}}{a}. \quad (12.8)$$

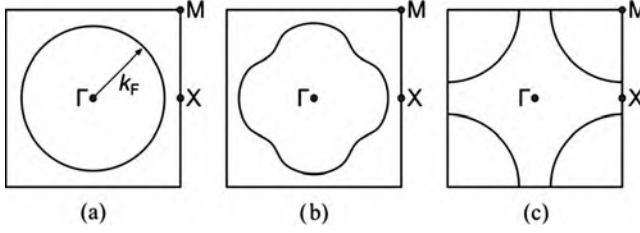


Fig. 12.5. The 1st BZ for a 2D square lattice and the Fermi line for *one* electron per primitive cell. The periodic potential is zero (a), or weak (b), or very strong (c)

In Fig. 12.5 we plot the 1st BZ of a square lattice together with the Fermi line, when $N_{\text{ep}} = 1$, for the free-electron case, Fig. 12.5a; for a weak periodic pseudopotential, Fig. 12.5b; and for a strong periodic pseudopotential, Fig. 12.5c. It is clear that the unperturbed Fermi circle lies entirely within the 1st BZ, since $k_F/(\Gamma X) = \sqrt{2\pi}/\pi = 0.798$, for $N_{\text{ep}} = 1$. The introduction of a weak periodic potential deforms the Fermi line, which develops bulges in the ΓX direction (and its symmetric ones) and depressions in the ΓM direction (and its symmetric ones), while keeping the area inside the Fermi line constant (according to (12.7)).

Question: Can you explain why the deformation has this shape?

As the periodic potential becomes stronger, the bulges become more pronounced, until eventually, they touch the boundary of the 1st BZ, Fig. 12.5c, which is not part of the Fermi line (except the eight points of intersection). Since the area inside the Fermi line is conserved, there is no way for the latter to disappear entirely no matter how strong the periodic potential is. Hence, the 2D periodic “solid” with one electron per primitive cell will always have a nonzero DOS at E_F and would never² become semiconducting or insulating. This result is in agreement with the general conclusion that a periodic solid with odd number of electrons per primitive cell is always a metal (within the independent-electron approximation).

Notice that there is a qualitative difference between the case (c) in Fig. 12.5c (in which part of the Fermi contour is missing by being “absorbed” by the boundary of the 1st BZ) and the other two cases: In case (c) the Fermi line is hole-like, while in cases (a) and (b) it is electron-like. This becomes clear in the repeated-zone scheme, where the four disjoint pieces of the Fermi line in Fig. 12.5c would give a closed contour, the interior of which has only empty states.

² This conclusion is valid within the periodic independent-electron approximation. If many-body effects are included, it is possible, under certain conditions, to have insulating behavior even in the case where there were an odd number of electrons per primitive cell.

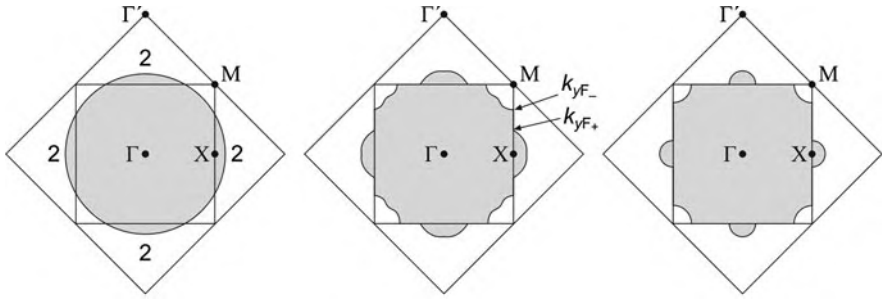


Fig. 12.6. The first two BZs of a square lattice and the Fermi line for *two* electrons per primitive cell. (a) The periodic potential is zero. (b) Weak periodic potential. (c) Stronger periodic potential

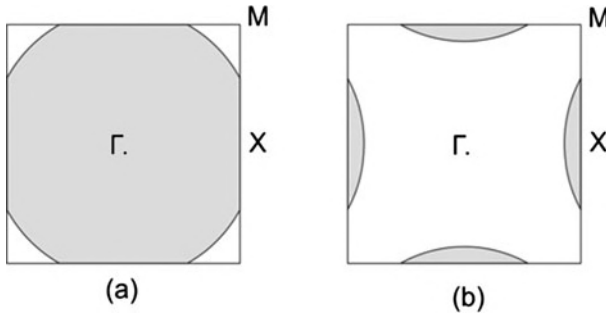


Fig. 12.7. The Fermi line of Fig. 12.6(a) plotted in the reduced-zone scheme. (a) The part of the Fermi line that was in *the* first BZ in Fig. 12.6(a) remains in the 1st BZ, corresponds to the lowest branch $E_1(\mathbf{k})$, and satisfies the equation $E_1(\mathbf{k}) = E_F$. (b) The part of the Fermi line that was in the 2nd BZ in Fig. 12.6(a) has been transferred to the 1st BZ, but as the second branch satisfying the equation $E_2(\mathbf{k}) = E_F$. The shaded areas correspond to occupied states

In Fig. 12.6 we show the first two BZs of a square lattice together with the Fermi line corresponding to *two* electrons per primitive cell. The area inside the Fermi line is now $\pi k_F^2 = 4\pi^2/a^2$ and remains invariant as the periodic potential is introduced (shaded area in Figs. 12.6a–c). Furthermore, πk_F^2 for $N_{\text{ep}} = 2$ is exactly equal to the area of the first BZ, $(2\pi/a)^2$. Notice that the Fermi line is partly in the first BZ and partly in the second BZ. If we adopt the reduced-zone scheme the parts of the Fermi line lying in the 2nd BZ would be transferred to the 1st BZ but as pieces belonging to the second band, $E_2(\mathbf{k})$. In Fig. 12.7 we replot Fig. 12.6a in the reduced-zone scheme. Let us see now how Fig. 12.6a (or 12.7) would change in the presence of a periodic pseudopotential. Every point, $(\pi/a, k_y > 0)$ in the segment XM of the first BZ has the same energy as its symmetric one in $X^{(1)}M^{(1)}$ (see Fig. 12.2) and it is coupled to it through a nonzero matrix $\tilde{v}(\mathbf{G})$, $\mathbf{G} = (2\pi/a)(1, 0)$. Hence, by employing degenerate perturbation theory and by diagonalizing the resulting 2×2 matrix as before, we obtain the following perturbed eigenenergies:

$$E_+ = \frac{\hbar^2}{2m} \left(\frac{\pi^2}{a^2} + k_y^2 \right) + |\tilde{v}(\mathbf{G})|, \quad (12.9)$$

$$E_- = \frac{\hbar^2}{2m} \left(\frac{\pi^2}{a^2} + k_y^2 \right) - |\tilde{v}(\mathbf{G})|. \quad (12.10)$$

By setting $E_{\pm}(\mathbf{k}) = E_F$ we shall find³ the intersections of the perturbed Fermi line with the segment XM ($0 \leq k_y \leq \pi/a$) of the 1st BZ. Because of the $\pm|\tilde{v}(\mathbf{G})|$ terms, we expect to find two intersections and not one as in Fig. 12.6a:

$$k_{Fy\pm}^2 = (E_F \mp |\tilde{v}(\mathbf{G})|)(2m/\hbar^2) - (\pi/a)^2. \quad (12.11)$$

The smaller one is the k_{Fy+} and the larger one the k_{Fy-} . Hence, the circle of Fig. 12.6a will break and deform as in Fig. 12.6b. Notice that the boundary of the 1st BZ does not belong to the perturbed Fermi line, since its points do not satisfy (12.11) (except at the 16 points of its intersection with this line). Furthermore, the Fermi line segments intersect the boundary of the 1st BZ at right angle (To explain why, think of the direction of the group velocity at the intersection points).

As the potential $|\tilde{v}(\mathbf{G})|$ increases, k_{Fy+} decreases and k_{Fy-} increases. As a result the pockets of empty states in the 1st BZ and the pockets of occupied states in the 2nd BZ (which in the reduced-zone scheme are pockets of occupied states in the second band) contract as shown in Fig. 12.6c, and tend to zero. Notice that the area of empty pockets in the 1st BZ is equal to the area of the occupied pockets in the 2nd BZ, since the total area of occupied states is constant and equal to the area of the 1st BZ. An equivalent way to describe the situation shown in Fig. 12.6c, is as in Fig. 12.4, which shows a few empty states (holes), in the valence band and a few occupied states (electrons, below the dotted E_{F_2} line) in the conduction band. This is the case of a semimetal where there is still a small overlap of the VB and the CB, and hence, no gap yet. The transition to a semiconductor will take place when $k_{Fy-} = \pi/a$ and $k_{Fy+} = 0$. The critical values, $|\tilde{v}(\mathbf{G})|_c$ and the resulting E_{Fc} , for this transition, taking into account (12.11), are as follows:

$$|\tilde{v}(\mathbf{G})|_c = \frac{\hbar^2}{4m} \left(\frac{\pi}{a} \right)^2, \quad (12.12)$$

$$E_{Fc} = \frac{3\hbar^2}{4m} \left(\frac{\pi}{a} \right)^2 = 3|\tilde{v}(\mathbf{G})|_c. \quad (12.13)$$

At this critical value $|\tilde{v}(\mathbf{G})|$, the Fermi line disappears altogether, the area of occupied states coincides with the 1st BZ, the pockets of empty states in the 1st BZ and of occupied states in the 2nd BZ disappear too, and there is no overlap of the valence and the conduction band. For $|\tilde{v}(\mathbf{G})| > |\tilde{v}(\mathbf{G})|_c$, a finite gap opens up.

³ The Fermi energy is not equal to its value in the unperturbed case.

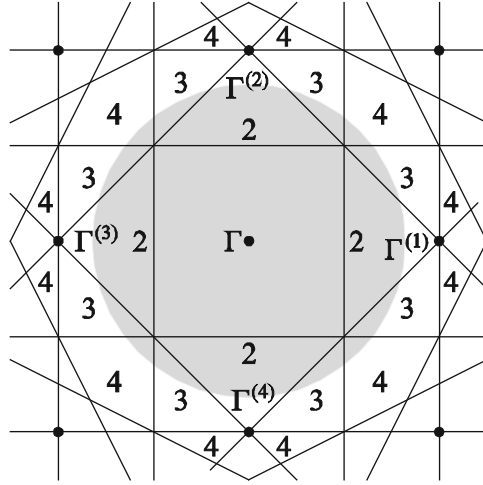


Fig. 12.8. The first four BZs (and pieces of some higher ones) for a square lattice are shown together with the unperturbed Fermi circle (in the extended zone scheme) for *four* electrons per primitive cell

The possibility of a metal–semiconductor transition exists also in the case of four electrons per primitive cell. In this case, the free-electron k_F is equal to $\sqrt{8\pi}/a$ and the area inside the Fermi circle is $8\pi^2/a^2$, i.e., equal to the sum of the first and second BZs. In Fig. 12.8 we plot the first four BZs for a square lattice together with the unperturbed Fermi circle (shaded) area. Because of the equality, $\pi k_F^2 = 2(2\pi/a)^2$, the Fermi line can disappear altogether and the area of occupied states may coincide with the square $\Gamma^{(1)}\Gamma^{(2)}\Gamma^{(3)}\Gamma^{(4)}$, if the pseudopotentials $|\tilde{v}(\mathbf{G}_i)|$, $i = 1, 2$ (where $\mathbf{G}_1 = (2\pi/a)(1, 0)$ and $\mathbf{G}_2 = (2\pi/a)(1, 1)$) are strong enough. Notice that the 1st BZ is fully occupied (since $k_F > \Gamma M = \sqrt{2}\pi/a$), while there are pockets of empty states in the 2nd BZ and pockets of occupied states in the 3rd and 4th BZs. In the reduced-zone scheme the parts of Fermi line, which are in the 2nd, the 3rd, and the 4th BZ, would be redrawn in the 1st BZ but as pieces of the 2nd, the 3rd, and the 4th band respectively as shown in Fig. 12.9. In Fig. 12.10 we replot the unperturbed Fermi line for the 3rd and the 4th bands in the repeated-zone scheme in order to make clear that they are closed contours, electron-like, since the states in their interior are occupied. In contrast, the closed contour corresponding to $E_2(\mathbf{k}) = E_F$ is hole-like, since the states in its interior are empty.

The three equivalent ways (Figs. 12.8–12.10) of plotting the Fermi line (for $N_{\text{ep}} = 4$) relative to the BZs of a square lattice allows us to get a qualitative picture of what are the effects of a weak periodic pseudopotential. The latter would lift in general the degeneracies (e.g., point A and its symmetric ones in Fig. 12.9a) would come closer to the Γ point, while point A and its symmetric ones in 12.9b would approach point M and the corresponding symmetric ones;

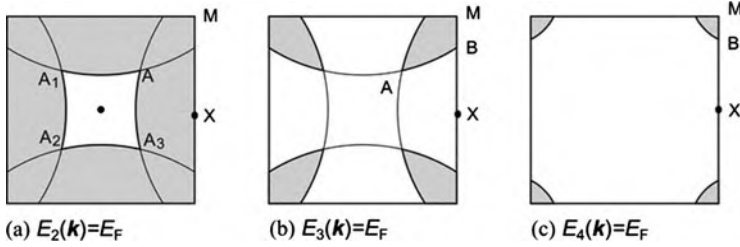


Fig. 12.9. Redrawing of Fig. 12.8 in the reduced-zone scheme. The index n in $E_n(\mathbf{k})$ has been determined so that its values for $\mathbf{k}$ in the 1st BZ to coincide with $E^{(0)}(\mathbf{k}) = \hbar^2 k^2/2m$ for $\mathbf{k}$ in the n th BZ. Notice that there is no solution of $E_1(\mathbf{k}) = E_F$, and as a result, the Fermi line for the first band does not exist. The shaded areas are the occupied ones

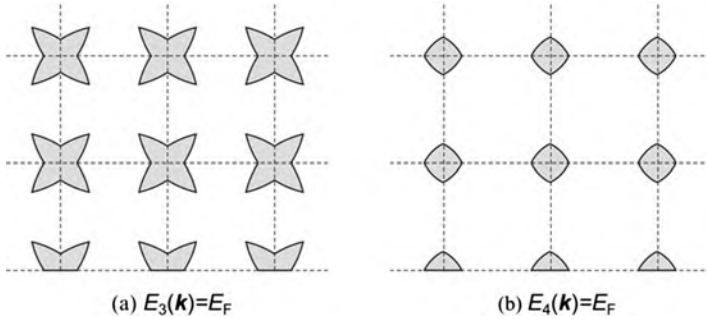


Fig. 12.10. Replot of the parts of Fermi line associated with the 3rd (a) and the 4th (b) band in the repeated-zone scheme

similarly point B in 12.9b would approach point M but not as much as point B in Fig. 12.9c).

Furthermore, the periodic pseudopotential would round off the corners and would make the Fermi line to intersect the BZ boundaries at right angle. Finally, as the periodic pseudopotential becomes stronger, the square-like pocket in Fig. 12.10b of the fourth band would disappear first, followed by the star-like regions of the third band. At the same time the hole-like contour $AA_1A_2A_3$ in Fig. 12.9a would become smaller and smaller and it would disappear at exactly the same strength that the third band Fermi line disappear. (The parts in the 4th disappeared earlier).

This marks the transition from a semimetallic to a semiconducting state. Keep in mind that the area of empty states in Fig. 12.9a is equal to the areas of occupied states of the 3rd and the 4th bands; this is a consequence of the total number of occupied states being conserved.

12.3 Harrison's Construction

We have seen that, when the periodic pseudopotential is weak, we can obtain a good qualitative picture of the shape of the Fermi line (or the Fermi surface for 3D solids) starting from the free-electron circle (or sphere for 3D) redrawn in the reduced or the repeated-zone scheme, and applying certain simple rules: That is, the lifting of the degeneracies, rounding-off of the corners, conservation of the occupied area (in 2D k -space) or volume (in 3D k -space), and normal intersection of the BZ boundaries by the Fermi line (in 2D) or the Fermi surface (in 3D). To apply these rules in the example of the square lattice with four electrons per primitive cell, we needed the first four BZs (the higher-order the BZ is of, the more complicated it becomes, see, e.g., the fourth one in Fig. 12.8). The situation becomes much more complicated in 3D and for lattices of reduced symmetry. Fortunately, there is the so-called *Harrison's construction*, which, in the repeated-zone scheme, partitions the unperturbed Fermi line (or Fermi surface in 3D) into sections each one of which belongs to one and only one BZ. This is achieved without having to separate the $\mathbf{k}$ -space into BZs. The recipe for Harrison's construction is as follows:

Draw equal circles (spheres in 3D) of radius k_F centered at every point $\mathbf{G}_n$ of the reciprocal lattice (including the origin $\mathbf{G}_n = 0$). The perimeters of these circles (or the surfaces of these spheres in 3D), which may or may not intersect depending on whether $2k_F > |\mathbf{G}_n|_{\min}$ or $2k_F < |\mathbf{G}_n|_{\min}$, form the unperturbed Fermi line (Fermi surface in 3D), S_F , in the repeated-zone scheme. The parts of S_F , if any, that separate regions belonging to one and only one circle (sphere in 3D) from regions belonging to none of these circles (spheres in 3D) lie within the 1st BZ, and are associated with the first (lowest) band as solutions of the equation $E_1(\mathbf{k}) = E_F$. The parts of S_F , if any, that separate regions belonging to two and only two circles (spheres in 3D) from regions belonging to one and only one circle (sphere in 3D) lie within the 2nd BZ, and are associated with the second band as solutions of the equation $E_2(\mathbf{k}) = E_F$. Generally, the parts of S_F , if any, that separate regions belonging to $n + 1$ and only $n + 1$ circles (spheres in 3D) from regions belonging to n and only n circles (spheres in 3D) lie within the $n + 1$ BZ and are associated with the $n + 1$ band as solution of the equation $E_{n+1}(\mathbf{k}) = E_F$. Furthermore, if a point $\mathbf{k}$ is in the interior of exactly ν circles (spheres in 3D), then and only then the eigenstates $\psi_{\mathbf{k}n}$, $n = 1, 2, \dots, \nu$ are occupied.

Problem 12.2t. Apply Harrison's construction for the case of Fig. 12.6a and reproduce Fig. 12.7

Solution: Dash-lines in the 1st BZ belong to the first band, while continuous lines in the 1st BZ belong to the second band, as in Fig. 12.11.

Problem 12.3t. Apply Harrison's construction to a square lattice with four electrons per primitive cell and reproduce Figs. 12.9 and 12.10.

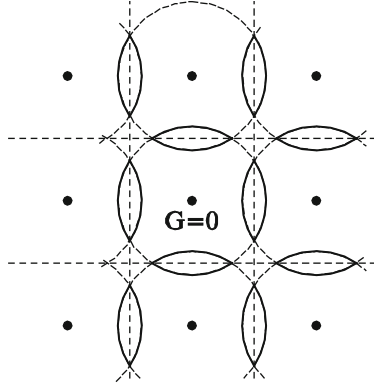


Fig. 12.11. Harrison's construction for a square lattice, with two electrons per primitive cell

Harrison's construction is based on the following theorem, which we state here without proof:

Consider any point $\mathbf{k}$ in the reciprocal space. Draw all equal circles (spheres in 3D) of radius $|\mathbf{k}|$ centered at every point $\mathbf{G}_n$ of the reciprocal lattice (excluding the origin, $\mathbf{G}_n = 0$). If the point $\mathbf{k}$ lies in the interior of $\nu - 1$ circles (spheres in 3D) and in the boundary of none, then and only then $\mathbf{k}$ belongs to the interior of the ν th BZ. If $\mathbf{k}$ lies in the interior of $\nu - 1$ circles (spheres in 3D) and in the boundaries of μ additional circles (spheres in 3D), then and only then the point $\mathbf{k}$ belongs to the surface bounding the ν th, $\nu + 1$ th, till the $\nu + \mu$ th BZ.

This theorem can be used to define the ν th BZ in an alternative way, which may be more convenient than the traditional one.

12.4 Second-Order Correction to the Total JM Energy

In Ch.4 we calculated the total energy of JM, $\langle \Psi_0 | \hat{H} | \Psi_0 \rangle$, assuming that the ground state wavefunction of the system is that of the JM. In other words we ignore the influence of the Coulomb forces on the wavefunction and thus we obtained the ground state energy to first-order in the potential. If we take the first order corrections to Ψ_0 , $\Psi_0 \rightarrow \Psi = \Psi_0 + \Psi^{(1)}$, we can obtain the second-order correction $E^{(2)}$, to the total energy. Taking into account (11.23), we have

$$E^{(2)} = 2 \sum_{\mathbf{q}} E_{\mathbf{q}}^{(2)} = 2 \sum_{\mathbf{q}} \sum_{\mathbf{k} \neq 0} \frac{|\tilde{v}(\mathbf{k}) S_{\mathbf{k}}|^2}{E_{\mathbf{q}}^{(0)} - E_{\mathbf{q}+\mathbf{k}}^{(0)}}, \text{ WRONG} \quad (12.14)$$

where $\tilde{v}(\mathbf{k}) S_{\mathbf{k}}$ is the screened (by electrons) ionic pseudopotential as given by (11.8) to (11.10). For a periodic system the $\mathbf{k}$'s must be replaced by the vectors

$\mathbf{G}$ s of the reciprocal lattice and $\mathbf{S}_{\mathbf{G}} = 1$. But (12.14) must be modified, as annotated by the “WRONG”: By summing in this equation over all the occupied single-electron states, we have overestimated the electron–electron interaction, since each electron is counted twice both as occupying the state $\mathbf{q}$ and as being a member of the cloud screening the ionic potential $\tilde{v}_i(\mathbf{k})$ according to the formula $\tilde{v}(\mathbf{k}) = \tilde{v}_i(\mathbf{k})/\varepsilon(\mathbf{k})$. To remedy this overestimation, we shall make the plausible, but not obvious, choice of screening only one of the two factors in $|\tilde{v}(\mathbf{k})|^2 = \tilde{v}(\mathbf{k})\tilde{v}^*(\mathbf{k})$, i.e., to replace $|\tilde{v}(\mathbf{k})|^2 = |\tilde{v}_i(\mathbf{k})|^2/(\varepsilon(k))^2$ by $|\tilde{v}_i(\mathbf{k})|^2/\varepsilon(k)$

$$E^{(2)} = 2 \sum_{\mathbf{q}} \sum_{\mathbf{k} \neq 0} \frac{|\tilde{v}_i(\mathbf{k})S_{\mathbf{k}}|^2}{\varepsilon(k) [E_{\mathbf{q}}^{(0)} - E_{\mathbf{q}+\mathbf{k}}^{(0)}]}. \quad (12.15)$$

The summation over $\mathbf{q}$ can be performed analytically giving finally

$$E^{(2)} = -\frac{4\pi\varepsilon_0 V}{8\pi e^2} \sum_{\mathbf{k} \neq 0} k^2 |\tilde{v}_i(\mathbf{k})S_{\mathbf{k}}|^2 \left[1 - \frac{1}{\varepsilon(k)} \right]. \quad (12.16)$$

Problem 12.4t. Starting from (12.15) prove (12.16) taking into account that $\varepsilon(k)$ is given by (11.12).

Problem 12.5t. Prove (12.16) directly (without employing (12.15)) by following an alternative approach starting from Problem 11.9s giving the interaction of the ionic pseudocharge $\tilde{\rho}_{i\mathbf{k}}$ with the electronic charge $\rho_{\mathbf{k}}$

$$\langle \hat{H}_{ie} \rangle^{(2)} = \sum_{\mathbf{k} \neq 0} \frac{4\pi}{4\pi\varepsilon_0 k^2} \tilde{\rho}_{i\mathbf{k}} \rho_{-\mathbf{k}}.$$

The $\mathbf{k} = 0$ term is excluded because it gives the interaction of a uniform ionic and electronic charge distribution, which has already been taken into account in Chap. 4. Next, use the definition of ε , $\varepsilon^{-1}(\mathbf{k}) \equiv 1 + (\rho_{\mathbf{k}}/\tilde{\rho}_{i\mathbf{k}})$, to obtain $\rho_{\mathbf{k}} = -\tilde{\rho}_{i\mathbf{k}}(1 - \varepsilon^{-1}(k))$. Furthermore, $\tilde{\rho}_{i\mathbf{k}} = -4\pi\varepsilon_0 \sqrt{V} k^2 \tilde{v}_i(\mathbf{k}) S_{\mathbf{k}} / 4\pi e$. Finally, take into account that $E^{(2)} = \langle \hat{H}_{ie} \rangle^{(2)} / 2$, since the total energy is half the potential energy.

12.5 Ionic Interactions in Real Space

For elemental solids, where $\tilde{v}_{i\ell}(k)$ in (11.9) is the same for all atoms ℓ , $\tilde{v}_{i\ell}(k) = \tilde{v}_i(k)$ can be taken out of the summation over $\mathbf{r}_{\ell}$ in (11.9), and (12.16) can be written as follows:

$$E^{(2)} = \frac{1}{N_a^2} \sum_{\mathbf{r}_{\ell} \mathbf{r}'_{\ell}} \sum_{\mathbf{k}} F(k) e^{-i\mathbf{k} \cdot (\mathbf{r}_{\ell} - \mathbf{r}'_{\ell})}. \quad (12.17)$$

where

$$F(k) = -\frac{4\pi\epsilon_0 V k^2 |\tilde{v}_i(k)|^2}{8\pi e^2} \left[1 - \frac{1}{\epsilon(k)} \right]. \quad (12.18)$$

We can rewrite $E^{(2)}$ by defining the indirect two-body ion-ion interaction $\mathcal{V}_{\text{ind}}(|\mathbf{r}_\ell - \mathbf{r}'_\ell|)$ in such a way that:

$$E^{(2)} = \frac{1}{2} \sum_{\mathbf{r}_\ell, \mathbf{r}'_\ell} \mathcal{V}_{\text{ind}}(|\mathbf{r}_\ell - \mathbf{r}'_\ell|). \quad (12.19)$$

Then, comparing (12.17) and (12.19), we have

$$\mathcal{V}_{\text{ind}}(\mathbf{r}_l - \mathbf{r}'_l) = \frac{2}{N_a^2} \sum_{\mathbf{k}} F(k) e^{-i\mathbf{k} \cdot (\mathbf{r}_\ell - \mathbf{r}'_\ell)}. \quad (12.20)$$

Problem 12.6t. Show that $\mathcal{V}_{\text{ind}}(r)$ is given by the following expression:

$$\mathcal{V}_{\text{ind}}(r) = \frac{V}{N_a^2 \pi^2} \frac{1}{r} \int_0^\infty dk k \sin kr F(k). \quad (12.21)$$

Separating the terms $\mathbf{r}_\ell = \mathbf{r}'_\ell$ from the rest, (12.19) becomes

$$E^{(2)} = \frac{1}{2} \sum_{\mathbf{r}_i \neq \mathbf{r}_l} \mathcal{V}_{\text{ind}}(|\mathbf{r}_l - \mathbf{r}'_l|) + \frac{1}{N_a} \sum_{\mathbf{k}} F(k). \quad (12.22)$$

Notice that the second term in the rhs of (12.22) is independent from the positions of the atoms and depends only on the volume of the solid. The same is true for the electronic kinetic energy and for the el-el, the el-ion, and the ion-ion potential energy as calculated in Ch.4. Hence, we can rewrite the total energy U in a form similar to (12.22)

$$E^{(2)} = \frac{1}{2} \sum_{\mathbf{r}_\ell \neq \mathbf{r}'_\ell} \left[\mathcal{V}_{\text{ind}}(|\mathbf{r}_\ell - \mathbf{r}'_\ell|) + \frac{(\zeta e)^2}{4\pi\epsilon_0 |\mathbf{r}_\ell - \mathbf{r}'_\ell|} \right] + U_V, \quad (12.23)$$

where the term U_V depends only on the volume, while the two terms in the brackets (including the bare Coulomb ion-ion interaction) define the effective ion-ion interaction $\mathcal{V}_i(d')$, where $d' = |\mathbf{r}_\ell - \mathbf{r}'_\ell|$, and depend explicitly on the distance d' between the two ions of each pair.

One can show that (see Pr. 12.5s)

$$\mathcal{V}_i(d') \simeq \frac{9\pi\zeta^2 |\tilde{v}(2k_F)|^2}{E_F} \frac{\cos 2k_F d'}{(2k_F d')^3}, \quad d' \gg d, \quad (12.24)$$

where d is the nearest neighbor equilibrium distance. Thus, for large distance d' , $\mathcal{V}_i(d')$ exhibits an oscillatory $1/d'^3$ dependence on d' ; this is a consequence of the singularity exhibited by the RPA dielectric function $\epsilon(k)$ for $k = 2k_F$ (see (D.26) and (D.28)); indeed, if, instead of the RPA $\epsilon(k)$, we use the Thomas-Fermi one, $\epsilon(k) = 1 + (k_{\text{FT}}/k)^2$, which has no singularity at

any finite k , the oscillatory $1/d'^3$ dependence disappears and in its place an exponentially screened Coulomb potential does show up

$$\mathcal{V}_i(d') \simeq (\zeta e)^2 e^{-k_{\text{TF}} d'} \frac{\cosh^2 k_{\text{TF}} r_c}{4\pi\epsilon_0 d'}, \quad d' \gg 2r_c, \quad (12.25)$$

(see Pr.12.5s). Oscillatory $1/d'^3$ behavior has been observed in the potential created by a foreign impurity in a metal. This behavior, known as *Friedel's oscillations*, plays an important role in explaining several phenomena. For example, is the nearest neighbor equilibrium distance d related to the distance at which $\mathcal{V}_i(d')$ exhibits the first minimum? The answer is yes (for details see the book by Harrison [SS76], p. 388). Furthermore, the $\cos 2k_F d'$ factor in (12.24) implies that $\mathcal{V}_i(d')$ can be either attractive or repulsive depending on the distance d' . This feature provides the basis for the understanding of the interesting topic of *spin-glasses*, where the coupling between nearest neighbor impurity spins (randomly located) is either ferromagnetic or antiferromagnetic depending on their distance.

12.6 Phononic Dispersions in Metals

The usefulness of expressing the total energy⁴ of the solid U explicitly on the ionic positions is revealed when one attempts to calculate the change in the energy U associated with a phonon $\mathbf{q}, s$. This change will only involve those terms, which depend on the ionic position, i.e., U_{ind} , and the unscreened Coulomb part of the ions. In the presence of a phonon $\mathbf{q}, s$ with displacements $\{\mathbf{u}_{\ell, qs}\}$ the indirect ion-ion interaction energy is given, according to (12.17), by the following expression:

$$U_{\text{ind}, qs} \equiv E_{qs}^{(2)} = \frac{1}{N_a^2} \sum_{\mathbf{k}} F(k) \left| \sum_{\mathbf{r}_{\ell}} e^{-i\mathbf{k} \cdot (\mathbf{r}_{\ell} + \mathbf{u}_{\ell})} \right|^2. \quad (12.26)$$

In Sect. 9.4 we calculated a quantity of the form $|f|^2 \left| \sum_{\mathbf{R}} \exp(i\mathbf{q} \cdot (\mathbf{R} + \mathbf{u})) \right|^2$, which becomes identical to (12.26) (except for the summation over $\mathbf{k}$) with the following replacements: $|f|^2 \rightarrow F(k)/N_a^2$, $\mathbf{q} \rightarrow -\mathbf{k}$, $\mathbf{k}s \rightarrow \mathbf{q}s$. Hence

$$U_{\text{ind}, qs} = \sum_{\mathbf{k}} F(k) \left\{ \delta_{-\mathbf{k}, G} \left(1 - \langle (\mathbf{k} \cdot \mathbf{u})^2 \rangle \right) + \left| \mathbf{k} \cdot \mathbf{b}_{qs} \right|^2 \left[\delta_{-\mathbf{k}+\mathbf{q}, G} n_{qs} + \delta_{-\mathbf{k}-\mathbf{q}, G} (1 + n_{qs}) \right] \right\} \quad (12.27)$$

where $\langle (\mathbf{k} \cdot \mathbf{u})^2 \rangle = |\mathbf{k} \cdot \mathbf{b}_{qs}|^2 (1 + 2n_{qs})$ and $n_{qs} = 1$ since there is only one phonon characterized by $\mathbf{q}, s$.

⁴ This energy does not include the kinetic energy of the ions.

To obtain the difference $\delta U_{\text{ind},qs} \equiv U_{\text{ind},qs} - U_{\text{ind},0}$, we must subtract from (12.27) a similar expression with $n_{qs} = 0$. We obtain then

$$\delta U_{\text{ind},qs} = \sum_{\mathbf{k}} F(k) |\mathbf{k} \cdot \mathbf{b}_{qs}|^2 [-2\delta_{-\mathbf{k},\mathbf{G}} + \delta_{-\mathbf{k}+\mathbf{q},\mathbf{G}} + \delta_{-\mathbf{k}-\mathbf{q},\mathbf{G}}]. \quad (12.28)$$

Exploiting the presence of the delta symbols, we can change the summation over $\mathbf{k}$ to a summation over $\mathbf{G}$:

$$\delta U_{\text{ind},qs} = \sum_{\mathbf{G}} \left[F(|\mathbf{G} - \mathbf{q}|) |(\mathbf{G} - \mathbf{q}) \cdot \mathbf{b}_{qs}|^2 + F(|\mathbf{G} + \mathbf{q}|) |(\mathbf{G} + \mathbf{q}) \cdot \mathbf{b}_{qs}|^2 - 2F(|\mathbf{G}|) |\mathbf{G} \cdot \mathbf{b}_{qs}|^2 \right]. \quad (12.29)$$

Since the bare ionic Coulomb potential, $(\zeta e)^2/4\pi\epsilon_0|\mathbf{r}_\ell - \mathbf{r}'_\ell|$ can be written as $\sum_{\mathbf{k}} (4\pi\epsilon^2\zeta^2/4\pi\epsilon_0Vk^2) \exp[-i\mathbf{k} \cdot (\mathbf{r}_\ell - \mathbf{r}'_\ell)]$, we can obtain $\delta U_{\text{Coulomb},qs}$ immediately by replacing in (12.28) $F(k)$ by $N_a^2 2\pi e^2 \zeta^2/4\pi\epsilon_0Vk^2$. Having the energy difference $\delta U_{qs} = \delta U_{\text{ind},qs} + \delta U_{\text{Coulomb},qs}$ due to the displacements $\{\mathbf{u}_{\ell,qs}\}$ associated with the phonon $\mathbf{q}, s$, the next step is to calculate the ionic kinetic energy connected with the phonon $\mathbf{q}, s$:

$$E_{K,qs} = \frac{1}{2} m_a \sum_{\ell} \dot{u}_{\ell}^2 = N_a m_a \omega_{qs}^2 |\mathbf{b}_{qs} \cdot \mathbf{b}_{qs}^*|. \quad (12.30)$$

Now we are in a position to obtain the eigenfrequency ω_{qs} of the phonon $\mathbf{q}, s$ exploiting the equality in a harmonic oscillation of the average kinetic energy with the average potential energy:⁵

$$\omega_{qs}^2 = \frac{\delta U_{qs}}{E_{k,qs}/\omega_{qs}^2} = \frac{\delta U_{qs}}{N_a m_a |\mathbf{b}_{qs} \cdot \mathbf{b}_{qs}^*|}, \quad (12.31)$$

where δU_{qs} depends on $|\tilde{v}_i(k)|^2$ and on $\epsilon(k)$ among others. For $|\tilde{v}_i(k)|^2$, we can use the empty-core pseudopotential (see 11.4) and for $\epsilon(k)$ the RPA dielectric function (see (11.12)). In Fig. 12.12 we plot the eigenfrequencies ω_{qs} for potassium, as obtained from (12.31) by Ashcroft [12.1] using the empty core pseudopotential; the corresponding experimental data are also shown.

The agreement between theory and experiment is impressive and it is due to the fact that the pseudopotential in potassium is weak, and hence, whatever errors enter in the empty core pseudopotential are overshadowed by the dominant contribution of the unscreened ion-ion Coulomb potential. It is worthwhile to point out that the present approach based on pseudopotentials, in contrast to the JM, calculates – and calculates correctly – not only the longitudinal phononic branch but also the transverse branches as well. The latter are associated with the $\mathbf{G} \neq 0$ terms in $\delta U_{\text{ind},qs}$ and in $\delta U_{\text{Coulomb},qs}$, while the $\mathbf{G} = 0$ contributes to the longitudinal branch.

⁵ Notice that the average ionic potential energy is equal to the change δU_{qs} of the total energy U due to the qs phonon.

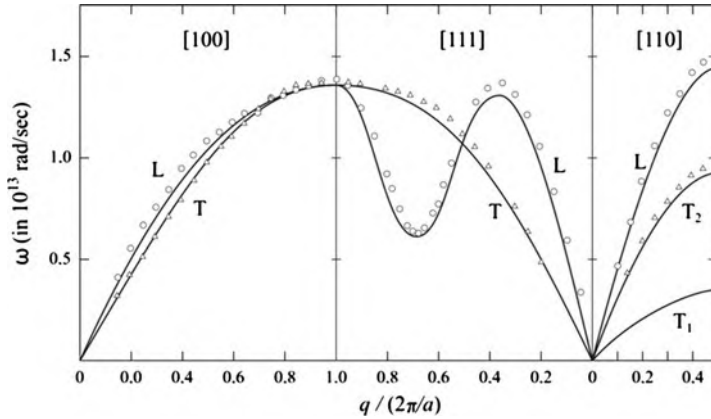


Fig. 12.12. Comparison of the experimental data [12.2] (circles and triangle) for the phononic dispersion relations in potassium with the theoretical results [12.1] (solid lines) based on (12.31) and the empty core pseudopotentials with $r_c = 1.13 \text{ \AA}$

Problem 12.7t. Show that the $\mathbf{G} = 0$ contribution to ω_{qs}^2 is given by

$$\omega_{qs}^2 = \frac{4\pi e^2 \zeta^2 n_a}{4\pi \varepsilon_0 m_a} \left(1 - \frac{\varepsilon(q) - 1}{\varepsilon(q)} \cos^2 qr_c \right), \quad \mathbf{G} = 0. \quad (12.32)$$

Using (12.32) prove that

$$\omega_{qs}^2 \rightarrow c_{\ell 0}^2 q^2 \quad (12.33)$$

where

$$c_{\ell 0}^2 = \frac{4\pi \zeta^2 e^2 n_a}{4\pi \varepsilon_0 m_a k_{\text{TF}}^2} (1 + k_{\text{TF}}^2 r_c^2) \quad (12.34)$$

show that $c_{\ell 0}^2$ as given by (12.34) and for $r_c = 0$ coincides with the Bohm–Staver expression (see (4.60)) obtained within the framework of the JM.

We conclude this section by pointing out that, as a result of the logarithmic singularity of the derivative $d\varepsilon/dk$ of the dielectric function at $k = 2k_F$, the quantity $dF(k)/dk$, as given by (12.18), will exhibit the same singularity, which in turn will be transferred to the derivative $d\omega_{ks}/dk$ for $|\mathbf{k} \pm \mathbf{G}| = 2k_F$. These singularities of $d\omega_{ks}/dk$ are known as *Kohn singularities*. Notice that the Kohn's singularities are weak and become weaker for small pseudopotentials. As a result, these singularities have not been observed in alkali metals, while in polyvalent metals and in particular in lead they are detectable and explainable through the pseudopotential approach.

12.7 Scattering by Phonons, Mean Free Path, and the Dimensionless Constant λ in Metals

In Sect. 5.4 of Chap. 5, we calculated the dimensionless el-ph couplings λ and λ_t and we compared their values with the corresponding experimental data in table 5.2. With the exceptions of the alkali metals *Na*, *K*, *Rb*, and *Cs*

and the noble metals *Cu*, *Ag*, and *Au*, we found severe discrepancies between theory and experiment, which reached a factor of ten for lead. It is only natural to examine if these discrepancies will be reduced or even disappear, if we abandon the JM and adopt the periodic pseudopotential approach. The latter modifies both the phonon-scattering mechanism and the electronic eigenfunctions, which from plane waves become Bloch waves. In Chap. 9, Sect. 9.4, we calculated the single-phonon inelastic cross-section⁶ (see (9.92))

Problem 12.8t. In (9.92) make the following approximations:

- (a) Integrate over ε_f to obtain $d\sigma/d\Omega$.
- (b) Set $\mathbf{G} = 0$ and $k_f = k_i = k_F$.
- (c) Omit the Debye–Waller factor, $\exp(-2W)$.
- (d) Take $n_{qs} \gg 1$ so that $n_{qs} + 1 \simeq n_{qs}$.
- (e) Omit the $\cos qr_c$ factor in the pseudopotential.
- (f) Set $\omega_{qs} = cq$, where $c^2 = B/\rho$.

Show then that $1/\ell_t$ and ρ_{ph} as calculated in the framework of the above approximations of (9.92) coincide with the ones obtained in Chap. 5 (5.43)–(5.59).

This verifies that keeping only the $\mathbf{G} = 0$ contribution, we end up with the same result as that of the JM; this is to be expected since the $\mathbf{G} = 0$ term corresponds to a constant potential. Having now the more accurate result (9.92) for the electronic cross-section due to a single phonon, we expect that we can obtain an improved expression for the phonon-due electronic transport mean free path, ℓ_t , the resistivity ρ_{ph} , and the dimensionless el-ph couplings λ , λ_t . The starting point for such a calculation is the following expression for $1/\ell_t$ (recall that $1/\ell_t = n_s \sigma_s = \sigma_s/V$):

$$\frac{1}{\ell_t} = \frac{1}{V} \sum_s \int d\Omega \delta\varepsilon_f \left(\frac{d^2\sigma}{d\Omega d\varepsilon_f} \right) (1 - \cos\theta) \{ [1 - f(\varepsilon_f)] f(\varepsilon_i) \beta d\varepsilon_i \}. \quad (12.35)$$

In (12.35) the angles θ and φ determine the direction of the final electronic wavevector $\mathbf{k}_f$ with respect to the initial one $\mathbf{k}_i$; (recall that $\mathbf{k}_i - \mathbf{k}_f \equiv \mathbf{k} = \pm \mathbf{q} + \mathbf{G}$, where $\mathbf{q}s$ specifies the phonon involved in the scattering and $\mathbf{k}_i$, $\mathbf{k}_f$ lie on the Fermi surface; hence, the angles θ and φ determine both $\mathbf{k}_f$, and $\pm \mathbf{q} + \mathbf{G}$, when $\mathbf{k}_i$ is given). The inelastic differential cross-section $d^2\sigma/d\Omega d\varepsilon_f$ is given by (9.92) and it is proportional to a quantity A , which is defined in (9.91). The last factor in curly brackets in (12.35) takes into account the availability of electrons in the initial energy ε_i (through the Fermi distribution $f(\varepsilon_i)$) and the availability of empty states in the final energy ε_f (through the factor $1 - f(\varepsilon_f)$ according to Pauli's principle).

⁶ The starting point in this calculation was (9.64) which assumes plane waves instead Bloch functions for the electrons.

Problem 12.9t. Show that the integral A_1 over ε_f and ε_i of A (which is defined in (9.91)) times the quantity in curly brackets in (12.35) is equal to

$$\begin{aligned} A_1 &= \sum_{\mathbf{G}} \hbar (1 + n_{qs}) \delta_{\mathbf{q}-\mathbf{k}, \mathbf{G}} \frac{y}{e^y - 1} + \sum_{\mathbf{G}} \hbar n_{qs} \delta_{\mathbf{q}+\mathbf{k}, \mathbf{G}} \frac{y}{1 - e^{-y}} \\ &= \hbar \frac{ye^y}{(e^y - 1)^2} \sum_{\mathbf{G}} [\delta_{\mathbf{q}-\mathbf{k}, \mathbf{G}} + \delta_{\mathbf{q}+\mathbf{k}, \mathbf{G}}], \end{aligned} \quad (12.36)$$

where $y = \beta \hbar \omega_{qs}$ and A is given by (9.91).

For high temperatures, $y \rightarrow 0$, while for $T \rightarrow 0$ $y \rightarrow \infty$.

Combining (12.35), (12.36) and (9.92), we obtain for $1/\ell_t$

$$\frac{1}{\ell_t} = n_a e^{-2W} \times \frac{1}{2m_a} \sum_s \int d\Omega (1 - \cos \theta) \frac{k_f}{k_i \omega_{qs}} |f|^2 |k \cdot \mathbf{w}_{qs}|^2 A_1. \quad (12.37)$$

Taking into account that the scattering amplitude f appearing in (12.37) is given by

$$f = -\frac{m_e}{2\pi \hbar^2 n_a} \tilde{v}(k) = \frac{m_e}{2\pi \hbar^2 n_a} \frac{4\pi \zeta e^2 n_a}{4\pi \varepsilon_0 k^2 \varepsilon(k)} \cos kr_c \quad (12.38)$$

we have

$$\begin{aligned} \frac{1}{\ell_t} &= e^{-2W} \frac{2m_e^2 \zeta^2 e^4 n_a}{(4\pi \varepsilon_0)^2 \hbar^3 m_a} \times \sum_{\mathbf{G}} \sum_s \int d\Omega (1 - \cos \theta) \frac{\cos^2 kr_c}{[k^2 \varepsilon(k)]^2} \\ &\times \frac{ye^y}{(e^y - 1)^2} \frac{1}{\omega_{qs}} \left\{ [(\mathbf{q} - \mathbf{G}) \cdot \mathbf{w}_{qs}]^2 + [(\mathbf{q} + \mathbf{G}) \cdot \mathbf{w}_{qs}]^2 \right\}. \end{aligned} \quad (12.39)$$

For a spherical Fermi surface $k_i = k_f = k_F$.

Problem 12.10t. For very low temperatures ($T \ll \Theta_D$), only very small values of q contribute to $1/\ell_t$. Hence, the equations $\mathbf{k} = \mathbf{q} + \mathbf{G}$ and $\mathbf{k} = -\mathbf{q} + \mathbf{G}$ are satisfied only for $\mathbf{G} = 0$ (Recall that $\mathbf{G} = 0$ processes are called normal). Since both $\mathbf{k}$ and $\mathbf{q}$ are very small, we have $\cos kr_c \rightarrow 1$, $\omega_{qs} = cq = ck$, and the summation over s includes only the LA branch. Taking into account these remarks and (12.39), show that the phonon due resistivity $\rho_{ph} = v_F / \mathbf{e}_0 \omega_{pf}^2 \ell_t$ at very low temperatures is given by (5.63) within the framework of the JM (in G-CGS $\mathbf{e}_0$ must be replaced by $1/4\pi$).

At high temperatures ($T \gtrsim \Theta_D$) all qs contribute; hence, it is not unusual for the vectors $\mathbf{q} - \mathbf{k}$ or $\mathbf{q} + \mathbf{k}$ to be outside the first BZ, which means that there are $\mathbf{G}s$ different than zero (Processes for which $\mathbf{G} \neq 0$ are called Umklapp Processes). $\mathbf{G}s$ different than zero imply that transverse branches (for which $\mathbf{q} \cdot \mathbf{w}_{qs} \simeq 0$) contribute also to $1/\ell_t$, since then the quantities $|(\mathbf{q} \pm \mathbf{G}) \cdot \mathbf{w}_{qs}|^2 \simeq |\mathbf{G} \cdot \mathbf{w}_{qs}|^2$ are not zero in general. We conclude that the value of $1/\ell_t$ will increase substantially, if there are nonzero $\mathbf{G}s$, (i.e., umklapp processes), because, then, several positive terms in addition to the one

corresponding to the JM will contribute to $1/\ell_t$. The increase of $1/\ell_t$ implies the increase of ρ_{ph} and the increase of λ_t and λ in comparison with their JM values. We expect this increase to be small in monovalent metals for two reasons: (a) their pseudopotential is weak; (b) the relation $\mathbf{k} \equiv \mathbf{k}_i - \mathbf{k}_f = -\mathbf{G} \pm \mathbf{q}$ with a nonzero $\mathbf{G}$ is satisfied for fewer electronic initial wavevectors $\mathbf{k}_i$ and for fewer phononic wavevectors $\mathbf{q}$, as the Fermi surface is entirely in the interior of the 1st BZ. In contrast, for polyvalent metals such as lead, $k_F/G_{\min} \simeq 1$. Hence, for polyvalent metals, we expect much higher values of λ_t and λ than those predicted by the JM.

12.8 Key Points

- In one-dimensional systems, degenerate perturbation theory transforms the free-electron parabola $E^{(0)} = \hbar^2 k^2/2m$ to a band structure $E_n(k)$ by opening gaps at $k_n = n\pi/a$ ($n = \pm 1, \pm 2, \dots$). The size of the n th gap E_{gn} equals $2|\tilde{v}(G_n)|$, where $G_n = 2n\pi/a$.
- In the two-dimensional case the first step is to plot the free-electron parabola $E_n^{(0)} = \hbar^2 (k_x^2 + k_y^2)/2m$ in the first BZ as in Fig. 12.3. The resulting intersection points can be n -fold degenerate ($n = 2, 4, \dots$). The next step is to apply degenerate perturbation theory to partially or fully lift the degeneracies through the nonzero matrix elements of the pseudopotential.
- An alternative way of visualizing the band structure in 2D periodic systems is to plot the lines $E_n(\mathbf{k}) = \text{const.}$ For free electrons, these lines are circles; their segments that are in the n th BZ can be transferred to the 1st BZ as the segments of the n th branch. Pseudopotentials modify these segments by lifting degeneracies, smoothing corners, and making the intersections with the boundary of the 1st BZ to occur at right angle.
- Among the lines $E_n(\mathbf{k}) = \text{const.}$ of particular interest is the Fermi line $E_n(\mathbf{k}) = E_F$. Under certain conditions, as the pseudopotential is increasing, the Fermi line can be partly or totally disappear; total disappearance, occurring when the area of occupied states coincides with a polygon bounded by Bragg lines, signals the onset of a gap and a metal-semiconductor transition.
- Harrison's construction is a direct graphical way to determine to which BZ an arbitrarily chosen point $\mathbf{k}$ belongs.
- By employing pseudopotentials, we can find the following correction to the total energy (without the ionic kinetic one) of the JM or RJM

$$E^{(2)} = -\frac{4\pi\epsilon_0 V}{8\pi e^2} \sum_{\mathbf{k} \neq 0} k^2 |\tilde{v}_i(\mathbf{k}) S_{\mathbf{k}}|^2 \left[1 - \frac{1}{\epsilon(k)} \right].$$

- By using this result, we can express the total ground-state energy (without the ionic kinetic energy) as a sum of two parts: the first one depends only on the volume, while the second one depends explicitly on the position of the

ions. By including the phononic displacements of the ions, we can calculate the change in the energy, δU_{qs} due to the displacements associated with any particular phonon qs . Then the eigenfrequency of the phonon qs can be calculated by employing the relation

$$\omega_{qs}^2 = \frac{\delta U_{qs}}{E_{K,qs}/\omega_{qs}^2},$$

where $E_{K,qs}$ is the average kinetic energy of the ionic motion associated with the phonon qs .

- Ionic vibrations change in general the character of the scattering from elastic to inelastic; this is true not only for external particles but also for the solid's mobile electrons. This inelastic electronic scattering reduces the low-temperature electronic mean free path, and hence, the electrical conductivity. The umklapp ($\mathbf{G} \neq 0$) scattering substantially increase the dimensionless el-ph interactions, λ, λ_t , and, hence, the resistivity especially of polyvalent metals.

12.9 Problems

- 12.1. Consider the 1D periodic Kronig–Penney model shown in Fig. 12.13 below. Examine the limiting case $b_1 \rightarrow 0$, $U \rightarrow \infty$, with $Ub_1 \rightarrow \text{const.} = \hbar^2 k_0/m$.

(a) Show that

$$\tilde{v}(\mathbf{G}) \equiv \frac{1}{a} \int_{-b_2}^{b_1} dx V(x) e^{-iGx} = \frac{U}{\pi n} e^{-i\pi n b_1/a} \sin \frac{\pi n b_1}{a}, \quad G = \frac{2\pi n}{a}.$$

- (b) What is the limit of $\tilde{v}(\mathbf{G})$, if $b_1 \rightarrow 0$, $U \rightarrow \infty$ and $Ub_1 \rightarrow \hbar^2 k_0/m$.
 (c) For this limiting case choose the constant $k_0 a = 4$ and use (11.25) to give a rough plot of $E_n(k)$ in the reduced- and the extended-zone scheme. Compare your results with the ones in problem 3.4 and those given in the book by Flügge [Q26] (Figs. 16–18, pp 66–67). Do the gaps tend to disappear as $E \rightarrow \infty$?

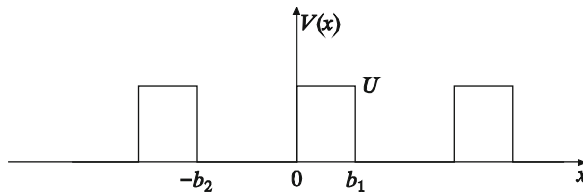


Fig. 12.13. The one-dimensional periodic Kronig–Penney potential. The period is $a = b_1 + b_2$

- 12.2. What is the threshold for optical absorption on the basis of Fig. 12.7 and for one electron per primitive cell? (See [SS75], p. 295).
- 12.3. Find the conditions in terms of the relevant pseudopotentials for the disappearance of the line $E_4(\mathbf{k}) = E_F$ in Fig. 12.9 and the line $E_3(\mathbf{k}) = E_F$ in the same figure.
- 12.4. Consider a 3D weak pseudopotential and obtain the dispersion relation $E(\mathbf{k})$ for $\mathbf{k}$ in the vicinity of a BZ boundary: $\mathbf{k} = \mathbf{G}/2 + \mathbf{k}_\perp + \mathbf{k}_\parallel$, where the normal, $\mathbf{k}_\perp$, and parallel, $\mathbf{k}_\parallel$, to $\mathbf{G}$ components are small in comparison with $\mathbf{G}/2$. Examine the intersection of the Fermi surface $E(\mathbf{k}) = E_F$ with the BZ boundary for various values of E_F .
- 12.5s. Prove (12.24) and (12.25) for the effective ion-ion interaction, $\mathcal{V}_i(d')$.
- 12.6. Justify (12.35).

Further Reading

- C. Kittel [SS74], pp. 223–232. (For Fermi lines or surfaces).
- W. A. Harrison [SS76], pp. 368–373. (For Fermi lines and surfaces) and pp. 384–398. (For Sects. 12.5–12.7).

Part IV

Materials

Simple Metals and Semiconductors Revisited

Summary. Starting from the jellium model(JM) and introducing pseudopotentials, we show how the band structure of monovalent, divalent, trivalent, and tetravalent metals and tetravalent semiconductors is shaped up. For semiconductors, the detailed form of the pseudopotential is given, and the disappearance of the Fermi surface (or equivalently, the opening of the gap) is described; furthermore, their mechanical, magnetic, optical, and transport properties are briefly examined. The band structure of two very important systems, the silicon dioxide and the graphene, is calculated in the framework of the LCAO. Finally, for the developing field of organic semiconductors, a brief outline is given.

13.1 Band Structure and Fermi Surfaces of Simple¹ Metals

13.1.1 Alkali Metals

Alkali metals crystallize by forming usually a bcc lattice with one atom per primitive cell. The reciprocal of a bcc lattice is an fcc with primitive vectors $\mathbf{b}_1 = (2\pi/a)(0, 1, 1)$, $\mathbf{b}_2 = (2\pi/a)(1, 0, 1)$, and $\mathbf{b}_3 = (2\pi/a)(1, 1, 0)$. The first BZ of a bcc lattice with lattice constant a is shown in Fig. 13.1. There are two atoms per cubic *unit* cell; taking into account that $\zeta = 1$, we have that the “free” electron concentration is $2/a^3$, and the Fermi wavenumber, $k_F = (3\pi^2 n)^{1/3}$, is equal to

$$k_F = \left(\frac{6\pi^2}{a^3} \right)^{1/3} \simeq \frac{3.9}{a}. \quad (13.1)$$

The shortest distance of the point Γ from a face of the first BZ is $(\Gamma N) = \sqrt{2}\pi/a \simeq 4.44/a$. Since $k_F < (\Gamma N)$, the Fermi sphere lies entirely in the interior of the first BZ.

¹ As simple elemental metals are classified those which are not transition metals or rare earths, or actinides.

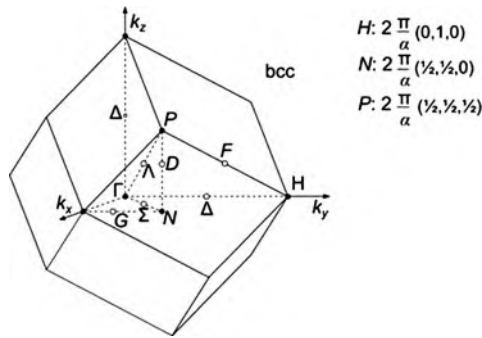


Fig. 13.1. The first BZ of a direct bcc lattice; the lattice constant is a

In Fig. 13.2a, the free electron energy, $E^{(0)}(k) = \hbar^2 k^2 / 2m$, has been plotted in the reduced-zone scheme following the same procedure as in the 2-D case (see Sect. 11.5.2.1). In Fig. 13.2b, the band structure of Na is plotted. The first comment has to do with the similarity of (a) and (b). On second thought, this is not surprising, since it must be clear by now that valence electrons in alkalis behave as being almost free. Coming to the differences, we note the partial (or total) lift of degeneracies in Na. Let us concentrate at the low energy points at N, P, and H: N is doubly degenerate (it is associated with $\mathbf{k}_{\pm} = \pm(\pi/a)(1, 1, 0)$); P is fourfold degenerate (the other three equivalent points are obtained by adding to the vector $\mathbf{\Gamma P}$ the following $\mathbf{G}$ s: $(\bar{1}, \bar{1}, 0)$, $(0, \bar{1}, \bar{1})$, and $(\bar{1}, 0, \bar{1})$ in units of $2\pi/a$); H is sixfold degenerate ($\mathbf{\Gamma H}$, $\mathbf{\Gamma H} + \mathbf{G}_i$, $i = 1, 2, \dots, 5$ where $\mathbf{G}_{1,2} = (2\pi/a)(\pm 1, \bar{1}, 0)$, $\mathbf{G}_{3,4} = (2\pi/a)(0, \bar{1}, \pm 1)$, and $\mathbf{G}_5 = (2\pi/a)(0, \bar{2}, 0)$).

Problem 13.1t. Reproduce the lowest branches of Fig. 13.2a along the segments ΓH , HP , PF , ΓN , NH where $\mathbf{k}$ is given respectively by $(0, x, 0)$, $(x/2, 1 - x/2, x/2)$, $(x/2, x/2, x/2)$, $(x/2, x/2, 0)$, $((1 - x)/2, (1 + x)/2, 0)$ (in units of $2\pi/a$ and with $0 \leq x \leq 1$). Show that $HP = \sqrt{3}\pi/a$ and $HN = \sqrt{2}\pi/a$. Reproduce some of the higher branches of Fig. 13.2a by adding to these values of $\mathbf{k}$, vectors of the reciprocal lattice $\mathbf{G} = n_1\mathbf{b}_1 + n_2\mathbf{b}_2 + n_3\mathbf{b}_3$ ($\mathbf{k} \rightarrow \mathbf{k}' = \mathbf{k} + \mathbf{G}$) and substituting the resulting values of $\mathbf{k}'$ in the $E^{(0)} = \hbar^2 k'^2 / 2m$.

Problem 13.2ts. Diagonalize the 2×2 , the 4×4 , and the 6×6 matrices at the point N, P, H, respectively. Employ the empty-core pseudopotential form factor. Take advantage of the high symmetry of the 4×4 and the 6×6 matrices in order to obtain analytical results for the eigenvalues. Compare the results with the corresponding results shown in Fig. 13.2b or the results in Papaconstantopoulos' book [SS81] (p. 36, and 38).

There are a few other points worth mentioning: (a) Several degeneracies have not been lifted at all. This happens because the corresponding matrix element of the perturbation is exactly zero as a result of the different symmetry properties of the two unperturbed eigenfunctions involved in the evaluation of the

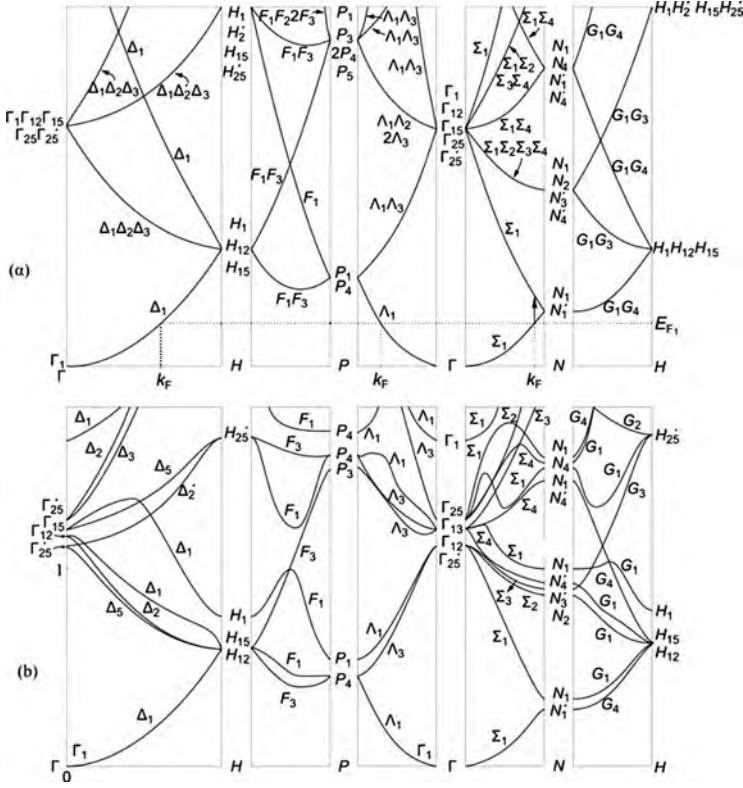


Fig. 13.2. (a) The free-electron parabola $E^{(0)} = \hbar^2 k^2 / 2m$ plotted in the reduced zone scheme of a bcc lattice. (b) The band structure of sodium (Na) (after Burns [SS77], p. 303). The dotted horizontal line denoted by E_{F1} marks the position of the Fermi level for one electron per primitive cell. Notice the impressive similarity between (a) and (b) indicating that the valence electrons in *Na* are almost free

matrix elements. (b) The local maxima and minima of $E_n(\mathbf{k})$ appear not only at the end points for the segments ΓH , HP , PT , ΓN , and NH but also at the internal points. (c) From the intersections of the Fermi line with the various branches of $E_n(\mathbf{k})$, we can determine the threshold of optical absorption (see arrow at k_F in the segment ΓN of Fig. 13.2a).

The Fermi surface of alkali metals is expected to be almost spherical with small bulges in the direction ΓN (and its equivalent) and small depressions in the ΓH directions. Using the empty-core pseudopotential, the deviation from sphericity of the Fermi surface is estimated to be of the order of 3%. In the book by Ashcroft and Mermin [SS75], where more information about monovalent metals is provided (pp. 284–297), it is mentioned that for Cs the deviation from sphericity is roughly 5% while for K and Na it is smaller.

We shall conclude this section by making some comments regarding the Fermi surface of the *noble metals*, which although of nominal valence $\zeta = 1$, as in the alkalis, have a more complicated band structure due to the influence of the d electrons. In Fig. 10.8, we have plotted the Fermi surface of Ag. The analog of the small bulges appearing in alkali metals are necks in noble metals; these necks touch the hexagonal faces of the first BZ of the fcc direct lattice giving rise to new qualitative phenomena such as open trajectories and magnetoresistance, hole-like closed trajectories, new periods in the de Haas–van Alphen effect, etc.

13.1.2 Alkaline Earths: Be, Mg, Ca, Sr, Ba, and Ra

Be and Mg crystallize in close-packed hexagonal structure (hcp), while Ca and Sr in fcc; Ba forms a bcc lattice. In this section, we shall examine the Ca elemental solid as a representative of alkaline earths.

In Fig. 12.3, we compare the free-electron E with $\mathbf{k}$ in the reduced-zone scheme for fcc lattice (and $\zeta = 2$) with the band structure $E_n(\mathbf{k})$ for Ca. To reproduce the plot of Fig. 13.3a, take into account the following: The basic vectors of the reciprocal lattice of fcc are $\mathbf{b}_1 = (2\pi/a)(\bar{1}, 1, 1)$, $\mathbf{b}_2 = (2\pi/a)(1, \bar{1}, 1)$, and $\mathbf{b}_3 = (2\pi/a)(1, 1, \bar{1})$. The points in the inset of Fig. 13.3a have the following coordinates (in units of $2\pi/a$): $L(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, $X(0, 1, 0)$, $K(\frac{3}{4}, \frac{3}{4}, 0)$, $W(\frac{1}{2}, 1, 0)$ and $U(\frac{1}{4}, 1, \frac{1}{4})$ (see Fig. 3.20). The radius, k_F , of the unperturbed Fermi sphere is equal to $(3\pi^2 8/a^3)^{1/3} = (24\pi^2)^{1/3}/a \simeq 6.19/a$; k_F is larger than the minimum distance, $(\Gamma L) = \sqrt{3}\pi/a \simeq 5.44/a$. The volume, $(4\pi/3)k_F^3 = 32\pi^3/a^3$, of the Fermi sphere is equal to the volume, V_{BZ} , of the first BZ, $V_{\text{BZ}} = (2\pi)^3/(a^3/4) = 32\pi^3/a^3$. Thus, alkaline earths had the possibility of becoming semiconductors if the periodic pseudopotential were strong enough. Actually, this does not happen, although we are close to the metal–semiconductor transition especially for Be, which is a semi-metal with very low DOS at the Fermi level $\rho_F/\rho_F^{(0)} = 3.5\%$ for Be, where $\rho_F^{(0)}$ is the free electron DOS at the unperturbed E_F . More information on the divalent metals (including Zn, Cd, and Hg) is given in the book by Papaconstantopoulos [SS81] and the book by Ashcroft and Mermin [SS75], pp. 298–300; in the latter, the Fermi surface of Be as determined experimentally is plotted (p. 300) together with the unperturbed Fermi sphere in the reduced-zone scheme in order to show how the pseudopotential shrinks the unperturbed surface to produce the actual one.

13.1.3 Trivalent Metals

Among those only Al is simple. Boron, in spite of expectations, is a semiconductor and not a metal;² the crystal structure of Ga is complicated (complex

² Already the diatomic molecule B_2 is special: in contrast to other diatomic molecules it is not of σ character (the reason is essentially the occupation of

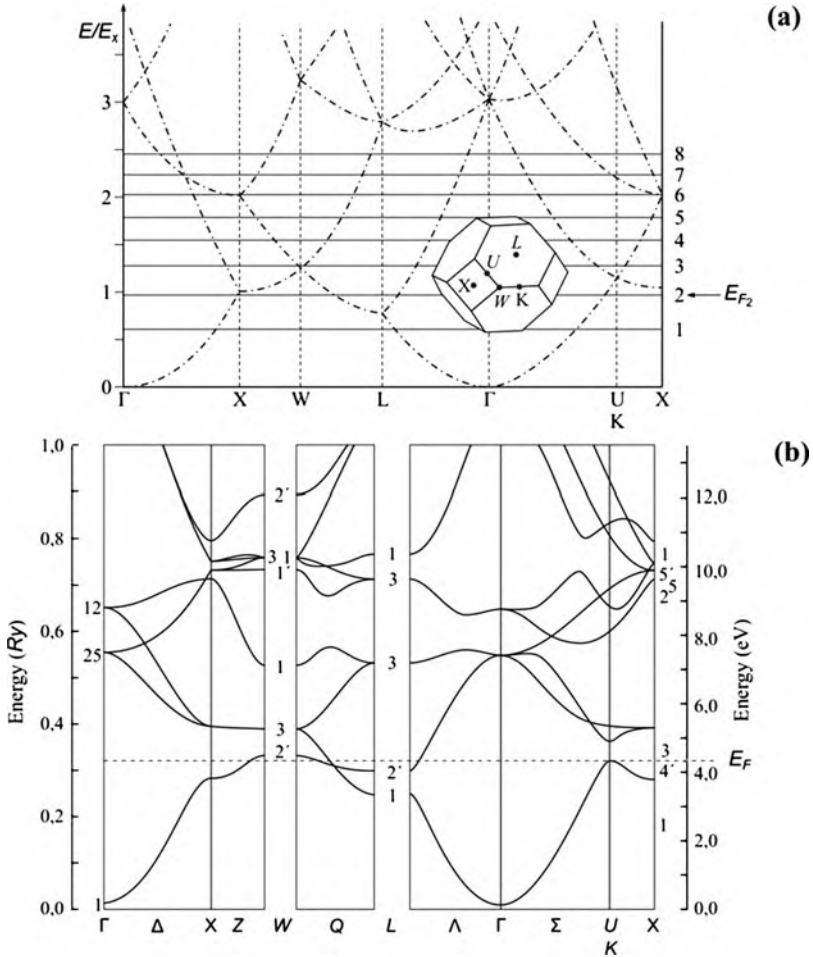


Fig. 13.3. (a) The free-electron energy $E^{(0)}(k) = \hbar^2 k^2 / 2m$ plotted in the first BZ (insert) of a fcc lattice; E_{F_2} denotes the position of the Fermi level for two electrons per atom. (b) The band structure of the fcc Ca (taken from the book by Papaconstantopoulos, [SS81], p. 64). Notice the similarities and the differences between (a) and (b) especially around the point X with energy $E_X = 2\pi^2 \hbar^2 / ma^2$

orthorhombic), while that of In can be viewed as a distorted fcc. Finally, Tl crystallizes in hcp. The Fermi wavenumber, k_F , of Al (taking into account its fcc structure and its valence $\zeta = 3$) is equal to

$$k_F = \left(3\pi^2 \frac{12}{a^3} \right)^{1/3} = (36\pi^2)^{1/3} / a \simeq 7.08/a. \quad (13.2)$$

the atomic s - and p - orbitals; the other exceptional diatomic molecule, more important in daily life, is molecular oxygen, O_2 .

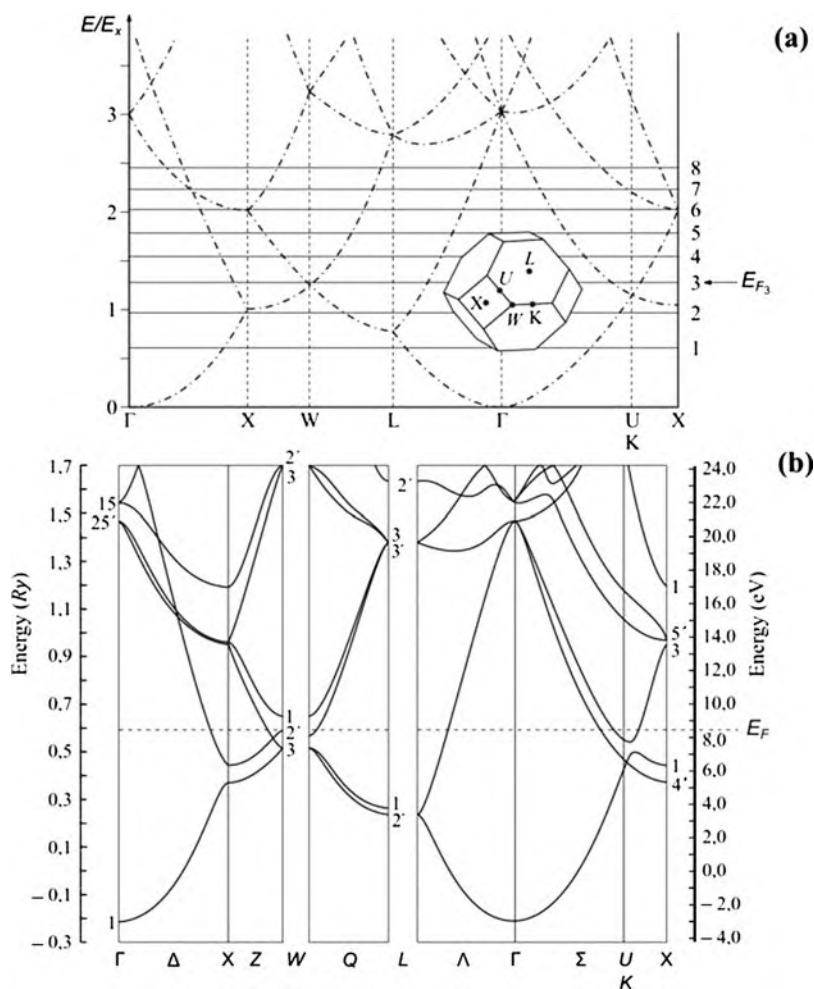


Fig. 13.4. (a) The same plot as in Fig. 13.3a with the Fermi level E_{F_3} corresponding to three electrons per atom. (b) The band structure of Al as given in the book by Papaconstantopoulos [SS81], p. 208

This value is larger than the largest distance, $\Gamma W = 2.236\pi/a \simeq 7.025/a$, in the first BZ. Thus, the Fermi sphere surrounds completely the first BZ. This is clear in Fig. 13.4a where it is shown that the Fermi level for $\zeta = 3$ is slightly above the lowest of the W energies.

Problem 13.3t. Using the empty core pseudopotential, determine the splitting at the lowest X point and compare it with the one shown in Fig. 13.4b.

In Fig. 13.5, the Fermi surface of the unperturbed case (i.e., the Fermi sphere) has been plotted in the reduced-zone scheme for fcc and $\zeta = 3$. Since

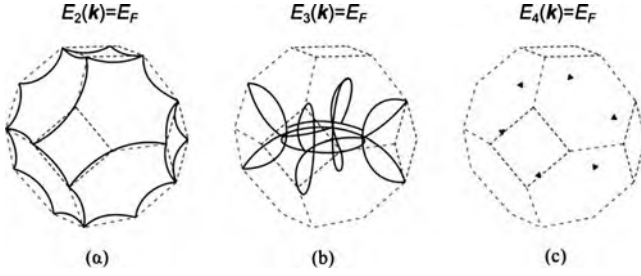


Fig. 13.5. The unperturbed Fermi surface has pieces in the second, in the third, and in the fourth BZs. These pieces in the reduced zone scheme are transferred to the first BZ as shown in (a), (b), and (c) respectively. In the presence of the periodic pseudopotential the tiny pockets in the fourth BZ disappear, and the (a) and (b) pieces are slightly modified as to round off corners. The interior of the closed surface of the second band consists of occupied states

$k_F > (\Gamma W)$, there is no solution to $E_1^{(0)}(\mathbf{k}) = E_F$, and hence, no Fermi surface for the first band.

Let us denote by n_i the number of electrons per atom in the i th band: We have $n_1 = 2$, since the first band is fully occupied. Hence, taking into account that $n_1 + n_2 + n_3 = 3$, we obtain:

$$n_2 + n_3 = 1. \quad (13.3)$$

Since $n_2 + p_2 = 2$, where p_2 is the unoccupied states in the second band, we have

$$p_2 - n_3 = 1. \quad (13.4)$$

There are no open orbits among the unoccupied states in the second band (since they are surrounded by a closed surface in the repeated zone scheme), nor among the occupied states in the third band; hence, the quantity $p_2 - n_3$ would determine the *high field* Hall coefficient, R , according to formula (10.65)

$$R \simeq \frac{1}{e(p_2 - n_3)c} = \frac{3}{enc} > 0, \text{ G-CGS}, \quad (13.5)$$

where $n = n_1 + n_2 + n_3 = 3$. This result agrees with the experiment, in contrast to the JM calculation, which gives a negative value of R and three times smaller in absolute value than that at (13.5). It is an impressive fact that a relatively small splitting of the unperturbed Fermi surface produces such a dramatic change in the Hall coefficient.

The optical absorption of Al exhibits a sharp threshold around $\hbar\omega = 1.5 \text{ eV}$. This is attributed by Ashcroft and Mermin [SS75], pp. 302–303 to vertical electronic transitions between occupied and unoccupied levels, especially the lowest parallel lines in the segment XW of Fig. 13.4b. For this interpretation to be valid, the Fermi level in Fig. 13.4b must be lower than the point 2' so as to make the upper branch of the two at least partly above E_F .

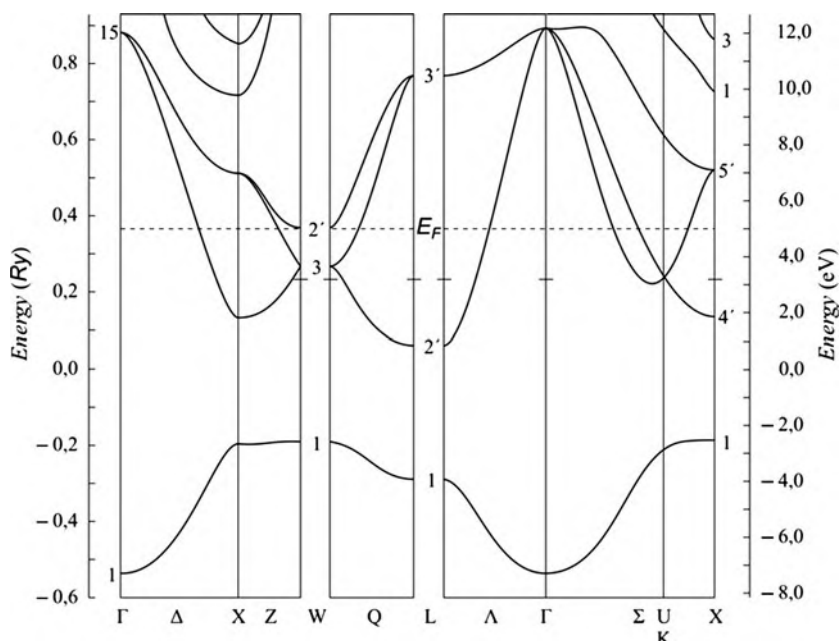


Fig. 13.6. The band structure of lead (Pb) (after Papaconstantopoulos [SS81], p. 224)

13.1.4 Tetravalent Metals

Among the elemental solids of the carbon column only lead (Pb) can be considered as a simple metal. Tin (Sn) is a borderline case, which can be found in tetrahedral zero gap “semiconducting” state (gray tin or α -tin) below 13°C or in a tetragonal metallic state (white tin or β -tin) above 13°C . The elemental solids above Sn (Ge, Si, C) are tetrahedral semiconductors; carbon can be found also as graphite (a semimetal) or as amorphous carbon, as well as in other forms.

In Fig. 13.6, we plot the band structure, $E_n(\mathbf{k})$, of lead (Pb), which forms an fcc lattice. There is a big gap between the lowest branch and the rest of them. Two out of the four electrons per atom reside in this lowest band and the other two partly fill up higher bands up to the Fermi level, E_F .

The LCAO approach allows an easy qualitative interpretation of the band structure shown in Fig. 13.6. The large bond length (due to the large size of the lead atom) makes the hybridized matrix element $|V_{2h}|$ small; this implies a small bonding energy gain unable to compensate for the energy cost of hybridization. Thus, the s state will not be substantially hybridized with the

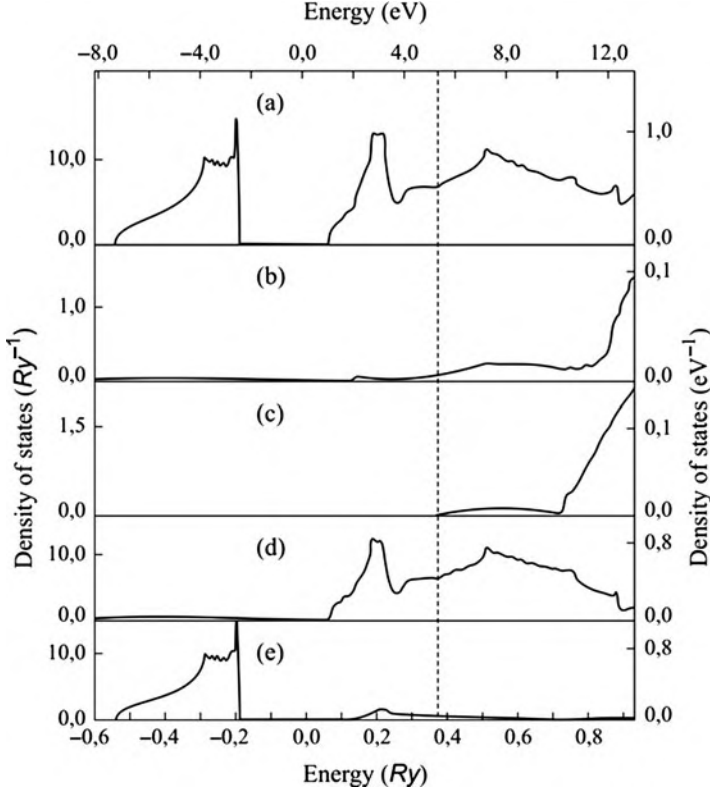


Fig. 13.7. (a) The total DOS per atom for the sum of the two spin orientations for Pb. (b) and (c): The contribution to the total DOS from the two components of different symmetry and of d-character. (Notice the different vertical scale for (b) and (c)) (d): The p contribution to the DOS (e): The s contribution to the DOS. The dashed vertical line denotes the Fermi level (after Papaconstantopoulos [SS81], p. 224)

p s . As a result, a band will be substantially created around the s level.³ This is the lowest band in Fig. 13.6. The other bands above the gap are of p character. This conclusion is verified in Fig. 13.7 where the total DOS has been decomposed into s , p , and d components. The lowest part is practically 100% s -like, while the upper bands are predominantly p -like.

³ Using Harrison's estimate for $V_{ss\sigma} = -1.32 \hbar^2/md^2$, the bandwidth comes out almost three times larger than the one in Fig. 13.6. However, the form of $E_1(\mathbf{k})$ is as expected (See Problem 10.4).

13.2 Band Structure of Semiconductors

We have already seen in Chaps. 6 and 7 that the LCAO method provides a reasonable (although not accurate) description of elemental and compound tetrahedral semiconductors of an average valence of four. In this section, we shall show that the pseudopotential/plane wave method, even in its simplest version, is also capable of accounting for the metal–semiconductor transition occurring as the pseudopotential exceeds a critical value. Thus, we confirm in the case of semiconductors that both LCAO and pseudopotential/plane wave methods offer themselves to the study of solids.⁴

To obtain the metal–semiconductor transitions, the pseudopotential must be strong enough to drive the opening of a gap around the Fermi level, or equivalently, to cause the total disappearance of the Fermi surface, which is, so to speak, replaced by the surface of a polyhedron defined by Bragg planes. In Fig. 13.8a, we replot the free electron parabola $E(k) = \hbar^2 k^2 / 2m$ in the reduced-zone scheme of an fcc lattice in order to be compared with the actual band structure of silicon shown in Fig. 13.8b. For case (a) to be reduced to (b), a large splitting of the degenerate levels at points X' (0, 1, 1), L' (3/2, -1/2, -1/2), and Γ' (1, 1, 1) must take place so that the resulting lower levels are below E_F and the resulting higher levels are above E_F . In addition, the splitting at points X, W, L, and K must be calculated to check whether they agree with the more elaborate calculation shown in Fig. 13.8b. Before we attempt any determination of the splitting at these points, we give the values of the pseudopotential form factor $\tilde{v}(\mathbf{q})$ according to (11.7) and (11.9)

$$\tilde{v}(\mathbf{q}) = \frac{1}{2} [\tilde{v}_1(\mathbf{q}) e^{-i\mathbf{q} \cdot \mathbf{r}_1} + \tilde{v}_2(\mathbf{q}) e^{-i\mathbf{q} \cdot \mathbf{r}_2}], \quad (13.6)$$

where $\tilde{v}_1(\mathbf{q})$ and $\tilde{v}_2(\mathbf{q})$ are the pseudopotential form factors for the atoms 1 and 2, respectively. Obviously, for elemental semiconductors $\tilde{v}_1(\mathbf{q}) = \tilde{v}_2(\mathbf{q}) = \tilde{v}_s(\mathbf{q})$. Equation (13.6) acquires a simpler form if we choose the origin of our fcc lattice to be midway between the positions of the two atoms in the primitive cell. Then $\mathbf{q} \cdot \mathbf{r}_1 = -[q_x + q_y + q_z] a/8$ and $\mathbf{q} \cdot \mathbf{r}_2 = [q_x + q_y + q_z] a/8$. Thus, for elemental semiconductors such as silicon we have

$$\tilde{v}(\mathbf{q}) = \tilde{v}_s(\mathbf{q}) \cos \mathbf{q} \cdot \mathbf{r}_2. \quad (13.7)$$

In Table 13.1, we give the empirical values of $\tilde{v}_s(\mathbf{q})$ for the relevant values of $\mathbf{q}$ for Si and Ge. For comparison, we give also the values of $\tilde{v}_s(\mathbf{q})$ according to the empty-core pseudopotential for Si (see Problem 11.8). In Table 13.2, we give the values of $\cos \mathbf{q} \cdot \mathbf{r}_2$ and $\sin \mathbf{q} \cdot \mathbf{r}_2$ for the relevant values of $\mathbf{q}$. Notice that $\sin(-\mathbf{q} \cdot \mathbf{r}_2) = -\sin \mathbf{q} \cdot \mathbf{r}_2$.

⁴ This is true for atomic concentrations around the equilibrium value. For much higher concentrations, the LCAO approach fails and only the metallic picture is relevant. For much lower concentration, the opposite is true.

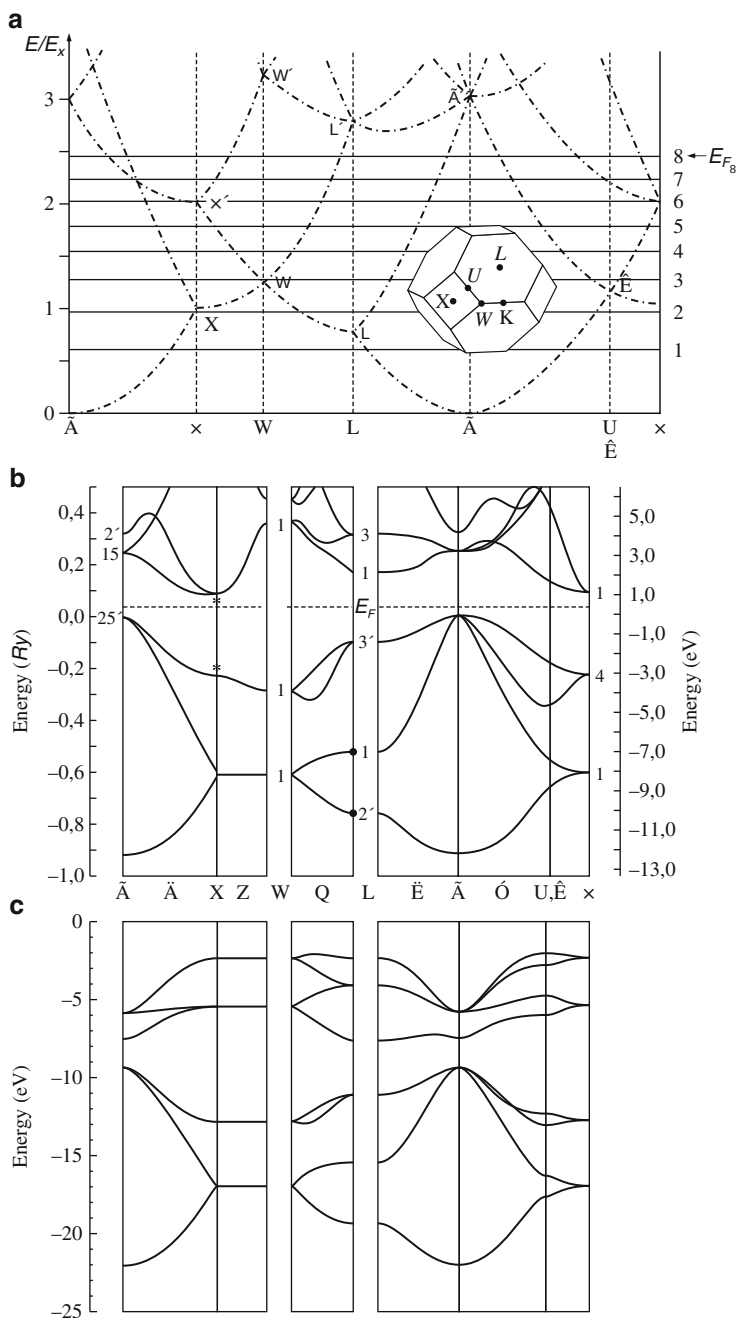


Fig. 13.8. (a) The free electron parabola $E(k) = \hbar^2 k^2 / 2m$ plotted in the reduced zone scheme of an fcc lattice. (b) The band structure, $E_n(\mathbf{k})$, of silicon (Papaconstantopoulos [SS81], p. 234). See, also, Fig. 7.7b. The unperturbed Fermi level E_{F_8} for eight electrons per primitive cell is also shown. Dots and asterisk show the results of the pseudopotential method (see text). (c) The LCAO band structure for Si

Table 13.1. Pseudopotential $\tilde{v}_s(\mathbf{q})$ for Si and Ge. (in eV)

$a\mathbf{q}/2\pi$	1, 1, 1	2, 0, 0	2, 2, 0	3, 1, 1
Si empirical	-2.87	-	0.54	1.1
Si empty core	-1.95	-	0.67	1.2
Ge empirical	-3.66	-	0.52	0.48
Ge empty core	-2.02	-	0.24	0.74

After Yu and Cardona [Se119], p. 63

Table 13.2. Values of $\cos \mathbf{q} \cdot \mathbf{r}_2$ and $\sin \mathbf{q} \cdot \mathbf{r}_2$ for the relevant $\mathbf{q}$'s

$a\mathbf{q}/2\pi$	1, 1, 1	$\bar{1}$, 1, 1	2, 0, 0	2, 2, 0	$\bar{2}$, 2, 0	3, 1, 1	3, $\bar{1}$, $\bar{1}$
$\cos \mathbf{q} \cdot \mathbf{r}_2$	$-\sqrt{2}/2$	$\sqrt{2}/2$	0	-1	1	$-\sqrt{2}/2$	$\sqrt{2}/2$
$\sin \mathbf{q} \cdot \mathbf{r}_2$	$\sqrt{2}/2$	$\sqrt{2}/2$	1	0	0	$-\sqrt{2}/2$	$\sqrt{2}/2$

Table 13.3. Symmetric and antisymmetric empirical pseudopotential form factors for compound semiconductors (in eV)

$a\mathbf{q}/2\pi$	1, 1, 1		2, 0, 0		2, 2, 0		3, 1, 1	
	$\tilde{v}_s$	$\tilde{v}_a$	$\tilde{v}_s$	$\tilde{v}_a$	$\tilde{v}_s$		$\tilde{v}_s$	$\tilde{v}_a$
GaAs	-3.43	0.92	-	0.90	0	-	1.09	0.16
GaP	-3.37	1.1	-	0.75	0.23	-	1.13	0.041
InAs	-3.67	1.06	-	0.52	0.27	-	0.56	0.49
InSb	-3.4	0.67	-	0.52	0.14	-	0.60	0.14
ZnSe	-3.13		-	1.63	0.14	-	0.82	0.41
CdTe	-3.33	1.21	-	1.14	-0.204	-	0.99	0.082

Atom 1 has been chosen as the anion (After Yu and Cardona [Se119])

For compound semiconductors, where $\tilde{v}_1(\mathbf{q})$ is different than $\tilde{v}_2(\mathbf{q})$, we define the symmetric and the antisymmetric parts

$$\begin{aligned}\tilde{v}_s(\mathbf{q}) &= [\tilde{v}_1(\mathbf{q}) + \tilde{v}_2(\mathbf{q})] / 2, \\ \tilde{v}_a(\mathbf{q}) &= [\tilde{v}_2(\mathbf{q}) - \tilde{v}_1(\mathbf{q})] / 2,\end{aligned}$$

so that (13.6) becomes

$$\tilde{v}(\mathbf{q}) = \tilde{v}_s(\mathbf{q}) \cos \mathbf{q} \cdot \mathbf{r}_2 - i v_a(\mathbf{q}) \sin \mathbf{q} \cdot \mathbf{r}_2. \tag{13.8}$$

In Table 13.3, we give the values of $\tilde{v}_s(\mathbf{q})$ and $\tilde{v}_a(\mathbf{q})$ for various compound semiconductors of an average valence 4 for the relevant values of $\mathbf{q}$.

Having explicit values for the matrix elements, let us return to the calculation of the split-up energies at the various points shown in Fig. 13.8a. The simplest point to calculate is the L point, which is doubly degenerate. The off-diagonal matrix element corresponds to $a\mathbf{q}/2\pi = 1, 1, 1$ and is

equal to 2 eV for Si according to the empirical value of the pseudopotential form factor (or 1.38 eV according to the empty core approximation). Thus, the splitting at L is about 4 eV, while the actual value is 3 eV, i.e., closer to the value 2.78 eV predicted by the empty-core pseudopotential. The discrepancy is due to our omission of the couplings between the subspace of the two degenerate states at L with the rest of the states. To obtain the splitting at the point X' , we observe that the 12 degenerate points $[\pm(110), \pm(\bar{1}10), \pm(011), \pm(0\bar{1}1), \pm(101), \pm(\bar{1}01)]$ fall into six independent pairs. For each of those pairs, the off-diagonal matrix elements, corresponding to $a\mathbf{q}/2\pi = \bar{2}\bar{2}0$, is equal to -0.54 eV for Si. Thus, the splitting is only 1.08 eV (or 1.34 eV if the empty core value is used): too small to account for the observed value of a little over 4 eV. What went wrong with this result is the fact that there are strong matrix elements connecting two pairs at X' (e.g., the $\pm(110)$ and the $\pm(\bar{1}10)$) with the one pair at X (e.g., the $\pm(001)$). Thus, there is a substantial mixing of these six states. Hence, we must diagonalize at least a 6×6 matrix in order to be more realistic. Using the values from Tables 13.1 and 13.2 and employing the software MATHEMATICA for the calculation of the six eigenenergies, we find three doubly degenerate eigenenergies at -9.76 , at -3.08 , and at 0.12 eV. Thus, the important splitting between points $X4$ and $X1$ (see Fig. 13.8b) around the gap turns to be 3.2 eV, still lower than the actual value of about 4 eV. To calculate the splitting at the point L' , we need to consider at least six degenerate states $[\pm(\frac{3}{2}\frac{1}{2}\frac{1}{2}), \pm(\frac{1}{2}\frac{3}{2}\frac{1}{2}), \pm(\frac{1}{2}\frac{1}{2}\frac{3}{2})]$. By employing MATHEMATICA we can diagonalize the resulting 6×6 matrix. The difference between the eigenvalues around the gap is 4.4 eV as against the observed value of 3.5 eV.

13.3 The Jones Zone and the Disappearance of the Fermi Surface

The metal–semiconductor transition (as a result of a strong pseudopotential) is accompanied by the opening of a gap around the Fermi level, and consequently, the disappearance of the Fermi surface, which is replaced⁵ by the surface of a suitable polyhedron bounded by Bragg planes. This polyhedron for tetrahedral fcc semiconductors is known as the *Jones Zone (JZ)* presented in Fig. 13.9. Since the number of particles is conserved, the number of occupied states (at $T = 0$ K), and hence the volume defined by the Fermi surface, is also conserved as the pseudopotential increases. It follows that the volume of the polyhedron, which “absorbs” the Fermi surface must be the same as the volume of the unperturbed Fermi sphere. The Fermi wavenumber, k_F , is given by

$$k_F = (3\pi^2 n_e)^{1/3} \simeq 9.82/a,$$

⁵ In the sense that the volume of the occupied states (defined by the Fermi surface) is replaced by this polyhedron.

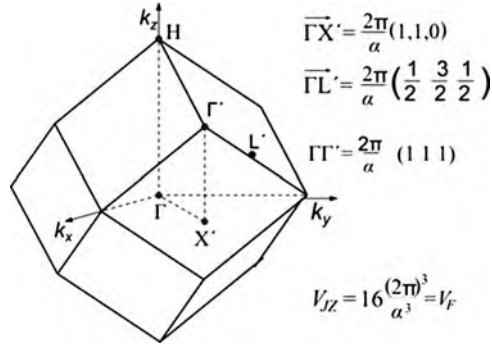


Fig. 13.9. The Jones Zone (JZ) is a rhombic dodecahedron with faces which bisect perpendicularly the following 12 vector of the reciprocal lattice of an fcc: $\pm(220)$, $\pm(022)$, $\pm(202)$, $\pm(\bar{2}20)$, $\pm(0\bar{2}2)$, $\pm(20\bar{2})$ (in units of $2\pi/a$). The JZ is the one which “replaces” the Fermi surface and thus gives rise to the gap in tetrahedral, tetravalent (on the average) semiconductors

where n_e , the electron concentration, in the case of tetravalent semiconductor with eight atoms per unit cell of the fcc lattice, is equal to $32/a^3$. Hence, $k_F = 9.82/a$ and the volume of the Fermi sphere is

$$V_F = \frac{4\pi}{3} k_F^3 = 4\pi^3 n_e = 128\pi^3/a^3. \quad (13.9)$$

The volume of the first BZ of an fcc lattice is equal to $(2\pi)^3$ over the volume of the primitive cell of the direct lattice, which is equal to $a^3/4$. Hence

$$V_{BZ} = 32\pi^3/a^3. \quad (13.10)$$

Since $V_F = 4V_{BZ}$, it follows that the first BZ is not the Jones Zone (JZ) we are looking for, and that points X, W, L, and K on the boundary of the first BZ are in the interior of the JZ. On the other hand, points X', L', and Γ' are expected to be on the boundary of the JZ, since their perturbed energies are on both sides of the gap. Further evidence for this expectation is the sizes of $|\Gamma X'| \simeq 8.88/a$, $|\Gamma L| \simeq 10.42/a$, and $|\Gamma \Gamma'| \simeq 10.88/a$, which imply the inequalities

$$|\Gamma X'| < k_F < |\Gamma L'|, |\Gamma \Gamma'|,$$

and indicate that the unperturbed Fermi sphere intersects the polyhedron on the surface of which points X', L', and Γ' (and their symmetric ones) lie. Let us make the reasonable hypothesis that point X' (and its symmetric ones) is closer to the center Γ than any other point on the boundary of the JZ we are looking for. It follows then that a face of this JZ is normal to the $\Gamma X' \simeq (2\pi/a)(011)$ vector and passes through point X'; there are eleven other such faces of the proposed JZ normal to the following vectors symmetrical to

$(2\pi/a) (011) : [2\pi/a] [(0\bar{1}\bar{1}), \pm(110), \pm(101), \pm(\bar{1}10), \pm(0\bar{1}1), \pm(\bar{1}01)]$. Thus, according to our hypothesis, the proposed JZ is a rhombic dodecahedron identical in shape to the first BZ of a bcc lattice (see Fig. 3.20 in p. 67.) but twice as big in linear dimensions and eight times as big in volume. To confirm our hypothesis, we must check whether the volume of this rhombic dodecahedron is equal to that of the Fermi sphere. Since the volume of the first BZ of an bcc lattice is equal to $(2\pi)^3$ divided by the volume $a^3/2$ of the primitive cell of the bcc lattice, we have for the volume of the proposed JZ the following result: $8 \times (2\pi)^3 / (a^3/2) = 128\pi^3/a^3$, i.e., equal to V_F . Hence, the rhombic dodecahedron shown in Fig. 13.9 is indeed the JZ.

13.4 Mechanical Properties of Semiconductors

We consider tetrahedral semiconductors with N atoms ($2N$ bonds, $N/2$ pairs, $N/2$ primitive cells, and eight electrons per pair). If ζ_a and ζ_c are the valence of the anion and the cation respectively, we have $\zeta_a + \zeta_c = 8$. The cohesive energy E_c per pair is the difference of the initial energy per pair, E_{in} , minus the final energy per pair, E_f , where

$$E_{in} = 2\varepsilon_{sc} + (\zeta_c - 2)\varepsilon_{pc} + 2\varepsilon_{sa} + (\zeta_a - 2)\varepsilon_{pa}, \text{ if } 2 \leq \zeta_c \leq 4, \quad (13.11)$$

$$= \zeta_c\varepsilon_{sc} + 2\varepsilon_{sa} + (\zeta_a - 2)\varepsilon_{pa}, \text{ if } 1 \leq \zeta_c \leq 2, \quad (13.12)$$

and

$$E_f = \frac{2}{(N/2)} \sum_{k,n} E_n(k) + 2E_o. \quad (13.13)$$

The sum is over all $2N$ occupied states of the valence band (four branches times $N/2$ different values of $\mathbf{k}$) and $2E_o$ is the increase of the final energy due to overlap of electronic eigenfunctions and the corresponding rise of the Coulomb repulsion energy. The sum over $\mathbf{k}$ and n can be written as $2N \langle E_n(\mathbf{k}) \rangle$, and the average value $\langle E_n(\mathbf{k}) \rangle$ over the valence band can be approximated by the energy of the bonding molecular orbital E_b . Thus

$$E_f \simeq 8E_b + 2E_o, \quad (13.14)$$

where

$$E_b = (\varepsilon_{hc} + \varepsilon_{ha})/2 - (V_{2h}^2 + V_{3h}^2)^{1/2}, \quad (13.15)$$

$\varepsilon_{hi} = (\varepsilon_{si} + 3\varepsilon_{pi})/4$, $i = c, a$, $V_{2h} \simeq -3.22\hbar^2/md^2$, and $V_{3h} = (\varepsilon_{hc} - \varepsilon_{ha})/2$. For elemental semiconductors, these expressions simplify so that the energies per atom become

$$E_{in} = 2(\varepsilon_s + \varepsilon_p), \quad (13.16)$$

$$E_f \simeq \varepsilon_s + 3\varepsilon_p - 4|V_{2h}| + E_o, \quad (13.17)$$

$$E_c \simeq 4|V_{2h}| - E_o - (\varepsilon_p - \varepsilon_s). \quad (13.18)$$

To proceed further, we need to find the value of E_o . This requires a full calculation as outlined in Sect. 8.4 and in addition some many-body corrections. To avoid this difficult and lengthy procedure, we can use a simple empirical expression for E_o of the form c_n/d^n , where the exponent n must be larger than 2 in order for E_c to have a minimum.

Problem 13.4t. Show that for elemental semiconductors at equilibrium ($\partial E/\partial d = 0$) the quantity c_n/d^n equals $(8/n)|V_{2h}|$. Hence, the cohesive energy per atom is approximately equal to

$$E_c \simeq 4 \frac{n-2}{n} |V_{2h}| - (\varepsilon_p - \varepsilon_s), \quad (13.19)$$

and the bulk modulus (at $T = 0$ K) is

$$B \simeq \frac{\sqrt{3}(n-2)}{3} \frac{|V_{2h}|}{d^3}. \quad (13.20)$$

Problem 13.5t. Choosing $n = 5$, compare E_c and B as given by (13.19) and (13.20), respectively with the corresponding experimental values for diamond, Si, Ge, and α -Sn.

The LCAO approach allows the determination of the other two elastic constants (besides B), which characterize a cubic crystal. The basic idea is to impose a distortion such that the only non-zero elements of the strain tensor are $u_{yy} = \partial u_y/\partial y = \varepsilon$ and $u_{zz} = \partial u_z/\partial z = -\varepsilon$. Then, according to 9.60, the distortion energy per unit volume, Δ/V , is given by

$$\Delta/V = (c_{11} - c_{12}) \varepsilon^2. \quad (13.21)$$

Because of this distortion, the sp^3 hybrid orbitals χ_o^1 and χ_1^1 (see Fig. 7.1) are not anymore on the same straight line, but each of them makes an angle θ with respect to the line that joins the atom (0) with the new position of the atom (1), where $\theta = \sqrt{2/3}\varepsilon$ (in the limit of $\varepsilon \rightarrow 0$). To prove that, take into account that the new position of atom (1) with respect to atom (0) is now $\mathbf{r}_o + \mathbf{u}$, where $\mathbf{u} = (a\varepsilon/4)(0, 1, \bar{1})$ and $\mathbf{r}_o = (a/4)(1, 1, 1)$. As a result of this misalignment, the matrix element V_{2h} will change by δV_{2h} , where

$$\delta V_{2h} = -\lambda V_{2h} \theta^2, \quad (13.22)$$

and $\lambda = 0.855$.

Problem 13.6ts. Prove (13.22). Taking into account (13.15) and (13.22), we obtain that

$$\delta E_b = \frac{\lambda V_{2h}^2 \theta^2}{(V_{2h}^2 + V_{3h}^2)^{1/2}} = \frac{2\lambda}{3} a_c |V_{2h}| \varepsilon^2, \quad (13.23)$$

Table 13.4. Comparison of the values of $c_{11} - c_{12}$ (in 10^{12} dyn/cm²) as obtained by (13.25) with the experimental values

	C	Si	Ge	$\alpha - \text{Sn}$	GaAs	ZnSe	InP
Equation (13.25)	8.34	1.018	0.82	0.418	0.65	0.335 ⁶	0.46
Experiment	9.51	1.018	0.827	0.397	0.652	0.366	0.446

where

$$a_c = \frac{|V_{2h}|}{(V_{2h}^2 + V_{3h}^2)^{1/2}} = \sqrt{1 - a_p^2} \quad (13.24)$$

is the covalency index. According to (13.14) (assuming that E_o does not change as a result of the distortion⁷), the energy per pair increases by $\Delta = 8\delta E_b$. Taking into account (13.23) and that the volume per pair is $a^3/4 = (4d/\sqrt{3})^3/4$, and comparing the resulting Δ/V with (13.21), we obtain that $c_{11} - c_{12} = \sqrt{3}\lambda a_c |V_{2h}|/d^3$. Actually, we expect $c_{11} - c_{12}$ to be smaller than this formula because of the expected decrease of E_o . If we modify this formula for $c_{11} - c_{12}$ by replacing $\sqrt{3}\lambda a_c = 1.48 a_c$ by $1.87 a_c^2$, we obtain good agreement with the experimental data.

$$c_{11} - c_{12} \simeq 1.87 a_c^2 |V_{2h}|/d^3. \quad (13.25)$$

In Table 13.4, we compare the values of $c_{11} - c_{12}$ as obtained by (13.25) with experimental values for several semiconductors.

By introducing a strain tensor such that the only non-zero element is $u_{xy} = \partial u_x / \partial y$, we can obtain the elastic constant, c_{44} , by comparing the general expression for the deformation energy per unit volume $\Delta/V = 2c_{44}u_{xy}$ with the one we shall calculate as before by taking into account the misalignment introduced by the deformation.

As we have mentioned in Chaps. 8 and 9, to obtain the phononic dispersion relations we need the spring constants, which in general cannot be obtained from the elastic constant unless we simplify the general expression 9.63. In the tetrahedral semiconductor, the simplest possible version of 9.39 is as follows:

$$\Delta \simeq \frac{1}{2}C_o \frac{(d' - d)^2}{d^2} + \frac{1}{2}C_1 (\delta\theta)^2. \quad (13.26)$$

Equation (13.26) describes the deformation energy per bond in terms of two spring constants, one, C_o , resisting the change of the bond length and the other, C_1 , resisting the change of the angle between any two bonds connected to the same atom. Obviously, C_o is proportional to the bulk modulus B and C_1 to the difference $c_{11} - c_{12}$.

⁶ Actually, because of the misalignment, we expect that E_o will decrease.

⁷ We have taken the ε_p of Zn as -2.5 eV.

Problem 13.7ts. Show that

$$C_o = \frac{3a^3}{16} (c_{11} + 2c_{12}) = \frac{9a^3}{16} B, \quad (13.27)$$

$$C_1 = \frac{a^3}{32} (c_{11} - c_{12}). \quad (13.28)$$

Furthermore, taking into account (13.26), prove that

$$c_{44} = \frac{32}{a^3} \frac{C_o C_1}{C_o + 8C_1}. \quad (13.29)$$

Problem 13.8t. Show that⁸ the low k longitudinal c_l and transverse c_t sound velocity is given by

$$c_l = \sqrt{c_{11}/\rho}, \quad (13.30)$$

$$c_t = \sqrt{c_{44}/\rho}. \quad (13.31)$$

Problem 13.9t. Taking into account (13.26), show that⁹ the transverse optical frequency, ω_T , in terms of the reduced mass m_a and for $k = 0$ is given by

$$\omega_T^2 = \frac{4}{3m_a d^2} (C_o + 8C_1). \quad (13.32)$$

13.5 Magnetic Susceptibility of Semiconductors

The magnetic susceptibility of tetrahedral semiconductors has in general three contributions coming from the core electrons, the valence electrons, and the free carriers (holes in the VB or electrons in the CB), if any. Thus,

$$\chi = \chi_c + \chi_v + \chi_f. \quad (13.33)$$

The core contribution, χ_c , is of the Larmor (or Langevin) type (see Sect. 5.5.3), since the electrons of the core form completely filled shells:

$$\chi_c = -\frac{e^2 n_c}{6m_e c^2} (Z_c^* \langle r_c^2 \rangle + Z_a^* \langle r_a^2 \rangle), \text{ G-CGS}^{10}, \quad (13.34)$$

where n_c is the concentration of cations ($n_c = n_a = 4/a^3$) and Z_j^* ($j = c, a$) is the number of electrons in the highest fully filled shell of cation or anion ($Z_j^* = 2, 8, 10, 10$ for the C, Si, Ge, and Sn row respectively). For the averages $\langle r_c^2 \rangle$ and $\langle r_a^2 \rangle$, we shall assume that $\langle r_j^2 \rangle = c_1^2 R_j^2$, where R_j ($j = c, a$) is the

⁸ See Harrison [SS76], 195–200.

⁹ See Harrison [SS76], 203–210.

¹⁰ In SI replace c^{-2} by μ_o .

radius of the highest fully filled shell and c_1 is a numerical factor close to unity. Thus,

$$\chi_c = -1.524c_1^2 (Z_c^* R_c^2 + Z_a^* R_a^2) \times 10^{-6}/d^3, \text{ G-CGS}, \quad (13.35)$$

In (13.35), R_c , R_a , and d are in Å. For GaAs, where $d = 2.45$ Å, $R_c = 0.62$ Å, $R_a = 0.46$ Å, and $Z_c^* = Z_a^* = 10$, (13.35) gives $\chi_{c,\text{G-CGS}} = -0.618 c_1^2 \times 10^{-6}$, while the experimental value is -0.51×10^{-6} ; the value of c_1 needed to establish agreement with experiment is $c_1 = 0.908$ for GaAs.

The valence band contribution, χ_v , as was mentioned in Problem 5.8, has two subcontributions, one is diamagnetic of the Larmor (or Langevin) type and the other is paramagnetic of the van Vleck type. In the present case, the role of atoms is played by the bonds. Thus,

$$\chi_v = \chi_L + \chi_{vV}, \quad (13.36)$$

where

$$\chi_L = -\frac{e^2 n_b Z^*}{6mc^2} \langle b | r^2 | b \rangle = -\frac{3.05c_2^2}{d} \times 10^{-6}, \text{ G-CGS}^{10}. \quad (13.37)$$

In (13.37), $n_b = 16/a^3 = 3\sqrt{3}/4d^3$ is the concentration of bonds, $Z^* = 2$, and $\langle b | r^2 | b \rangle = c_2^2 d^2/4$, where c_2 is a numerical factor of the order of one. In the last relation of (13.37), d is in Å. (Remember that $\chi_{L,SI} = 4\pi\chi_{L,\text{G-CGS}}$). The van Vleck contribution, according to Problem 5.8, is given by the following expression

$$\chi_{vV} = 2 \times 2n_b \mu_B^2 \sum_j |\langle a_j | \ell_z | b_i \rangle|^2 / (E_c - E_v), \text{ G-CGS}^{11}, \quad (13.38)$$

where the extra factor 2 was introduced, because there are two electrons per bond, $\mu_B = e\hbar/2m_e c$ (in G-CGS), and $E_C - E_V \simeq 2 [V_{2h}^2 + V_{3h}^2]^{1/2}$ is the typical energy separation between the centers of the VB and the CB. The matrix element of the orbital angular momentum (with respect to the center of the bond) between bonding state, b_i , in the VB and antibonding, a_j , in the CB sharing the same atom (n), can be expressed in terms of the two hybrids of this atom as follows: $\langle a_j | \ell_z | b_i \rangle \simeq a_c \langle h_n^{(1)} | \ell_z | h_n^{(2)} \rangle / 2 \simeq c_3 a_c / 2$, where c_3 is a numerical factor of the order of one and $a_c = \sqrt{1 - a_p^2} = |V_{2h}| / \sqrt{V_{2h}^2 + V_{3h}^2}$. Substituting these in (13.38), we obtain finally

$$\chi_{vV} = \frac{n_b e^2 \hbar^2 c_3^2 a_c^3}{8m^2 c^2 |V_{2h}|} = 1.423 \frac{c_3^2 a_c^3}{d} \times 10^{-6}, \text{ G-CGS}^{10} \quad (13.39)$$

In Table 13.5, we give the numerical values of c_1 , c_2 , and c_3 in order to obtain agreement with the experimental values for χ_c , χ_L , and χ_{vV} for several semiconductors.

¹¹ In SI replace $\mu_{B,\text{G-CGS}}^2$ by $\mu_{B,SI}^2 \mu_o$ (in (13.38)) where $\mu_{B,SI} = e\hbar/2m_e$.

Table 13.5. Values of the dimensionless quantities c_1 , c_2 , and c_3 (for some semiconductors) which make formulas (13.34), (13.37), and (13.39) to coincide with the experimental values of χ_c , χ_L , and χ_{vV} respectively

	c_1	c_2	c_3	$\chi = \chi_c + \chi_L + \chi_{vV}$ (G-CGS) (exp)
C	0.89	1.34	1.44	-1.7×10^{-6}
Si	0.78	1.12	1.61	-0.26×10^{-6}
Ge	0.93	1.21	1.8	-0.58×10^{-6}
GaAs	0.91	1.18	1.67	-1.22×10^{-6}
GaP	0.81	1.21	1.68	-1.23×10^{-6}

Notice that $c_2 = c_3/\sqrt{2}$ (with the exception of diamond).

The free carriers (electrons or holes), if any, contribute to the magnetic susceptibility in two ways: through their spin (Pauli paramagnetism, χ_P) and through their quantized motion¹² (Landau diamagnetism, χ_L). In Sect. 5.5.3, we have calculated χ_P for metals (for which only electrons around the Fermi level contribute). We have also stated that $\chi_L = -\chi_P/3$. These relations must be modified for semiconductors, since (a) the free carriers are distributed over a range of energies and (b) their effective mass, m^* , is not the same as m . To obtain χ_P , we shall calculate the magnetization $M = -\mu_B(N_\uparrow - N_\downarrow)/V$, where N_σ ($\sigma = \uparrow, \downarrow$) is the number of electrons with spin σ . According to (C.44), we have

$$N_\sigma = \int_{\varepsilon_{\min}}^{\infty} dE \rho_\sigma(E) f(E) = \int_{\varepsilon_{\min}}^{\infty} \frac{dE \rho_\sigma(E)}{e^{\beta(E-\mu)} + 1}, \quad (13.40)$$

where, from Fig. 5.5, $\rho_\uparrow(E) = \rho(E - \mu_B B)$ and $\rho_\downarrow(E) = \rho(E + \mu_B B)$. Thus,

$$\begin{aligned} M &= \frac{-\mu_B}{V} \int dE f(E) [\rho(E - \mu_B B) - \rho(E + \mu_B B)] \\ &= \frac{2\mu_B^2 B}{V} \int dE f(E) \rho'(E), \end{aligned}$$

The form of the above equations for M is valid for both the G-CGS and the SI systems. Hence, $\chi_P \equiv M/H$ is equal to

$$\chi_P = \frac{2\mu_B^2}{V} \int_{\varepsilon_{\min}}^{\infty} dE f(E) \rho'(E) = -\frac{2\mu_B^2}{V} \int_{\varepsilon_{\min}}^{\infty} dE \rho(E) f'(E), \quad \text{G-CGS.} \quad (13.41)$$

(In SI μ_B^2 must be replaced by $\mu_B^2 \mu_o$). For metals, where $k_B T \ll E_F$, $-f'(E) \simeq \delta(E - E_F)$ and (13.41) reduces to (5.109). For non-degenerate semiconductors, for which $f'(E) \simeq -\beta f(E)$, we have that

¹² The existence of holes will slightly modify χ_v

$$\chi_P \simeq \beta \frac{2\mu_B^2}{V} \int_{\varepsilon_{\min}}^{\infty} dE \rho(E) f(E) = \frac{n\mu_B^2}{k_B T}, \text{ G-CGS,} \quad (13.42)$$

where the concentration of electrons (or holes), n , is by definition equal to $2 \int_{\varepsilon_{\min}}^{\infty} dE \rho(E) f(E) / V$. For intrinsic semiconductors the concentration, n , is proportional to $m^{*3/2}$ (see the caption of Fig. 7.6 and 7.73). Thus, in the case of intrinsic nondegenerate semiconductors,¹³ the replacement $m \rightarrow m^*$ would multiply χ_P by $(m^*/m)^{3/2}$; notice that μ_B in (13.42) will remain unchanged under the replacement $m \rightarrow m^*$, since, in calculating χ_P , μ_B appears because of the relation $\mathbf{m} = -2\mu_B \mathbf{s}$, which is an intrinsic property of the electron spin and it does not depend on m^* . On the other hand, in calculating χ_L , only the orbital motion of the electron enters, and as a result, m must be replaced by m^* everywhere, both in $\mu_B^2 = (e\hbar/2mc)^2$ and in ρ , so that $\chi_L(m^*)/\chi_L(m) = (m/m^*)^2 (m^*/m)^{3/2} = (m/m^*)^{1/2}$. Hence, in general

$$\frac{\chi_P}{\chi_L} = -3 \left(\frac{m^*}{m} \right)^2, \quad k_B T \gg \hbar\omega_c, \quad (13.43)$$

13.6 Optical and Transport Properties of Semiconductors

In Fig. 7.5 (p. 190), we have plotted the imaginary part, $\varepsilon_2(\omega)$, of the dielectric function, which is related to the absorption coefficient $\alpha' = \alpha/n_1 = \omega\varepsilon_2/c_1 n_1$; both $\alpha'(\omega)$ and $\varepsilon_2(\omega)$ have a threshold E'_g and two peaks denoted by E_1 and E_2 . These peaks have been attributed to optical transitions between almost parallel branches in the VB and the CB (see Fig. 7.7). For direct gap semiconductors (such as GaAs), the optical gap, E'_g , coincides with the thermodynamic gap, E_g . By calculating the band structure (either by the LCAO method or by the pseudopotential method), we can obtain E'_g , E_1 , and E_2 .

Problem 13.10t. By employing the LCAO method, calculate E_2 for GaAs. *Hint:* Identify E_2 as the difference at $\mathbf{k} = 0$ between the lowest p-character point in the CB and the top of the VB (see Fig. 7.7).

13.6.1 Excitons

During the absorption of a photon of energy $\hbar\omega$ comparable to E_g , an electron-hole pair is created.¹⁴ Since each partner of the pair carries opposite electric charges, there is a Coulomb attraction between the two, which may lead to an electron-hole bound state called *exciton*. An exciton, being a bound state, has a lower energy than the difference between an electron

¹³ For metals also, if the DOS at the Fermi level is free-like with m replaced by m^* , the same factor $(m^*/m)^{3/2}$ would multiply the free-electron result.

¹⁴ A direct-gap semiconductor is assumed.

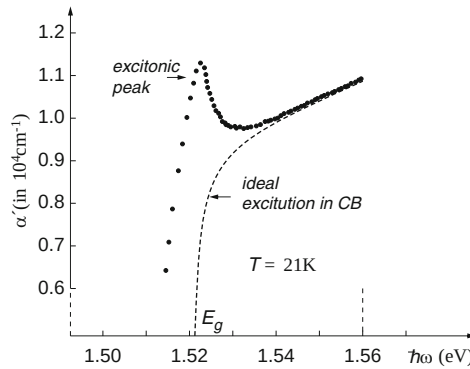


Fig. 13.10. Optical absorption in GaAs for $\hbar\omega \simeq E_g$ and at low temperature

at the bottom¹⁴ of the CB and a hole at the top of the VB, non-interacting with each other. This lowering of the energy would allow a photon with an energy $\hbar\omega = E_g - E_b$ below threshold to create an exciton (E_b is the binding energy of the exciton). The conclusion is that excitons will appear as peaks in the absorption coefficient for $\hbar\omega$ below the VB/CB absorption threshold as shown in Fig. 13.10.

In ionic solids where the electron–hole Coulomb interaction is very strong, the binding energy of the exciton is of the order of 1 eV and the exciton more or less remains in the vicinity of an ion. Thus, to a first rough approximation such excitons may be considered as an internal electronic excitation of a single ion. Such entities are called *Frenkel excitons*.

In semiconductor-excitons, the average electron–hole distance is of the order of tens of Angstroms. Hence, the electron–hole Coulomb interaction is weak and becomes even weaker, because it is screened by a large dielectric constant. Under these circumstances, the exciton, to a first approximation, can be treated as a two-body system interacting through a screened Coulomb interaction. Thus, its Hamiltonian can be brought to the form

$$\hat{H} = -\frac{\hbar^2 \nabla_{\mathbf{R}}^2}{2M^*} + \mathcal{V}(\mathbf{R}) - \frac{\hbar^2 \nabla_{\mathbf{r}}^2}{2m^*} - \frac{e^2}{4\pi\epsilon_0\epsilon r}, \quad (13.44)$$

where $M^* = m_h^* + m_e^*$, $m^* = m_h^* m_e^* / (m_h^* + m_e^*)$, and $\mathcal{V}(\mathbf{R})$ is any weakly varying non-periodic potential experienced by the center of mass of the exciton. Such a potential may be due to defects or foreign atoms (e.g., donors or acceptors) and may trap the center of mass of the exciton around it. In the absence of such a potential, the center of mass $\mathbf{R}$ of exciton moves as a free particle with a kinetic energy $\hbar^2 K^2 / 2M^*$. The relative electron–hole motion, described by the vector $\mathbf{r}$, is clearly hydrogenic and as a result the size and the binding energy of the electron–hole pair are given by the following expressions:

Table 13.6. Values in meV of the electron–hole binding energies for several excitons

Ionic solids (Frenkel excitons)		Extreme cases of ionic solids (Wannier–Mott excitons)		Semiconductors (Wannier–Mott excitons)	
KI	480	AgBr	20	Si	14.3 ^a
KCl	400	AgCl	30	Ge	4.18 ^a
KBr	400	BaO	56	GaAs	4.9 ^a
RbCl	440	–	–	GaP	3.5
LiF	1,000	–	–	CdS	29
				CdSe	15
				InP	5.1 ^a
				InSb	0.4

^aNumbers quoted in the book by Yu and Cardona [Se119]. The rest are those in the book by Kittel [SS74] (6th ed.)

$$\left\langle \frac{1}{r} \right\rangle_n = \frac{1}{a_B} \frac{1}{n^2} \frac{m^*}{em}, \quad n = 1, 2, \dots, \quad (13.45)$$

$$|E_n| = \frac{\hbar^2}{2ma_B^2} \frac{1}{n^2} \frac{m^*}{e^2m}, \quad n = 1, 2, \dots \quad (13.46)$$

Problem 13.11t. Calculate $\langle 1/r^{-1} \rangle$ and $|E_1|$ for GaAs and $n = 1$. Use the light hole mass and $\epsilon(\infty)$.

Answer: $\langle 1/r^{-1} \rangle_1^{-1} = 70 \text{ \AA}$, $|E_1| = 4.24 \text{ meV}$. The quoted experimental value for $|E_1|$ is between 4.14 and 4.9 meV.

The excitons in semiconductors for which their binding energy is much less than 1 eV and their size is much larger than 5 Å are called *Wannier–Mott* (or simply Wannier) *excitons*. In Table 13.6, the values of the electron–hole binding energies for several semiconductor or ionic solid excitons are given.

Excitons may interact with an injected electron in the CB forming a three-body bound state called *trion*. Excitons may interact strongly with photons creating thus a mixed exciton–photon state called (exciton) *polariton*. Furthermore, excitons in Ge or Si may condense to form macroscopic droplets of linear dimensions of up to 0.1 mm. These droplets are in metastable states that can be sustained up to 600 μs under conditions of liquid He temperatures, external radiation, and applied voltage. The condensed excitons lower their total energy relative to that of independent excitons. Within each droplet, excitons break into electrons and holes each of concentration of the order of $2 \times 10^{17} \text{ cm}^{-3}$. For more details, the readers may consult the Kittel book [SS74] book or that by Yu and Cardona [Se119].

13.6.2 Conductivity and Mobility in Semiconductors

Combining (G.7) and (G.14) together with $j_\nu = \sigma_{\nu\mu} E_\mu$, we obtain for the conductivity tensor

$$\sigma_{\nu\mu} = 2e^2 \int \frac{d^3k}{(2\pi)^3} v_\nu v_\mu \tau \left(-\frac{\partial f}{\partial E} \right), \quad (13.47)$$

where $\mathbf{v} = \partial E_n(\mathbf{k}) / \hbar \partial \mathbf{k}$ and $f(E)$ is the equilibrium Fermi distribution. The elementary volume d^3k can be written as $dS dk_\perp = dS dE / |v| \hbar$, where dS is the elementary area of a surface of constant energy and $dk_\perp$ is normal to this surface element; $dk_\perp = dE / |v| \hbar$, since $dE = \hbar \mathbf{v} \cdot d\mathbf{k}_\perp = \hbar v dk_\perp$. Furthermore, in the absence of a magnetic field, because of mirror symmetry, $\sigma_{\nu\mu} = 0$ if $\nu \neq \mu$. Moreover, for a lattice of cubic symmetry, $\sigma_{xx} = \sigma_{yy} = \sigma_{zz} = \sigma$. Hence, by introducing the DOS ρ_V per volume and per spin, we have

$$\sigma(T) = \int dE \tilde{\sigma}(E; T) (-\partial f / \partial E), \quad (13.48)$$

where

$$\tilde{\sigma}(E; T) = \frac{2e^2}{3} \frac{1}{(2\pi)^3} \int \frac{dS}{\hbar v} v^2 \tau \quad (13.49)$$

$$= \frac{e^2}{12\pi^3 \hbar} \int dS \ell \quad (13.50)$$

$$= \frac{2e^2}{3} \rho_V v \ell. \quad (13.51)$$

with $v\ell$ being an average of the product of the velocity v times the mean free path ℓ , averaged over the surface of constant energy E . For a metal, for which $k_B T \ll E_F$, $-\partial f / \partial E = \delta(E - E_F)$. Hence, (13.50) is reduced to (5.34), and (13.51) to (5.35), $v\ell$ being the average of the product of the velocity times the mean free path over the Fermi surface. For semiconductors we have in general contributions from both the electrons in the CB and the holes in the VB. For the CB the Fermi distribution is almost equal to the Boltzmann distribution (assuming that $k_B T \ll E_g - \mu$)

$$f(E) \simeq \exp[-\beta(E - \mu)] = \exp[-\beta(E_g - \mu)] \exp[-\beta(E - E_g)]. \quad (13.52)$$

From (13.52), it follows that $-\partial f / \partial E = \beta f = f / k_B T$. Similarly, for the VB, the Fermi distribution $f(E)$ is almost equal to $1 - \exp[\beta(E - \mu)]$. Thus, again $-\partial f / \partial E = \beta \exp[\beta(E - \mu)]$. Substituting in (13.51) $v\ell$ by $v^2 \tau$, setting $v^2 = 2E' / m_e^*$ and $v^2 = 2E' / m_h^*$ in the CB and the VB respectively where $E' = E - E_g$ for the CB and $E' = -E$ for the VB, we have

$$\sigma_e = \frac{4e^2 \exp[-\beta(E_g - \mu)]}{3m_e^* k_B T} \int_0^\infty dE' e^{-\beta E'} \rho_{Ve}(E') E' \tau_e(E'), \quad (13.53)$$

$$\sigma_h = \frac{4e^2 \exp(-\beta\mu)}{3m_h^* k_B T} \int_0^\infty dE' e^{-\beta E'} \rho_{Vh}(E') E' \tau_h(E'). \quad (13.54)$$

To proceed with the computation of σ , we need the dependence of $\tau(E)$ on E (and on T). Since $\tau = \ell/v \sim \ell/E^{1/2}$, we have on the basis of the results of Sect. 5.4

$$\ell \sim \frac{1}{T} \Rightarrow \tau \sim \frac{1}{TE^{1/2}}, \quad T > \frac{\Theta_D}{5}, \quad (13.55)$$

$$\ell \sim \text{const} \Rightarrow \tau \sim \frac{1}{E^{1/2}}, \quad T \ll \Theta_D/5, \quad (13.56)$$

Moreover, for scattering by electrically charged impurities, we have approximately

$$\tau \sim E^{3/2}, \quad T \ll \Theta_D/5, \quad (13.57)$$

Thus, the temperature dependence of the conductivity for the CB is of the form

$$\sigma_e \sim T^a e^{-\beta(E_g - \mu)}, \quad (13.58)$$

while for the valence band is

$$\sigma_h \sim T^a e^{-\beta\mu}, \quad (13.59)$$

where $a = 0, 1$, and 3 for the three cases (13.55)–(13.57), respectively.

It is instructive to write the conductivity in semiconductors as a product of two terms: one is the equilibrium concentration of carriers (either in the CB or in the VB), which provides the strong exponential temperature dependence; the other characterizes how mobile the carriers are. With this in mind, we define the *microscopic mobility*, $\mu_i(E, T)$, $i = e, h$, by the relation

$$\delta \mathbf{v}_i(E, T) \equiv \mu_i(E, T) \mathbf{E}, \quad i = e, h, \quad (13.60)$$

where E is the electric field inducing an average velocity $\delta \mathbf{v}_i$ to an electron or a hole of energy E when the semiconductors is at temperature T . However, $\delta \mathbf{v}_i/\mathbf{E} = q_i \tau_i/m_i^*$, $i = e, h$, ($q_e = -e$, $q_h = e \equiv |e|$) by the definition of the microscopic relaxation time τ_i . Hence, we have

$$\mu_i(E, T) = \frac{q_i}{m_i^*} \tau_i(E, T), \quad i = e, h, \quad (13.61)$$

According to (13.61), μ_e is negative and μ_h is positive. Rewriting $v\ell$ as $v^2\tau = 2(E/m^*)\tau$ in (13.51) and substituting τ from (13.61), we have¹⁵ [13.1]

¹⁵ It has been proposed (see M.H. Cohen et al, Phys. Rev. B30, 4493 (1984)) that a more general relation between $\tilde{\sigma}$ and μ is as follows: $|e|\rho_V\mu = -\frac{3}{4}\frac{\partial\tilde{\sigma}(E)}{\partial E}$.

Table 13.7. Size of the average mobilities at $T = 300\text{ K}$ in $\text{cm}^2\text{V}^{-1}\text{s}^{-1} = 10^{-4}\text{ m}^2\text{V}^{-1}\text{s}^{-1}$

	C	Si	Ge	AlN	GaAs	InAs	GaSb	PbTe
Electron	2000	1450	3900	–	8000	30000	(Γ point) 3750	2500
Hole	1200	505	1800	14	320	450	680	1000

$$q_i \rho_{V_i}(E) \mu_i(E, T) = \frac{3}{4} \frac{\tilde{\sigma}_i(E; T)}{E}. \quad (13.62)$$

We define also the *average relaxation time*, $\bar{\tau}_i(T)$, and the *average mobility*, $\bar{\mu}_i(T)$, through the relations

$$\bar{\mu}_i(T) \equiv \frac{q_i}{m_i^*} \bar{\tau}_i(T), \quad i = e, h, \quad (13.63)$$

$$\bar{\tau}_i(T) \equiv \frac{m_i^*}{q_i^2 n_i(T)} \sigma_i(T), \quad i = e, h, \quad (13.64)$$

where $n_i(T)$ is the concentration of carriers in the i band

$$n_e(T) = 2 \int_{E_g}^{\infty} dE f(E) \rho_{V_e}(E) \quad (13.65)$$

$$n_h(T) = 2 \int_{-\infty}^0 dE (1 - f(E)) \rho_{V_h}(E). \quad (13.66)$$

Show that $\bar{\tau}_i = \tau_i$ and $\bar{\mu}_i = \mu_i$, if τ_i and μ_i do not depend on the energy E .

From (13.63) and (13.64), we obtain the following relation:

$$\sigma_i(T) = q_i n_i(T) \bar{\mu}_i(T), \quad i = e, h, \quad (13.67)$$

Equation (13.67) clearly distinguishes between the two factors that determine the conductivity $\sigma(T) = \sigma_e(T) + \sigma_h(T)$ in semiconductors: the concentration of carriers and mobility of carriers. In Table 13.7, the average mobilities of some semiconductors are given.

Problem 13.12t. Estimate the value of the average electron mobility in Si at $T = 300\text{ K}$.

Hint: Use the result of Sect. 5.4 to estimate the average mean free path and take $v = (2k_B T / m^*)^{1/2}$.

Problem 13.13t. Calculate the magnetoresistance and the Hall coefficient, starting from Shockley's tube-integral formula and employing the following simplifications:

$$E_i(k) = \frac{1}{2} m_i^* v^2 = \frac{\hbar^2 k^2}{2m_i^*}, \quad i = e, h, \text{ and } \tau_i \text{ independent of } \mathbf{k}.$$

Hint: $v_x(\phi') = v \sin \theta \cos \phi'$, $v_y(\phi' + \phi) = v \sin \theta \sin(\phi + \phi')$, where θ is the angle of the wavevector $\mathbf{k}$ with the z-axis; the latter coincides with the direction of the magnetic field $\mathbf{B}$.

The results for the magnetoconductivity tensor according to (5.83), (13.63), and (13.67) and taking into account both the CB and VB are

$$\sigma_{xx} = \sigma_{yy} = \frac{e_h \mu_h n_h}{1 + (\mu_h B/c)^2} + \frac{|e_e \mu_e| n_e}{1 + (\mu_e B/c)^2}, \quad \text{G-CGS}, \quad (13.68)$$

$$\sigma_{xy} = -\sigma_{yx} = \frac{eB}{c} \left[\frac{\mu_h^2 n_h}{1 + (\mu_h B/c)^2} - \frac{\mu_e^2 n_e}{1 + (\mu_e B/c)^2} \right], \quad \text{G-CGS}, \quad (13.69)$$

In SI, delete c . These formulae are based on the assumption of an isotropic effective mass and independence of the microscopic relaxation time (or equivalently of the microscopic mobility) on E . In reality, both μ and τ are functions of E : $\mu = \mu(E, T)$ and $\tau = \tau(E, T)$. Thus, μ 's that enter in (13.68) and (13.69) must be replaced by $c_{ia} \bar{\mu}_i(T)$, $i = e, h$, where c_{ia} are numerical factors different for the numerator and the denominator and different for σ_{xx} and σ_{xy} . For weak field B , where the denominator can be replaced by one, μ_i in (13.68) must be replaced by $\bar{\mu}_i(T)$ as defined by (13.63) and (13.64), while μ_i^2 in (13.69) must be replaced by $\tilde{\mu}_i^2 = r_{Hi} \bar{\mu}_i^2$, where $r_{Hi} = \langle \tau_i^2 \rangle / \langle \tau_i \rangle^2 > 1$. The off-diagonal element of the resistivity tensor ρ_{yx} is given in terms of σ_{xx} and σ_{xy} :

$$\rho_{yx} = \frac{\sigma_{xy}}{\sigma_{xx}^2 + \sigma_{xy}^2}. \quad (13.70)$$

Hence, the Hall coefficient, $R \equiv \rho_{yx}/B$, is given as follows in the limits of weak field and strong field:

$$R \simeq -\frac{r_{He}}{ec} \frac{n_e - n_h b^2 x}{(n_e + n_h b)^2}, \quad \bar{\mu}_i B/c \ll 1, \quad \text{G-CGS}, \quad (13.71)$$

$$R \simeq -\frac{1}{ec(n_e - n_h)}, \quad \bar{\mu}_i B/c \gg 1, \quad \text{G-CGS}, \quad (13.72)$$

where $b \equiv \bar{\mu}_h/|\bar{\mu}_e|$ and $x = r_{Hh}/r_{He}$. Notice that (13.72) is identical to (10.65). In (13.68)–(13.72), c must be replaced by one in order to obtain the corresponding formulae in SI. To conclude this section, we mention that we define also the Hall mobility, μ_H , in the case of weak field by the relation

$$\mu_H \equiv cR\sigma_{xx} = \frac{n_h \tilde{\mu}_h^2 - n_e \tilde{\mu}_e^2}{n_h \bar{\mu}_h + n_e |\bar{\mu}_e|}, \quad (13.73)$$

or

$$\mu_H = \frac{r_{Hh} \bar{\mu}_h - y r_{He} |\bar{\mu}_e|}{1 + y}, \quad (13.74)$$

where $y = n_e |\bar{\mu}_e| / n_h \bar{\mu}_h$.

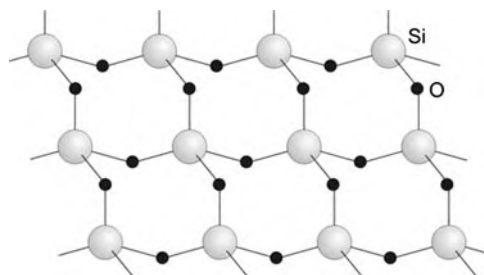


Fig. 13.11. 2-D schematic representation of the structure of SiO_2

13.7 Silicon Dioxide (SiO_2)

Silicon dioxide is a very important compound from many points of view: It is the most abundant compound on the Earth's crust; it is very common in our everyday life as the main component of the common glass; it is very important in the semiconductor industry both as a source of silicon and as the insulating component in the semiconductor devices. It forms also aerogel, the lightest solid composed of 99.9% air and 0.1% SiO_2 with many applications.

To visualize the structure of SiO_2 , consider the tetrahedral structure of Si and introduce one oxygen atom at the middle of each bond. This leads to the 1:2 ratio of Si to O, since at each Si atom correspond two bonds. The oxygen introduction increases substantially the nearest neighbor Si – Si distance from 2.35 Å to 3.06 Å, while the nearest neighbor O – Si distance is 1.61 Å $>$ (3.06/2) Å. It follows from the last relation that the angle Si – O – Si is less than 180° (it is about 144°) and it allows enough structural freedom leading to either crystalline or amorphous states. For example, the crystalline structure of SiO_2 , known as α -quartz, has three Si atoms and six O atoms per primitive cell, while the common glass is amorphous with admixtures of Na_2O and CaO .

In Fig. 13.11, we show a 2-D sketch of the essential structural properties of SiO_2 .

To find the main features of the electronic structure of SiO_2 , we shall employ the LCAO approach to find the molecular levels of the unit $(\frac{1}{4}\text{Si}) - \text{O} - (\frac{1}{4}\text{Si})$ around which the bands will be formed. Since the configuration of the Si atoms is tetrahedral, it is advantageous to use sp^3 hybridization for the four Si atomic orbitals. On the other hand, it does not look promising to employ either the sp^1 or the sp^2 hybridization for oxygen, since the resulting angles of 180° or 120° are not any near the actual angle of 144° , while the energy cost of hybridization is very high given the deep s level of oxygen. As a result, the relevant atomic orbitals describing the coupling of each oxygen with the two neighboring silicon atoms are the p_x and p_y of oxygen and one sp^3 hybrid for each silicon as shown in Fig. 13.12. To proceed with the calculation of the four molecular orbitals of the unit $(\frac{1}{4}\text{Si}) - \text{O} - (\frac{1}{4}\text{Si})$, it

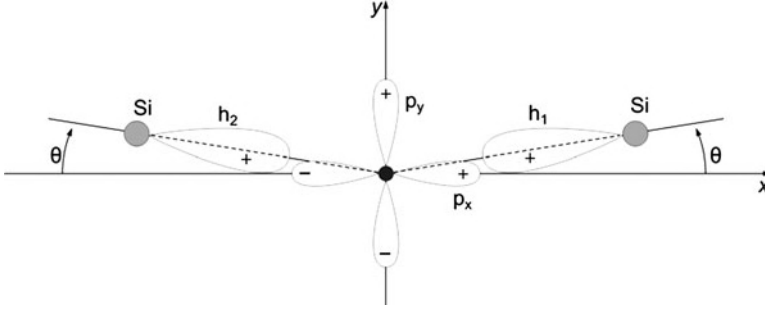


Fig. 13.12. The two orbitals p_x and p_y (each one with two lobes) involved in the bonding of the oxygen atom with the nearest neighbors silicon atoms. The couplings of the fully occupied p_z and s orbitals of oxygen are ignored. The angle θ is equal to 18°

is convenient to take advantage from the very beginning of the symmetry of the configuration shown in Fig. 13.12 by introducing the symmetric and antisymmetric combination of h_1 and h_2 : $h_{\pm} \equiv (h_1 \pm h_2)/\sqrt{2}$. The matrix elements of the Hamiltonian in the basis h_+ , h_- , p_x , p_y are:

$$\langle h_{\pm} | \hat{H} | h_{\pm} \rangle = \varepsilon_h, \quad \langle p_x | \hat{H} | p_x \rangle = \langle p_y | \hat{H} | p_y \rangle = \varepsilon_p, \quad (13.75)$$

$$\langle h_- | \hat{H} | h_+ \rangle = \langle p_x | \hat{H} | p_y \rangle = 0, \quad (13.76)$$

$$\langle h_+ | \hat{H} | p_x \rangle = \langle h_- | \hat{H} | p_y \rangle = 0, \quad (13.77)$$

$$\langle h_+ | \hat{H} | p_y \rangle = \sqrt{2}V_2 \sin \theta, \quad \langle h_- | \hat{H} | p_x \rangle = \sqrt{2}V_2 \cos \theta, \quad (13.78)$$

where $\varepsilon_h = (\varepsilon_{s\text{Si}} + 3\varepsilon_{p\text{Si}})/4 = -9.38 \text{ eV}$, $\varepsilon_p = -16.72 \text{ eV}$, and $V_2 = \frac{1}{2} \left[\langle p_x | \hat{H} | s \rangle - \sqrt{3} \langle p_x | \hat{H} | p_x \rangle \right] = -2.63 \hbar^2 / m d_{\text{SiO}}^2 = -7.73 \text{ eV}$.

It is clear from these values of the matrix elements that the 4×4 Hamiltonian matrix is reduced to two uncoupled 2×2 matrices, the diagonal elements of which are ε_h and ε_p ; the off-diagonal matrix element for one of the two is $\sqrt{2}V_2 \cos \theta$ and for the other is $\sqrt{2}V_2 \sin \theta$. Introducing the numerical values, we obtain for the four molecular eigenenergies of the unit $(\frac{1}{4}\text{Si}) - \text{O} - (\frac{1}{4}\text{Si})$ the following values: $\varepsilon_{x-} = -24.08$, $\varepsilon_{y-} = -18.04$, $\varepsilon_{y+} = -8.06$, and $\varepsilon_{x+} = -2.03$ all in eV. In Fig. 13.13, we compare these values (and the unperturbed atomic levels $\varepsilon_{pz} = \varepsilon_{po}$, ε_{so}) with sophisticated band structure calculations for α -quartz. The correspondence between the calculated molecular levels and the bands is rather satisfactory (with the exception of the ε_{so} level), especially if we take into account the effects of level repulsion. Furthermore, the number of branches in the band structure is equal to the degeneracy of each molecular level for the primitive cell, which contains six times our unit of $(\frac{1}{4}\text{Si}) - \text{O} - (\frac{1}{4}\text{Si})$.

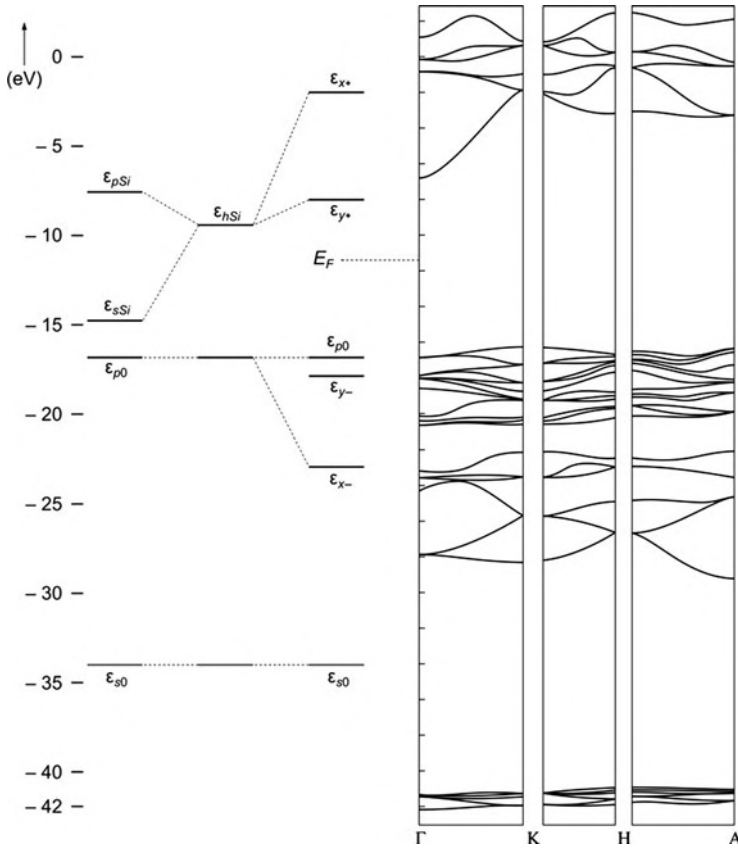


Fig. 13.13. Comparison of the molecular levels of the unit $(\frac{1}{4}\text{Si}) - \text{O} - (\frac{1}{4}\text{Si})$ shown in Fig. 13.12 with the bands of the α -quartz whose primitive cell contains six units of $(\frac{1}{4}\text{Si}) - \text{O} - (\frac{1}{4}\text{Si})$. The correspondence of the levels ε_{p0} , ε_{y-} , ε_{x-} with the relevant bands is rather satisfactory. So is the size of the gap and the position of the Fermi energy

13.8 Graphite and Graphene

Carbon atoms in graphite arrange themselves in planar structures, only one atom thick, called *graphenes*. Graphenes are stacked on top of each other, being held together by weak van der Waals forces. Within each graphene the carbon atoms form a 2-D honeycomb lattice as shown in Fig. 13.14.

It is obvious from the structure of the graphene that the relevant hybridization is sp^2 with the hybrids of atom A given by (F.50)–(F.52). The relevant matrix elements among hybrids of the same atom are given by (F.54) and (F.55), while the big matrix element $\langle \chi_A^1 | \hat{H} | \chi_B^1 \rangle$ is equal to $-3.259\hbar^2/md^2 = -12.3\text{ eV}$. The p_z orbital of each carbon atom is perpendicular to the plane of

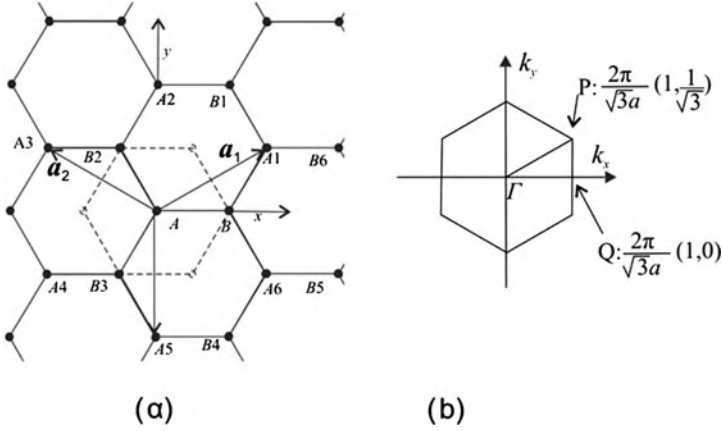


Fig. 13.14. (a) The honeycomb lattice structure formed by carbon atoms within each graphene. The bond length is $d = 1.42 \text{ \AA}$; the primitive vectors are $\mathbf{a}_1 \equiv (3d/2)\mathbf{i} + (\sqrt{3}d/2)\mathbf{j}$ and $\mathbf{a}_2 = -(3d/2)\mathbf{i} + (\sqrt{3}d/2)\mathbf{j}$; $\mathbf{a}_3 = -\mathbf{a}_1 - \mathbf{a}_2$; $|\mathbf{a}_1| = |\mathbf{a}_2| = |\mathbf{a}_3| = a = \sqrt{3}d$; within each W-S cell (dotted hexagon) there are two atoms and three bonds. (b) The first BZ of the honeycomb direct lattice; $P : (2\pi/3d)(1, 1/\sqrt{3})$ and $Q : (2\pi/3d)(1, 0)$ in Cartesian coordinates

the graphene; notice that the coupling of the p_z orbitals is maximized when these orbitals are parallel to each other.

Hence, this coupling favors, as far as the energy is concerned, a perfect planar structure for graphene.

On the basis of the lattice structure of graphene, we expect its band structure to consist of three composite bands as shown in Fig. 13.15: One of them would be built around the bonding molecular level ε_b and it will consist of three branches, fully occupied (since there are three bonds per primitive cell); the second one, half filled, will be built out of p_z orbitals and it will consist of two branches (since there are two atoms per primitive cell); finally, the third one will be built around the antibonding molecular level ε_a in a similar way as the bonding band. We shall make the approximation to treat each of these three bands independently. Let us start with the p_z band; the eigenfunctions are linear combinations of the p_z orbitals:

$$\psi = \sum_{n=-\infty}^{\infty} c_{An} |p_z\rangle_{An} + \sum_{n=-\infty}^{\infty} c_{Bn} |p_z\rangle_{Bn}, \quad (13.79)$$

where, according to Bloch's theorem, the $\{c_{An}\}$ and the $\{c_{Bn}\}$ are connected among themselves:

$$c_{A1} = \exp(i\varphi_1)c_A, \quad c_{A6} = \exp(-i\varphi_2); \quad c_{B2} = c_B \exp(i\varphi_2), \quad c_{B3} = c_B \exp(-i\varphi_1), \quad (13.80)$$

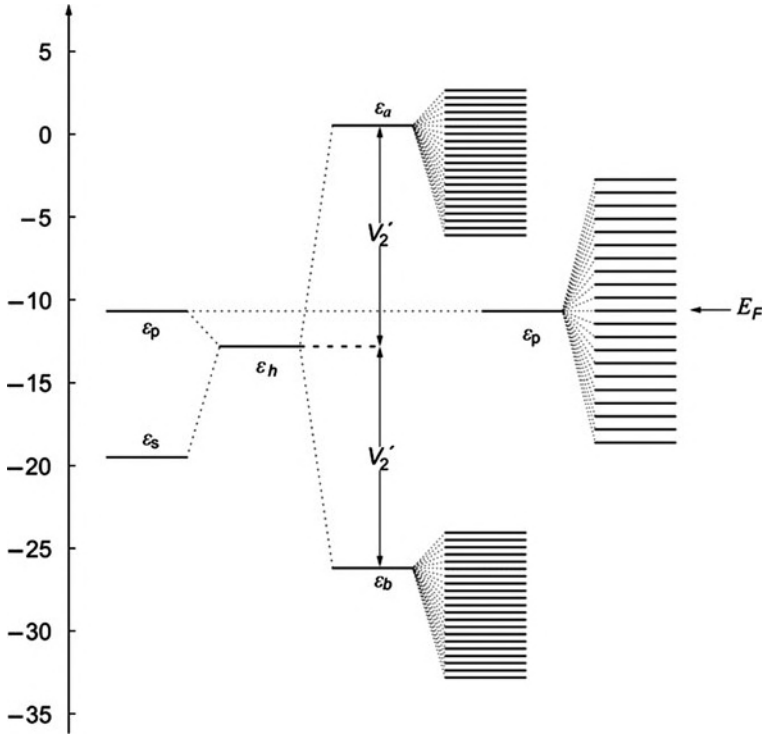


Fig. 13.15. Schematic presentation of the band structure of graphene. The atomic levels ε_s and ε_p of carbon, together with the $sp^2\varepsilon_h$ hybrid level and the bonding ε_b and the antibonding ε_a molecular levels are shown. These levels give rise to the bonding and antibonding bands, while the unhybridized ε_p level develops into the half full p_z band

where $\varphi_1 = \mathbf{k} \cdot \mathbf{a}_1$ and $\varphi_2 = \mathbf{k} \cdot \mathbf{a}_2$. Taking into account (13.79), (13.80), and that there are off-diagonal matrix elements $V \equiv V_{pp\pi}$ only between nearest neighbors, Schrödinger's equation $\hat{H}\psi = E\psi$ becomes

$$\begin{vmatrix} \varepsilon_p & Vf \\ Vf^* & \varepsilon_p \end{vmatrix} \begin{vmatrix} c_A \\ c_B \end{vmatrix} = E \begin{vmatrix} c_A \\ c_B \end{vmatrix}, \quad (13.81)$$

where

$$f = 1 + e^{-i\varphi_1} + e^{i\varphi_2}. \quad (13.82)$$

Problem 13.14t. Calculate the value of f at the point P of the BZ where $\mathbf{k}_P = (2\pi/3d) (1, 1/\sqrt{3})$

Hint: Show that $\varphi_{1P} = 4\pi/3 = (-2\pi/3) + 2\pi$ and $\varphi_{2P} = -2\pi/3$.

Problem 13.15t. Let $\delta\mathbf{k} \equiv \mathbf{k} - \mathbf{k}_P$. Calculate f to first order in the small quantity $\delta\mathbf{k}$ and show that

$$f \simeq \frac{3d}{2} (\delta k_y + i\delta k_x). \quad (13.83)$$

Equation (13.83) can be brought to a more elegant form, if we express the vector $\delta \mathbf{k}$ in a new coordinate system, which is rotated clockwise by 90° with respect to the one shown in Fig. 13.14b; the Cartesian components of $\delta \mathbf{k}$ in the new system are $q_x = -\delta k_y$ and $q_y = \delta k_x$. Then (13.83) becomes

$$f \simeq -\frac{3d}{2} (q_x - iq_y). \quad (13.84)$$

The Hamiltonian matrix appearing in (13.81) can be written in view of (13.84) as follows:

$$H \simeq \begin{pmatrix} \varepsilon_p & 0 \\ 0 & \varepsilon_p \end{pmatrix} + \frac{3}{2} |V| d \begin{pmatrix} 0 & q_x - iq_y \\ q_x + iq_y & 0 \end{pmatrix}, \quad q_x a, \quad q_y a \ll 1. \quad (13.85)$$

Problem 13.16t. Recalling the definition of the Pauli matrices (see 11.61), show that H in (13.85) can be brought to the form:

$$H \simeq \begin{pmatrix} \varepsilon_p & 0 \\ 0 & \varepsilon_p \end{pmatrix} + \frac{3}{2} d |V| \boldsymbol{\sigma} \cdot \mathbf{q}, \quad q a \ll 1. \quad (13.86)$$

From (13.81), it follows that the eigenenergies are

$$E_{\pm} = \varepsilon_p \pm |Vf|. \quad (13.87)$$

The reader is urged to plot $E_{\pm}$ vs. $\mathbf{k}$ as the latter follows the path $\Gamma Q P \Gamma$, especially near the point P of the BZ . There $|\delta \mathbf{k}| \equiv |\mathbf{q}|$ is small, (13.84) is valid, and we have a linear *isotropic* behavior.

$$E_{\pm} = \varepsilon_p \pm \frac{3}{2} |Vd| |\delta \mathbf{k}|. \quad (13.88)$$

The eigenfunctions $\psi_{\pm}$ corresponding to the eigenenergies $E_{\pm}$ are:

$$\psi_+ = \begin{pmatrix} c_A \\ c_B \end{pmatrix}_+ = |A| \begin{vmatrix} q_x - iq_y \\ |\mathbf{q}| \end{vmatrix}; \quad \psi_- = \begin{pmatrix} c_A \\ c_B \end{pmatrix}_- = |A| \begin{vmatrix} -q_x + iq_y \\ |\mathbf{q}| \end{vmatrix}, \quad (13.89)$$

where $|A|$ is a normalization factor. Notice that the state ψ_+ is an eigenstate of the helicity $h \equiv \boldsymbol{\sigma} \cdot \mathbf{q} / |\mathbf{q}|$ with eigenvalue 1, while ψ_- is an eigenstate of the helicity with eigenvalue -1 .

The velocity $\mathbf{v}_g \equiv \partial E_{\pm} / \hbar \partial \mathbf{q}$ for small $|\mathbf{q}|$ is along the direction of $\mathbf{q}$ and its magnitude is constant and it is given by

$$|\mathbf{v}_g| = \frac{3}{2\hbar} |Vd| = \frac{3}{2} \times 0.63 \frac{\hbar}{md} = 7.7 \times 10^5 \text{ m s}^{-1}. \quad (13.90)$$

Probably, it did not escape the attention of the readers that the Hamiltonian (13.86), which describes the motion of an electron with crystal momentum $\hbar\mathbf{k}$ near the point P (and its equivalent points) in the BZ of graphene, is equivalent to that of a Dirac relativistic particle with zero rest mass and with fixed helicity (+1 for the positive energy, $E - \varepsilon_p$, solutions and -1 for the negative energy solutions (antiparticles)). In other words, the low-energy $|E - \varepsilon_p|$ electrons in graphene, according to our analysis, behave like zero mass, charged pseudo-neutrinos, and antineutrinos,¹⁶ moving with a constant velocity of about 10^6 m s^{-1} . This opens up the possibility of testing two of the most counterintuitive predictions of the relativistic Dirac equation: the *Klein paradox*, according to which a relativistic particle can pass a high and wide potential barrier with 100% probability; and the so-called *Zitterbewegung*, an oscillatory jittery motion around its instantaneous classical position $\langle \mathbf{r} \rangle = v \cdot t$. These are not the only possibilities for new physics. The 2-D character of graphene together with the massless Dirac Hamiltonian (13.86) has led to the reexamination (in the framework of this “relativistic” 2-D solid state system) of several intriguing solid state effects (to be presented in later chapters) such as the quantum hall effect (QHE)¹⁷ several many-body effects,¹⁸ weak localization effects,¹⁹ etc.

The research on graphene took a turning point when in 2004 a free-standing graphene was obtained²⁰ after many years of futile efforts (for a brief review of the early work see A.K. Geim and K.S. Novoselov, *Nature Materials* **6**, 13–171 (2007) and references therein; see also A.K. Geim, *Science*, 324, 1530 (2009)). This was achieved in spite of theoretical predictions that strictly 2-D crystals at any finite temperature are unstable. Actually, graphene shows small departures from a perfect flat shape by exhibiting warping such that the normal to the flat surface deformations can reach up to 1 nm. These deformations are thought to offer one mechanism to stabilize the structure.

Following the discovery of free-standing graphene, a number of amazing properties were discovered in this extraordinary truly 2-D material. The list includes long mean free paths approaching the micron range and very high mobility of the order of $20,000 \text{ cm}^2 \text{ Vs}^{-1}$, which is due mainly to extrinsic disorder and it is weakly temperature dependent. This indicates that the electron–phonon interaction is very weak and that the elimination (or drastic reduction) of the extrinsic disorder may lead to mobilities in excess of $200,000 \text{ cm}^2 \text{ Vs}^{-1}$.²¹ Such high mobilities are consistent with the theoretical picture emerging from a Dirac-like Hamiltonian as in (13.84). Moreover, the

¹⁶ According to recent experiments, the real neutrinos of particle physics seem to have a small but finite mass.

¹⁷ see, e.g., F.D.M. Haldane, *Phys. Rev. Lett.* **61**, 2015 (1988)

¹⁸ K. Nomura et al., *Phys. Rev. Lett.* **96**, 256602 (2006)

¹⁹ S.V. Morozov et al., *Phys. Rev. Lett.* **97**, 016801 (2006)

²⁰ K.S. Novoselov et al. *Science* **306**, 666 (2004)

²¹ S.V. Morozov et al., *Phys. Rev. Lett.* **100**, 016602 (2008).

metallic DC conductivity²² persists even at the point $E - \varepsilon_p = 0$ (where the DOS and the Fermi surface are zero) with values around $4e^2/h$, while theoretical work predicts $4e^2/h\pi$. This discrepancy was resolved (see F. Miao et al., *Science*, **317**, 1530 (2007)): For short and very wide specimens, the transport is ballistic and σ approaches the minimum theoretical value of $G_o = 4e^2/h\pi$, while for long specimens boundary scattering makes the transport diffusive with a near-universal value of ~ 3 to $4 G_o$. It is not only the DC conductivity that seems to depend exclusively on universal constants: the AC opacity, $1 - T$, where T is the transmission coefficient under normal incident conditions, is equal to $\pi\alpha$, to an accuracy of 5% or less;²³ α is the fine structure constant. Graphene exhibits high thermal conductivity as well.

This wealth of extraordinary properties has opened, at this point of time (2008), many possibilities for applications: graphene transistor (based on the quantum dot design shown schematically in Fig. 19.7) optical displays, battery improvement, field emission, sensors, etc.

Graphene has not only remarkable transport properties but also extraordinary mechanical strength as well,²⁴ due to the strong $sp^2 - sp^2$ bond and the fact that it can be prepared to be practically defect-free. This leads us to study (within the framework of the simple LCAO approach) the bonding (and the antibonding) bands:

Problem 13.17t. Show that the nearest neighbors and the next nearest neighbors matrix elements of the Hamiltonian among molecular bonding (and molecular antibonding) states are:

$$\begin{aligned} V_b &\equiv \langle \psi_{bAB} | H | \psi_{bBA1} \rangle = -0.0347 \frac{\hbar^2}{md^2} - \frac{\varepsilon_p - \varepsilon_s}{6} = -1.514 \text{ eV}, \\ V_2 &\equiv \langle \psi_{bAB} | H | \psi_{bA1B1} \rangle = -0.228 \frac{\hbar^2}{md^2} = -0.859 \text{ eV}, \\ V'_2 &\equiv \left\langle \psi_{bAB} \left| \hat{H} \right| \psi_{bA1B6} \right\rangle = 0.0873 \frac{\hbar^2}{md^2} = 0.328 \text{ eV}, \\ \bar{V}_b &\equiv \langle \psi_{aAB} | H | \psi_{aBA1} \rangle = 0.0347 \frac{\hbar^2}{md^2} - \frac{\varepsilon_p - \varepsilon_s}{6} = -1.252 \text{ eV}, \\ \bar{V}'_2 &\equiv \langle \psi_{aAB} | H | \psi_{aA1B1} \rangle = 0.228 \frac{\hbar^2}{md^2} = 0.859 \text{ eV}, \\ \bar{V}_2 &\equiv \langle \psi_{aAB} | H | \psi_{aA1B6} \rangle = -0.0873 \frac{\hbar^2}{md^2} = -0.328 \text{ eV}. \end{aligned}$$

Problem 13.18t. Define c_1 , c_2 , c_3 as the coefficients of ψ_{bAB} , ψ_{bAB2} , and ψ_{bAB3} in a linear combination of bonding molecular orbitals and use Bloch's theorem to show that

²² In 2-D, the dimensions of conductivity and conductance coincide.

²³ R. R. Nair et al., *Science* **320**, 1308 (2008).

²⁴ J. Hone et al., *Science* **321**, 385 (2008).

$$[\epsilon_b + 2V'_2 (\cos \phi_1 + \cos \phi_2) - E] c_1 + [V_b (1 + e^{-i\phi_2}) + V_2 (\epsilon^{i\phi_1} + \epsilon^{i\phi_3})] c_2 + [V_b (1 + \epsilon^{i\phi_1}) + V_2 (\epsilon^{-i\phi_2} + \epsilon^{-i\phi_3})] c_3 = 0.$$

Show also that two more equations for c_1, c_2, c_3 are produced by cyclic permutation of the indices 1, 2, and 3 in c_1, c_2, c_3 and ϕ_1, ϕ_2, ϕ_3 where $\phi_3 = -\phi_1 - \phi_2$. Solve this system for $\mathbf{k} = 0$ (point Γ in the first BZ) and for $\mathbf{k} = (2\pi/a) (1/\sqrt{3}, 1/3)$ (Point P in the first BZ). Do a similar calculation for the antibonding branches. Plot $E_n(\mathbf{k})$ for all eight branches (three bonding, three antibonding, and two p_z). Compare your results with those of Fig. 2, p. 631 of the paper by Zunger, Phys.Rev. B17, 626 (1978) or with Fig. 4.6, p. 146, in Kaxiras book [SS83].

To conclude this section, we must stress that the grapheme is an extraordinary material from many points of view: (1) It is a truly free standing 2-D system. (2) It exhibits pseudo-relativistic behavior. (3) It is extremely hard. (4) Its electrical and optical properties are quite impressive.

13.9 Organic semiconductors

Organic semiconductors find many uses in light-emitting diodes (LEDs), photovoltaic, and even in field-effect transistors (FETs). They possess several advantageous features such as tunability of their energy gap (through proper interventions in their chemical synthesis) and various easy ways of processing resulting in low-cost and large-scale fabrication. Their main disadvantage is their low mobility (usually many orders of magnitude lower than that of tetrahedral inorganic semiconductors), which makes them inappropriate for fast integrated electronics.

Organic semiconductors fall naturally in two broad groups of materials: small molecules (such as pentacene consisting of five benzene rings next to each other) or long linear conjugated polymers (conjugation means, in chemical language, alternating single and double bonds along the polymers backbone). The common feature in both groups of materials is the sp^2 hybridization (which provides structural stability and the possibility of planar geometry) combined with parallel-oriented p_z orbitals, which actually give rise to delocalized molecular orbitals capable of transporting electrons.

The situation is similar to graphene but with two important differences: In organic semiconductors the occupied states are separated from the empty states by a finite gap (in contrast to graphene where the two overlap slightly giving rise to semimetallic behavior). Furthermore, in small molecules and in conjugated polymers, the intermolecular transfer matrix elements V'_2 is much smaller than the intramolecular matrix elements V_2 . (typical values $V'_2 \lesssim 0.1$ eV vs. $V_2 \simeq 2$ eV). This is one reason for the low mobility of organic semiconductors.

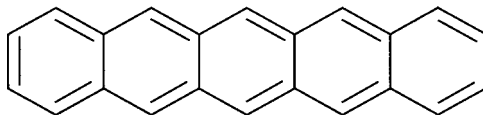


Fig. 13.16. The pentacene molecule. At each corner there is a p_z atomic orbital, which couples with all other nearest neighbors (and not only with the nearest neighbor connected by the second bond)

Problem 13.19t. Find the p_z energy levels of pentacene. (Fig. 13.16). In particular, find the level of the highest occupied molecular orbital (HOMO) and that of the lowest unoccupied molecular orbital (LUMO).

Hint: Keep only nearest neighbor matrix elements. The four orbitals per primitive cell can be reduced to two for the symmetric and antisymmetric solution. The coefficient of the molecular orbitals can be written as

$$\begin{aligned} c_{2n+1} &= A \sin(2n+1)\phi \\ c_{2n} &= B \sin 2n\phi. \end{aligned}$$

And the boundary conditions are $c_0 = c_{12} = 0$.

Both disorder and electron–electron electrostatic interactions tend to localize the p_z electrons, and hence, to reduce their mobility, sometimes to the point where the band picture fails completely. Disorder in small molecule organic semiconductors is usually associated with the noncrystalline arrangements of the individual molecules, while in conjugated polymers disorder is due to random conformation of the chain. Coulomb interactions are stronger in organics than in inorganic tetrahedral semiconductors, because the dielectric function, ϵ , is much lower in the former than in the latter (typical values 3 vs. 12). Another mechanism that reduces mobility further is the electron–phonon interaction, which leads to the creation of polarons. On the other hand, in polymers, such as trans-isomer of polyacetylene, soliton-like excitations can be formed, which facilitate transport (for a short description of polarons and solitons see Chap. 8).

The anticipated wider use of organic semiconductors is in LEDs and photovoltaics. In the former, external current drives electrons and holes to the interface of two different organic semiconductors (one n-type and the other p-type); there, electrons and holes annihilate each other giving rise to photons of proper color. In photovoltaic diodes the process is reversed, i.e., the external photons set up a voltage difference that can drive a current if the device is connected to be part of a closed circuit.

Thus, it is not surprising that optical properties, i.e., electron–hole excitation and deexcitation, draw a lot of attention. The lowest energy electronic excitation is of the exciton type, more specifically of the Frenkel type. The exciton radius in atomic units is about 6 (i.e., about 3 Å). This value combined with a dielectric function of about 3 gives a binding energy of

$13.6/3 \times 6 \simeq 0.75\text{eV}$. Notice that the singlet spin excitonic state having a symmetric spatial wavefunction leads to a smaller e – h distance and hence to a stronger binding and a lower excitonic energy than that of triplet state; the latter, however, needs spin–orbit coupling to emit a photon.

13.10 Key Points

- Electrons in alkali metals are almost free with an almost spherical Fermi surface enclosed entirely within by the first BZ.
- The DOS of divalent metals has a dip at the Fermi level that is more pronounced in Be, being, for this reason, a semimetal.
- Among the trivalent metals, only Al has a simple electronic and lattice structure; its Fermi surface consists of a closed surface for the second band containing occupied states and closed pieces of occupied states for the third band. This band structure leads to the conclusion that the high field Hall coefficient is positive and three times larger in absolute value than the corresponding JM result.
- The tetravalent nontransition elements are insulators (diamond), semiconductors (Si, Ge), zero-gap “semiconductor” (gray tin), and metal (white tin and lead). In lead, the 5s level does not hybridize; thus, the main band around the Fermi level is of 5p character.
- The pseudopotential for tetrahedral semiconductors can be brought to the form

$$\tilde{v}(\mathbf{q}) = \tilde{v}_s(\mathbf{q}) \cos \mathbf{q} \cdot \mathbf{r}_2 - i\tilde{v}_a(\mathbf{q}) \sin \mathbf{q} \cdot \mathbf{r}_2,$$

where $\tilde{v}_s(\mathbf{q}) = [\tilde{v}_1(\mathbf{q}) + \tilde{v}_2(\mathbf{q})]/2$ and $\tilde{v}_a(\mathbf{q}) = [\tilde{v}_2(\mathbf{q}) - \tilde{v}_1(\mathbf{q})]/2$; the relevant values of $\mathbf{q}$ are: (1,1,1), (2,0,0), (2,2,0), and (3,1,1) in units of $(2\pi/a)$. For elemental semiconductors $\tilde{v}_1 = \tilde{v}_2$ and hence, $\tilde{v}_a = 0$.

- The strength of these pseudopotentials is such that the unperturbed Fermi spherical surface is fully “replaced” by a Bragg plane-polyhedron called Jones Zone and a full gap around the Fermi level opens up.
- For elemental semiconductors, the cohesive energy, E_c , can be approximated as follows:

$$E_c \simeq 4|V_{2h}| - E_o - (\varepsilon_p - \varepsilon_s),$$

where E_o is of the empirical form c_n/d^n with $n \simeq 5$.

- The elastic constants c_{11}, c_{12}, c_{14} of cubic tetrahedral semiconductors are given by the following expressions:

$$\begin{aligned} c_{11} - c_{12} &\simeq 1.87a_c^2 |V_{2h}|/d^3, \\ c_{44} &\simeq \frac{32}{a^3} \frac{C_o C_1}{C_o + 8C_1}, \\ C_o &= \frac{3a^3}{16} (c_{11} + 2c_{12}) = \frac{9a^3}{16} B, \end{aligned}$$

$$C_1 = \frac{a^3}{32} (c_{11} - c_{12}),$$

$$B \simeq \sqrt{3} \frac{|V_{2h}|}{d^3}.$$

- The magnetic susceptibility of semiconductors has three contributions $\chi = \chi_c + \chi_v + \chi_f$.
- The ratio of Pauli χ_P to Landau χ_L magnetic susceptibility is $\frac{\chi_P}{\chi_L} = -3 \left(\frac{m^*}{m} \right)^2$, $k_B T \gg \hbar \omega_c$.
- Large binding energy excitons ($\varepsilon_b \simeq 1$ eV) are called Frenkel excitons and occur in strong ionic insulators and organic semiconductors, while small binding energy excitons ($\varepsilon_b \simeq 0.1$ eV) occurring in semiconductors are called Wannier–Mott excitons. The binding energy of the latter is equal to $(13.6 m^* / \varepsilon^2 m)$ eV.
- The conductivity, σ , in semiconductors has contributions, in general, from both electrons in the CB and holes in the VB: $\sigma = \sigma_e + \sigma_h$, where

$$\sigma_i(T) = q_i n_i(T) \bar{\mu}_i(T), \quad i = e, h.$$

- The Hall coefficient in semiconductor is given by

$$R \simeq -\frac{r_{\text{He}}}{ec} \frac{n_e - n_h b^2 x}{(n_e + n_h b)^2}, \quad \bar{\mu}_i B / c \ll 1,$$

$$R \simeq -\frac{1}{ec(n_e - n_h)}, \quad \bar{\mu}_i B / c \gg 1,$$

where $b = \bar{\mu}_h / |\bar{\mu}_e|$ and $x = r_{\text{Hh}} / r_{\text{Hc}}$. In SI set $c = 1$.

- The lattice structure of SiO_2 can be visualized by inserting an oxygen at the middle of each Si – Si bond, increasing its size and bending it. The electronic structure of SiO_2 can be roughly understood by considering the eigenenergies of the unit $\frac{1}{4}\text{Si}-\text{O}-\frac{1}{4}\text{Si}$ with two sp^3 Si hybrids and the p_x and p_y of O.
- Graphene is a planar honeycomb carbon structure. Its electronic structure consists of a composite bonding band, a half full p_z band, and an empty antibonding band. The E vs. $\mathbf{k}$ relation around the Fermi level is mathematically similar to a massless Dirac particle–antiparticle. Graphenes have been isolated and exhibit impressive transport, optical, and mechanical properties. Many graphenes held together by van der Waals forces comprise graphite.

13.11 Questions and Problems

- 13.1 Find the intersection of the free-electron Fermi surface of Be with the k_x, k_y plane (see Fig. 3.20) within the reduced-zone scheme. Are your results consistent with those shown in Fig. 15.13 (p. 300) of the book by Ashcroft and Mermin [SS75]?

- 13.2 Using the results of Problem 10.4, calculate the band structure of the s band of Pb. Is the predicted shape of the s -DOS consistent with the one shown in Fig. 13.7e?
- 13.3 Calculate $\tilde{v}_s(\mathbf{q})$ for Si and Ge according to empty core approximation and for the values of $\mathbf{q}$ shown in Table 13.1.
- 13.4 Calculate $\tilde{v}_s(\mathbf{q})$ and $\tilde{v}_a(\mathbf{q})$ for InAs and for the values of q shown in Table 13.1 (according to the empty core approximation). Compare them with the corresponding empirical values ($a = 6.058 \text{ \AA}$ and $r_c = (r_{\text{cIn}} + r_{\text{cAs}})/2$).
- 13.5 Find the line of intersection of the unperturbed Fermi surface of $k_F = 9.82/a$ with the face of the JZ normal to the vector $(2\pi/a)(1, 1, 0)$.
- 13.6 Prove (13.23) starting from (13.22).
- 13.7 What is the value of $\langle r^{-1} \rangle_1$ and $|E_1|$ if $m_h^* = m_e^* = m$ and $\varepsilon = 1$ according to (13.45) and (13.46) respectively? Is $\langle r^{-1} \rangle_1 = a_B^{-1}$ and $|E_1| = 13.6 \text{ eV}$?
- 13.8 Calculate $|E_1|$ and $\langle r^{-1} \rangle_1^{-1}$ for an exciton in InSb. Use the light hole mass and compare with the corresponding experimental value. What would the results be, if you use the heavy hole mass or the split-off mass?
- 13.9 Prove (13.58) and (13.59) for the three cases shown in (13.55)–(13.57).
- 13.10 Write down the 4×4 Hamiltonian matrix for the $\frac{1}{4}\text{Si} - 0 - \frac{1}{4}\text{Si}$ unit in the basis h_+, p_y, h_-, p_x . Diagonalize the resulting two decoupled 2×2 matrices and find the corresponding eigenfunctions. Express the corresponding four eigenfunctions as linear combinations of the h_1, h_2, p_x, p_y orbitals.
- 13.11 Prove (13.81) and (13.82).
- 13.12 Calculate the DOS for E around the neutral point ε_p of grapheme (see (13.88)). What is the temperature dependence of the specific heat of graphite?
- 13.13 What is the width of the p_z band in graphene?

Further Reading

- References to the books by Burns [SS77], Papaconstantopoulos [SS81], Ashcroft and Mermin [SS75], and Yu and Cardona [Se119], regarding specific topics were given in the text. The Yu and Cardona book [Se119] treats the magnetoresistance in semiconductors, pp. 232–237, and the exciton topic, pp. 276–292 in details.
- In Harrison's book [SS76] the topics of energy, pp. 167–178, elastic constants, pp. 180–200, and magnetic susceptibility, pp. 419–422, in semiconductors are treated in more detail than here; in the same book, more information regarding SiO_2 can be found (pp. 257–287).

- Some recent (2008) references regarding organic semiconductors follow:
 1. S.S. Sun, N.S. Sariciftci, Organic Photovoltaics: mechanisms, materials and devices (Taylor and Francis, Boca Raton, FL, 2005)
 2. G. Malliaras, R. Friend, Physics Today, May 2005, p. 53
 3. J.Y. Kim et al., Science **317**, 222 (2007)
 4. P. Peumans, S.R. Forrest, Chem. Phys. Lett. **398**, 27 (2004)
 5. M.L. Tang et al., J. Am. Chem. Soc. **128**, 16002 (2006)

Closed-Shell Solids

Summary. For closed-shell solids consisting of neutral noble gas atoms (Ne, Ar, Kr, Xe) or nonpolar neutral molecules (H_2 , N_2 , O_2 , CO_2 , etc), their structure is determined by the competition of the van der Waals attraction and the overlap repulsion. In closed-shell solids consisting of ions, such as the NaCl, the Coulomb energy, instead of the van der Waals, provides the main attraction, while the repulsion is still coming from the overlap energy. The lattice structure, the mechanical properties, and the electromagnetic response of these types of materials will be examined in this chapter by employing, when needed, the LCAO approach.

14.1 Van Der Waals Solids

For simplicity we shall restrict our study to the solids made up from atoms of the so-called noble gases (He, Ne, Ar, Kr, Xe). In Table 14.1 we show the freezing and the boiling temperatures of these substances. Notice how low the freezing point is and how small the difference between boiling point and freezing point is. This is a direct consequence of the weakness of the $-1/d'^6$ van der Waals attraction (see (2.10)). The repulsive overlap energy can be approximated for simplicity by an inverse power law of the form D/d'^v where v ought to be larger than 6 (in order for the overlap energy to dominate at small d'); actually it must be much larger than 6 because the overlap energy rises very fast, since the complete shells of the noble gas atoms do not tolerate any overlap. For convenience v is usually chosen to be equal to 12. Thus, the so-called *Lennard-Jones* two-body interaction results, which is usually expressed in terms of a length σ and an energy ε as follows:

$$E(d'_{ij}) = 4\varepsilon[(\sigma/d'_{ij})^{12} - (\sigma/d'_{ij})^6]. \quad (14.1)$$

The minimum of E is equal to $-\varepsilon$ and it is obtained at

$$d'_{ij} = d_0 = 2^{1/6}\sigma = 1.12\sigma. \quad (14.2)$$

Table 14.1. Freezing and boiling points (in K), under normal pressure (with the exception of He, which does not solidify under normal pressure), of the noble gas elements

	He	Ne	Ar	Kr	Xe
Freezing point (K)	0.95 for 25 atm	24.553	83.81	115.78	161.36
Boiling point (K)	4.215	27.096	87.30	119.80	165.03

Thus, ε gives the bond energy of the diatomic molecule (for atoms at rest, i.e., without taking into account the zero point motion) and σ is the distance at which the repulsive and the attractive energy terms are equal in size. The total ground state energy (excluding the zero point energy) is obtained by adding (14.1) over all pairs

$$E'_t = \frac{1}{2} \sum_{ij} E(d'_{ij}) = \frac{1}{2} N_a \sum_j E(d'_{ij}). \quad (14.3)$$

The last equation can be written in terms of the nearest neighbor distance d' by introducing the quantities $p_{ij} = d'_{ij}/d'$:

$$E'_t = 2N_a \varepsilon [(\sigma/d')^{12} \sum_j (1/p_{ij})^{12} - (\sigma/d')^6 \sum_j (1/p_{ij})^6]. \quad (14.4)$$

The value of the sums depends on the lattice structure as is shown below

	fcc	hcp	bcc	sc
$s_{12} \equiv \sum_j 1/p_{ij}^{12}$	12.13188	12.13229	9.1142	6.20
$s_6 \equiv \sum_j 1/p_{ij}^6$	14.45392	14.45489	12.2519	8.40

Minimizing E'_t with respect to d' we find the equilibrium nearest neighbor distance d and the equilibrium ground state energy $E'_t(d)$ for the solid (excluding zero point energy).

$$d = (2s_{12}/s_6)^{1/6} \sigma = 1.09\sigma, \quad (14.5)$$

$$E'_t(d) = -(s_6^2/2s_{12})N_a \varepsilon = -8.61N_a \varepsilon, \quad (14.6)$$

where the last expression in both (14.5) and (14.6) is for the *fcc* lattice. The bulk modulus B at $T = 0$ K can be calculated by the relation $B = V(\partial^2 E_t / \partial V^2)$ and (14.4). The result is

$$B = \left(4s_6^{5/2}/s_{12}^{3/2}\right) (\varepsilon/\sigma^3) = 75.185(\varepsilon/\sigma^3). \quad (14.7)$$

To compare with experimental data, we need the values of ε and σ for each material. These values can be estimated theoretically by measurements in the

Table 14.2. Comparison of theoretical and experimental values of the nearest neighbor distance d , the total energy per atom, E'_t/N_a , and the bulk modulus B at $T \rightarrow 0$ K ignoring the zero point motion

	$\sigma(\text{\AA})$	$\varepsilon(\text{eV})$	$d(\text{\AA})$		$-E_{0\lambda}/N_a(\text{eV})$		$B(\text{Mbar})$	
			Theory	Exp.	Theory	Exp.	Theory	Exp.
Ne	2.74	0.0031	2.99	3.13	0.027	0.02	0.0182	0.011
Ar	3.40	0.0104	3.71	3.75	0.089	0.080	0.0319	0.027
Kr	3.65	0.014	3.98	4.01	0.121	0.116	0.0347	0.035
Xe	3.98	0.02	4.34	4.35	0.172	0.17	0.0382	0.036

gas phase. In Table 14.2 we compare the experimental values of d , E'_t , B with the corresponding theoretical values based on (14.5), (14.6), and (14.7).

Notice that, as we move from Xe to Ne, the comparison of the theoretical results with the experimental data deteriorates from excellent (discrepancies of about 1%) to fair (discrepancies of 10% or even more). The main reason for this is our omission of the zero point motion, which contributes to the total energy by an amount that is inversely proportional to the square root of the atomic mass m_a (The zero point energy per atom $U_i^{(0)}/N_a$ is equal to $9\hbar\omega_D/8$ according to (4.78) where ω_D is the Debye frequency; obviously the frequency is proportional to $1/\sqrt{m_a}$). By dimensional analysis, one can conclude that

$$U_i^{(0)}/N_a = c_1(\hbar/\sigma)\sqrt{\varepsilon/m_a}. \quad (14.8)$$

Problem 14.1ts. Prove (14.8) by dimensional analysis taking into account its $1/\sqrt{m_a}$ dependence; c_1 is a numerical constant that depends on the ratio $f \equiv \tilde{c}/c_0$ (see (4.67)).

The relative importance of the zero point energy can be quantified by the ratio $U_i^{(0)}$ as given by (14.8) over E'_t as given by (14.6). This ratio, apart from numerical constants, is equal to $\hbar/(\sigma\sqrt{m_a\varepsilon})$, and it is known as the *de Boer parameter*, and it is denoted by the Greek capital letter Λ :

$$\Lambda = \frac{\hbar}{\sigma\sqrt{m_a\varepsilon}}. \quad (14.9)$$

Problem 14.2t. Prove that Λ is proportional to the dimensionless ratio $\langle\delta d'^2\rangle/d^2$.

An explicit calculation, using (14.5) for the equilibrium value of d , and (14.7) for B shows that

$$\Theta_D = 33.3(\hbar f/k_B\sigma)\sqrt{\varepsilon/m_a}, \quad f = \tilde{c}/c_0, \quad (14.10)$$

$$U_i^{(0)} = 37.46(N_a\hbar f/\sigma)\sqrt{\varepsilon/m_a}. \quad (14.11)$$

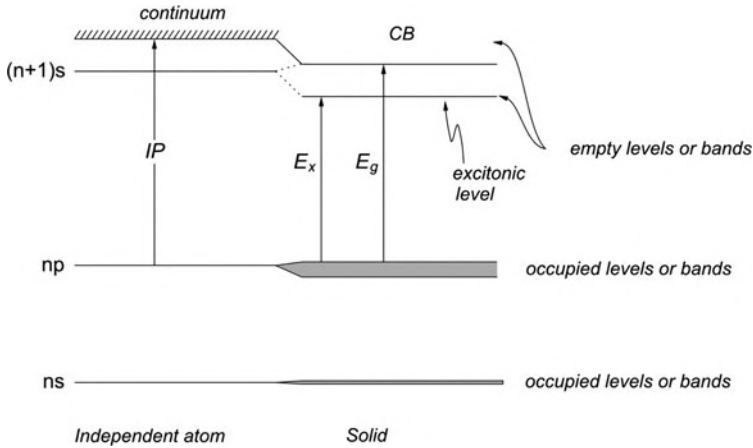


Fig. 14.1. The energy levels of an independent atom of noble gas and the bands of the corresponding solid (schematically). The value of n is 2, 3, 4, 5 for Ne, Ar, Kr, Xe respectively

The bands of the noble gas solids are in very close alignment with the energy levels of the corresponding atom as shown schematically in Fig. 14.1. The reason is that the bands are very narrow, because the nearest neighbor distance is much larger than the atomic diameter (see Table 14.8). Thus, the ns bandwidth is practically negligible (n is the highest occupied principal quantum number); the np bandwidth is given by the usual formula of $\eta\hbar^2/md^2$, where the numerical factor η has been estimated to be about 4.2 for all noble gases. The exciton is of Frenkel type, since it is mainly an intra atomic excitation with small spreading to the neighboring atoms. The CB is wide, Bloch-like, with E_g smaller than the energy difference between the $(n+1)s$ and the np levels.

We shall conclude this section by briefly examining the possibility of estimating the basic quantities σ and ε theoretically. Since a pair of noble gas atoms does not tolerate any overlap it is reasonable to assume that $\sigma \simeq 2r_M$, where r_M is the atomic radius beyond which the electronic density is practically zero. Hence, the most external occupied atomic orbital, which is p -like, is fitted within a sphere of radius r_M ; this implies that $\lambda \simeq 2r_M \simeq \sigma$, where λ is the wavelength of the p orbital. The wavelength λ can be expressed in terms of the kinetic energy ε_K : $\varepsilon_K = \hbar^2(2\pi)^2/2m\lambda^2$; furthermore, ε_K is equal to the absolute value of the total energy of the p orbital because of the virial theorem for Coulomb potential; the magnitude of this total energy is approximately equal to the first ionization potential, IP. Thus, in atomic units, $\sigma = 4.44c_1(\text{IP})^{-1/2}$, where c_1 is a numerical constant of the order of unity. This formula reproduces reasonably well the experimental data, if we choose $c_1 = 1.045$ and change the exponent from -0.5 to -0.6 :

$$\sigma = 4.64(\text{IP})^{-0.6}. \quad (14.12)$$

To estimate ε we notice that $4\varepsilon\sigma^6$ is equal to the quantity A of (2.10). In the footnote 5 of p. 24 we have obtained that $A = \eta\zeta^2 e^4 R_a^4 / (2(\text{IP}))$, where η is a numerical factor. Hence

$$\varepsilon = \frac{\eta\zeta^2}{8} \frac{e^4 R_a^4}{(\text{IP})\sigma^6} \simeq 0.4 \frac{\tilde{a}^2}{\sigma^6} (\text{IP}), \text{ G-CGS} \quad (14.13)$$

where R_a is the radius at which the highest occupied p orbital gives the maximum density, and $\tilde{a}$ is the atomic polarizability ($\tilde{a} = 0.39, 1.62, 2.46$, and 3.99 (in $\text{\AA}^3$) for Ne, Ar, Kr, and Xe respectively). The last expression in (14.13) is more accurate than the one before it; in deriving it the relations $(\text{IP})^2 \sim \zeta^2 e^4 / R_a^2$ and $\alpha \sim R_a^3$ were taken into account.

14.2 Ionic Compounds I: Types and Crystal Structures

The simplest ionic solids are the ones that consist of an equal number of alkali and halogen atoms, e.g., NaCl, or alkaline earths and column VI atoms, e.g., CaO. As was pointed out in Chap. 7, the ionic character decreases and the lattice changes from close-packed Coulomb dominated to open band-formation dominated ZnS structure, as we move from the I–VII, to II–VI, to III–V, and finally to IV–IV compounds.

It is instructive to consider the similarities and the differences between an ionic compound, e.g., the KCl and a corresponding van der Waals atomic solid, such as Ar. Indeed the Cl^- and K^+ ions have exactly the same electronic configuration as the Ar atom: $1s^2 2s^2 2p^6 3s^2 3p^6$. Thus, we can think of the electronic structure of KCl as coming from that of Ar solid by transferring mentally one proton from every second atom of Ar to a neighboring atom of Ar. The Ar atoms with the extra proton behave as the K^+ ions and the Ar atoms with the missing proton as Cl^- ions. Because of the extra proton the radius of K^+ is smaller than that of Ar and the energy levels deeper, while the radius of Cl^- would be larger than that of Ar and its levels more shallow. In Fig. 14.2, the atomic levels of Ar, the levels of K^+ and Cl^- and the bands in KCl are shown schematically.

The noble metals, Cu, Ag, and Au may take the place of alkalis in forming I–VII compounds, e.g., AgBr, and the Zn, Cd, and Hg may take the place of alkaline earths; however, the d-levels of these transition elements are involved in the bonding and affect the cohesive energy and other properties of these compounds. Lead also may act as a divalent cation transferring the two electrons occupying the 6p orbital to a column VI element and thus forming a compound such as PbS. Hydrogen also forms ionic compounds, e.g., LiH, in which it acts as being in the VII column (since with one electron it completes its s shell) and not in the first (because its large ionization potential sets it apart from the alkalis).

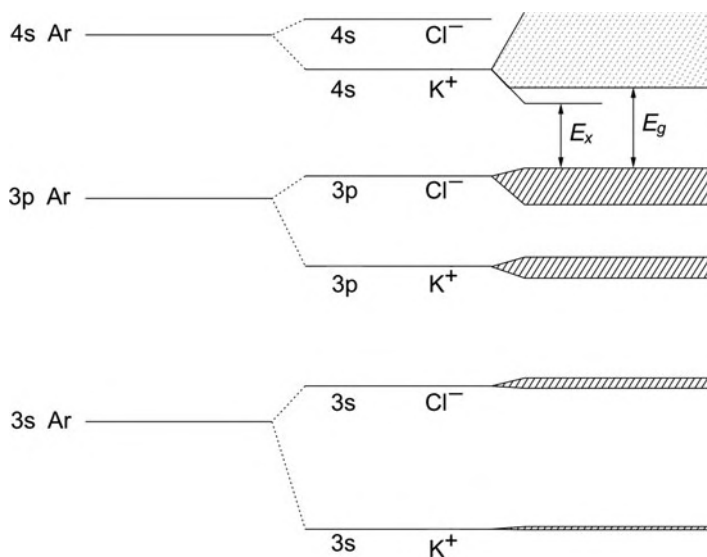


Fig. 14.2. Schematic representation of the atomic levels of Ar, of ionic levels of K^+ and Cl^- , and the bands of the KCl solid. The 3p levels of Cl^- become the VB, while the lower part of the CB is dominated by the 4s states of K^+ . E_g is equal to 8.4 eV

There are more complicated ionic compounds with unequal number of cations and anions such as $A_m^{-n}C_n^{+m}$, e.g., $CaCl_2$, $AlCl_3$, V_2O_5 . We shall return to some of them in the next chapter.

The strong ionic compounds of the type A^-C^+ form either the *sodium chloride*, otherwise called *rock salt* structure, or the *cesium chloride* structure. In the sodium chloride structure cations and anions are placed alternately at the sites of a *simple cubic* lattice so that each anion is surrounded by six cations and vice versa. As a result, two interpenetrated *fcc* sublattices are formed, one occupied by anions and the other by cations, displaced from each other by the vector $a(\mathbf{i} + \mathbf{j} + \mathbf{k})/2$, where a is the lattice constant of each *fcc* sublattice; the nearest neighbor anion–cation distance d is equal $a/2$. In the cesium chloride structure the anions and the cations are placed alternately at the sites of a *bcc* lattice so that each anion is surrounded by eight cations and vice versa. Thus, two interpenetrated *sc* sublattices are formed (one occupied by the anions and the other by the cations), which are displaced relative to each other by the vector $a(\mathbf{i} + \mathbf{j} + \mathbf{k})/2$, where a is the lattice constant of each *sc* sublattice; the nearest neighbor anion–cation distance d is equal to $\sqrt{3}a/2$ (see also Table 3.3, p. 71). The NaCl structures are the ones that maximize the Coulomb interactions among ions. In contrast, in the zincblende structure preferred by compound semiconductors, the Coulomb interactions among ions play a secondary role, while the energy gain due to band formation is the dominant factor in determining the lattice structure.

14.3 Ionic Compounds II: Mechanical Properties

In strongly ionic solids, each ion has a practically complete outer shell as the noble gas atoms. As a result, the occupied bands are of practically negligible width and the band formation energy is so small that it can be ignored at least to a first approximation. Thus, the cohesive energy is as in the case of (14.4), with two additional important contributions:

1. The energy cost for the formation of the ions, which is approximately equal to $N_{\text{P}}(\text{IP}_{\text{c}} - \text{EA}_{\text{a}})$, where $N_{\text{P}} = N/2$ is the number of anion–cation pairs; IP_{c} is the energy needed to change a neutral atom to a cation of charge $\zeta|e|$ and EA_{a} is the energy gained by transferring ζ electrons to form an anion of charge $-\zeta|e|$.
2. The Coulomb attraction among ions

$$\frac{1}{2} \frac{(\zeta e)^2}{4\pi\epsilon_0} \sum_{ij} \frac{\pm 1}{r_{ij}} \equiv -N_{\text{P}} \frac{(e\zeta)^2}{4\pi\epsilon_0 d'} \alpha. \quad (14.14)$$

Equation (14.14) is essentially the definition of the dimensionless quantity α , called *Madelung constant*; its value¹ depends on the lattice structure ($\alpha = 1.762675$, $\alpha = 1.747565$, and $\alpha = 1.63806$ for CsCl, NaCl, and ZnS structures). Thus, the total energy is

$$E_{\text{t}} = N_{\text{P}}(\text{IP}_{\text{c}} - \text{EA}_{\text{a}}) - N_{\text{P}} \frac{(e\zeta)^2}{4\pi\epsilon_0 d'} \alpha + E'_{\text{t}}, \quad (14.15)$$

where d' is the nearest neighbor anion–cation distance and E'_{t} is given by (14.4). Instead of (14.4) other forms for E'_{t} have been used in the literature: Ashcroft and Mermin [SS75], (p. 405–408) employ a form c_1/d'^m with the exponent m between 6 and 9.5 (with the smaller values for the smaller ionic radii); Kittel [SS74], (p. 60–66) is using an exponential form, $\lambda \exp(-d'/p)$, which seems to give more accurate results. Here we shall present some results based on (14.4) with ϵ and σ taken as the averages of the values for the corresponding noble gas atoms.

We see from Table 14.3 that (14.15) with E'_{t} according to (14.4) underestimates the equilibrium distance d , while overestimating the binding energy E_{b} . As a result the bulk modulus, which is proportional to E_{b}/d^3 , is seriously overestimated by a factor that, in some cases, may approach 3.

There is a simpler –and happily– more accurate way to obtain the equilibrium distance d based on the concept of *ionic radius*, r_{i} , given in Table H.9.

$$d \simeq r_{\text{a}} + r_{\text{c}} \quad (14.16)$$

Equation (14.16) gives 2.31 Å, 2.76 Å, and 3.64 Å for NaF, NaCl, and CsBr respectively. These values are closer to the experimental data than those in

¹ The evaluation of the Madelung constant is a real challenge in numerical analysis (see, e.g., the book by Ashcroft and Mermin [SS75], p. 403–404).

Table 14.3. Comparison of theoretical results (based on (14.15)) with experimental data for some ionic crystals

	$d(\text{\AA})$		$(E_b/N_p)(\text{eV})^a$		$B(\text{Mbar})$	
	Theory	Exp	Theory	Exp	Theory	Exp
NaF	2.19	2.317	10.75	9.45	1.2	0.465
NaCl	2.59	2.82	9.25	8.04	0.65	0.24
CsBr	3.63	3.71	6.98	—	0.205	0.158

^a The binding energy E_b does not include the first term in the rhs of (14.15)

Table 14.3. The reason that the simple formula (14.16) works rather well is that the strong Coulomb attraction squeezes the ions until they touch each other; at this point the squeezing stops because the overlap energy rises very fast as to give the ions the character of almost rigid tiny spheres.

The binding energy E_b to a large extent is due to the Coulomb interaction among the ions. Hence

$$E_b/N_p = c_1 \frac{(\zeta e)^2}{4\pi\epsilon_0 d} \alpha, \quad (14.17)$$

where c_1 is less but close to one (if the ions were exactly rigid spheres c_1 would be 1). Reasonable values for E_b are obtained by the choice $c_1 \simeq 0.9$. Finally, from dimensional analysis, B must be of the form

$$B = c_2 \frac{E_b/N_p}{d^3}, \quad (14.18)$$

where the numerical factor c_2 is about $1/2$, while the Coulomb energy contribution alone at the equilibrium distance gives, according to (14.17), $c_2 = 0.4$.

We can calculate also the elastic constant c_{44} by introducing a strain, the only nonzero element of which is u_{xy} as in Fig. 9.8b. Then, $c_{44} = \Delta/(2Vu_{xy}^2)$, where Δ/V is the energy per unit volume as a result of the strain u_{xy} . Since u_{xy} leaves the bond length unchanged, Δ is due exclusively to the electrostatic term. Then, the calculation of Δ/V , although lengthy, is purely a geometric sum, which has been performed for various lattices. For NaCl structure with $\pm\zeta e$ ionic charges, the final result for c_{44} is as follows: (See [SS76], p. 312),

$$c_{44} \approx 0.348 \frac{(\zeta e)^2}{4\pi\epsilon_0 d^4}. \quad (14.19)$$

Since the forces are to a very good approximation central, we expect the Cauchy relation, $c_{12} \approx c_{44}$, to be valid (see footnote in Table 9.2, p. 263). This relation together with (14.19), (14.18) and (9.62) allows us to determine approximately the three elastic constants c_{11} , c_{12} , c_{44} , which characterize the behavior of cubic crystals. In Table 14.4 we compare the theoretical results based on (14.16) till (14.19) with the corresponding experimental data.

Table 14.4. Comparison of theoretical results based on (14.16) till (14.19) with the corresponding experimental data for some ionic crystals of NaCl structure. See also [SS76], p. 313

	$d(\text{\AA})$		$B(\text{Mbar})$		$c_{11}(\text{Mbar})$		$c_{12}(\text{Mbar})$		$c_{44}(\text{Mbar})$	
	Theory	Exp.	Theory	Exp.	Theory	Exp.	Theory	Exp.	Theory	Exp.
LiF	2.0	2.014	1.1	0.671	2.32	1.12	0.488	0.45	0.488	0.632
LiBr	2.59	2.751	0.32	0.238	0.68	0.394	0.140	0.187	0.140	0.193
NaCl	2.77	2.820	0.29	0.240	0.618	0.485	0.126	0.125	0.126	0.127
KF	2.69	2.674	0.35	0.305	0.736	0.656	0.157	0.146	0.157	0.125
KI	3.49	3.533	0.12	0.117	0.256	0.275	0.052	0.045	0.052	0.0369
RbBr	3.43	3.445	0.13	0.130	0.276	0.314	0.057	0.048	0.057	0.0383

The binding energy E_b according to (14.15) and (14.14) satisfies the relation

$$-\frac{E_b}{N_p \varepsilon} = -\alpha \gamma x + 4s_{12}x^{12} - 4s_6x^6, \quad (14.20)$$

where α is Madelung's constant, γ is the dimensionless ratio of the electrostatic energy scale over ε , $\gamma = (\zeta e)^2/4\pi\varepsilon_0\sigma\varepsilon$, and $x = \sigma/d'$.

This expression is minimized when x satisfies the relation

$$48s_{12}x^{11} = a\gamma + 24s_6x^5. \quad (14.21)$$

Problem 14.3t. For each of the three lattices, NaCl, CsCl, and ZnS, solve (14.21) numerically for $\gamma = 0, 100, 200, 300, 400, 500, 600, 700$ to obtain the equilibrium value of x ; then substitute this value in (14.20) to find the minimum value of $-E_b/N_p\varepsilon$ for each of the three lattices and for each of the above values of γ . Plot this minimum value vs. γ (by interpolation) for each of the three lattices. Show that for large values of γ the NaCl structure is preferable, while for small values of γ the CsCl structure is preferable. Remember that the ZnS structure would become the preferable one for very low γ , if a more realistic formula (than (14.20)) for E_b were used.

The values of α , s_{12} and s_6 are given below

	α	s_{12}	s_6
NaCl	1.747565	6.20	8.40
CsCl	1.762675	9.1142	12.2519
ZnS	1.63806	4.04	4.9

14.4 Ionic Compounds III: Optical Properties

To calculate optical quantities such as the dielectric function $\varepsilon(\omega)$, we need the band structure and the corresponding Bloch functions; in particular, for a rough estimate we need the size of the gap E_g . In Fig. 14.2 (p.398) the

bands of KCl, a representative I–VII ionic solid, are shown schematically. A very simple rough estimate of E_g is given by (6.38) (see also Fig. 6.6, p. 158): $E_g = \varepsilon_A - \varepsilon_B$. Pantelides [14.1] has proposed the following formula for the gap of $A^{-\zeta}C^{\zeta}$ ionic compounds:

$$E_g \simeq \eta_g \frac{\hbar^2}{md^2}, \quad (14.22)$$

where η_g has been adjusted to be 9.1, 5.3, and 1.6 for $\zeta = 1, 2$, and 3. Another approximate formula for the alkali halides is as follows

$$E_g \simeq \frac{e^2 [2(\alpha - 1)q_c + 1]}{d} + \text{EA}_A - \text{IP}_C \simeq \frac{2e^2}{d} + \text{EA}_A - \text{IP}_C, \quad (14.23)$$

where q_c is the effective charge of the cation, α is Madelung's constant, EA_A is the electron affinity of the anion and IP_C is the ionization potential of the cation. The argument in support of (14.23) is as follows: E_g is the energy required to transfer an electron from the highest occupied orbital of the anion A^- to the lowest empty orbital of the cation C^+ . If there were only a pair of anion–cation separated from each other by an infinite distance $d = \infty$, then this energy would be $\text{EA}_A - \text{IP}_C \equiv \delta E(\infty)$. If their distance were finite, equal to d , then the required energy would be $\delta E(d) + e^2/d$, where $\delta E(d)$ would be about equal to $\delta E(\infty)$ and e^2/d appears because the p level of the anion would be lower by $-e^2/d$ due to the presence of the cation. When all the other anion–cation pairs are present, the levels of the anion would be lower by an amount equal to $(\alpha - 1)q_c e^2/d$, while the levels of the cation would be higher by the same amount; the minus one, (-1) , appears, because we should not include in the contribution of the other anion–cation pairs, the contribution of either the anion or the cation of the pair under examination. The effective charge q_c is expected to be around 0.7 (for $\zeta = 1$), a little higher for the more ionic compounds, such as NaF , and a little lower of the less ionic compound, such as CsI . In Table 14.5 we compare the theoretical results based on (14.22) and (14.23) with the corresponding experimental data.

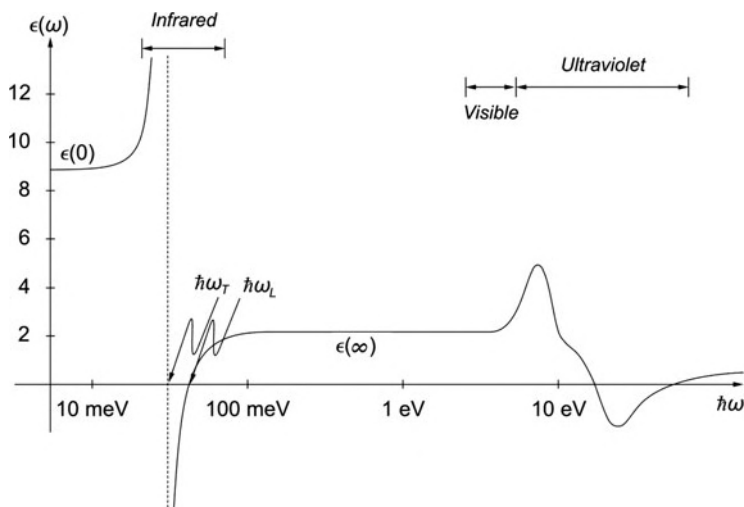
In Fig. 14.3 we plot schematically the dielectric function vs. frequency for a typical ionic material. The qualitative features are the same as in Fig. 7.12, where the $\varepsilon(\omega)$ -vs.- ω relation was plotted for GaAs, a typical III–V ionic semiconductor. We can easily distinguish four regimes:

1. $\omega \ll \omega_{\text{TO}} \simeq 3 \times 10^{13} \text{ rad/s}$ ($\Leftrightarrow 20 \text{ meV}$)
2. $\omega_{\text{TO}} \lesssim \omega \lesssim \omega_{\text{LO}}$, $\omega_{\text{LO}} - \omega_{\text{TO}} \simeq 3 \times 10^{13} \text{ rad/s}$
3. $\omega_{\text{LO}} \ll \omega < E_g/\hbar$ ($E_g \simeq 10 \text{ eV}$)
4. $E_g/\hbar < \omega$

In the first regime $\varepsilon(\omega)$ is constant and rather large of the order of 5 to 10 (Remember that $\varepsilon(0)$ in compound semiconductor is usually larger). This large value is mainly due to the relative motion of the anions vs. cations, which sets up polarization producing dipoles; hence, a large electric susceptibility χ_e

Table 14.5. Comparison of theoretical results for the gap E_g of A^-C^+ with the corresponding experimental data

	$-(EA_B - IP_A)$ (eV)	E_g (eV)			
		$\varepsilon_A - \varepsilon_B$	$9.1\hbar^2/md^2$	Equation (14.23)	Exp. Data
LiF	2	14.52	17.1	12.3	13.6
LiCl	1.78	8.44	10.5	9.4	9.4
LiBr	2.03	7.09	9.2	8.4	7.6
Lil	2.32	5.63	7.7	7.3	—
NaF	1.71	14.91	12.9	10.7	11.6
NaCl	1.53	8.83	8.7	8.7	8.5
NaBr	1.78	7.48	7.8	7.6	7.5
NaI	2.07	6.02	6.6	6.8	—
KF	0.92	15.85	9.7	9.8	10.7
KCl	0.73	9.77	7.0	8.4	8.4
KBr	0.97	8.42	6.4	7.8	7.4
KI	1.27	6.96	5.6	6.9	6.0
RbF	0.75	16.11	8.7	9.5	10.3
RbCl	0.56	10.03	6.4	8.2	8.2
RbBr	0.81	8.68	5.8	7.5	7.4
Rbl	1.11	7.22	5.1	6.7	6.1
CsF	0.47	16.5	—	—	9.9
CsCl	0.28	10.42	5.4	7.8	8.3
CsBr	0.53	9.07	5.0	7.2	7.3
Csl	0.82	7.61	4.4	6.5	6.2

**Fig. 14.3.** Schematic plot of the real part of $\varepsilon(\omega)$ vs. ω for a typical ionic insulator. For simplicity it was assumed that the $\text{Im}\varepsilon(\omega)$, for $\omega \leq E_g/\hbar$, is identically zero

is produced and a large dielectric function $\varepsilon(0) = 1 + 4\pi\chi_e$ (χ_e in G-CGS) results. In the second regime the frequency is comparable to the transverse optical phononic eigenfrequency(ies); as a result a resonance response is exhibited at ω_{TO} followed by the zero of ε at $\omega = \omega_{\text{LO}}$. In the third regime the frequency is so high and the period of the AC field is so short that the ions have no chance to move and set up ionic dipoles; thus only the “bound” electrons contribute to χ_e and $\varepsilon(\infty)$.

Finally, for $\omega > E_g/\hbar$, electrons are excited from the VB to the CB giving rise to strong absorption, i.e., a substantial $\text{Im } \varepsilon(\omega)$, and a complicated $\text{Re } \varepsilon(\omega)$ related to the $\text{Im } \varepsilon(\omega)$ by the well-known Kramers–Kronig relation (see (A.53)).

We shall conclude this section by estimating the magnitude of $\varepsilon(0)$, $\varepsilon(\infty)$, ω_{TO} , and ω_{LO} ; we remind the readers that these four quantities satisfy the LST relation: $\varepsilon(0) = \varepsilon_\infty \omega_{\text{LO}}^2 / \omega_{\text{TO}}^2$ (see (7.87) in Chap. 7). There are two approaches for obtaining these quantities: The *local* approach, which is based on the assumption that the electronic polarization is due to the *intraionic* rearrangement of the electrons without any interionic phenomena; and the other approach takes into account interionic electronic rearrangement by employing the *LCAO bands*, which mixes cation and anion orbitals. However, even the local approach implicitly incorporates some partial electron transfer from the anion to the cation due to solid formation (this is the reason that q_c in (14.23) is around 0.7 and not one). This transfer leads to an increased (decreased) electronic polarizability $\tilde{\alpha}_+$ ($\tilde{\alpha}_-$) of the cations (anions) in solids compared with that of isolated cations (anions), as shown in Table 14.6.

The local picture in combination with the cubic symmetry leads to the *Clausius – Mossotti* formula connecting the dielectric constant ε_∞ to the electronic polarizabilities of the ions (in solids)

$$\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} = \frac{4\pi}{3V_p}(\tilde{\alpha}_+ + \tilde{\alpha}_-), \quad (14.24)$$

where V_p is the volume of the primitive cell ($V_p = 2d^3$ for NaCl structure, and $V_p = (8/3\sqrt{3})d^3$ for CsCl structure; d is the anion–cation nearest distance)

Table 14.6. Electronic G-CGS polarizabilities for monovalent ions (in $\text{\AA}^3$). After [SS73], p. 465

	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺	F [−]	Cl [−]	Br [−]	I [−]
Isolated ions (Pauling [14.2] estimates)	0.029	0.179	0.83	1.40	2.42	1.04	3.66	4.77	7.10
Ions in solids (Shockley’s estimates)	0.045	0.28	1.13	1.79	2.85	0.86	2.92	4.12	6.41
(JS-TKS) [14.3, 14.4] Ions in Solids	0.029	0.29	1.133	1.679	2.743	0.858	2.947	4.091	6.116

Problem 14.4t. Using the values $\tilde{\alpha}_+$ and $\tilde{\alpha}_-$, calculate the values of ε_∞ for LiF, LiBr, NaCl, RbI, KCl and compare with the experimental values, which are 1.9, 3.2, 2.25, 2.6, and 2.1 respectively.

In the framework of the local approach, the values of ω_{TO} and ω_{LO} can be calculated as follows: (see problem 14.5t).

$$\omega_{\text{TO}}^2 = \frac{V_p}{d^2 M} \left(3B - \frac{4\pi(\varepsilon_\infty + 2)q_c^2 e^2 d^2}{9V_p^2} \right), \quad (14.25)$$

$$\omega_{\text{LO}}^2 - \omega_{\text{TO}}^2 = 4\pi \frac{q_c^2 e^2}{MV_p \varepsilon_\infty} \left(\frac{\varepsilon_\infty + 2}{3} \right)^2, \quad (14.26)$$

where $M = M_1 M_2 / (M_1 + M_2)$ is the reduced ionic mass, $q_c e$ is the ionic charge, and B is the bulk modulus. The first term in (14.25), $3V_p B / d^2 M \sim Bd/M$ is of the form κ/M , where the “spring constant” κ is for dimensional reasons proportional to the product Bd . The second term in (14.25) is due to the difference between the average field $\mathbf{E}$ and the local field $\mathbf{E}_l$ (at the site of each ion):

$$\mathbf{E}_l = \mathbf{E} + \frac{4\pi}{3} \mathbf{P}, \text{ G-CGS} \quad (14.27)$$

where $\mathbf{P} = \chi_e \mathbf{E}$ is the polarization. Finally, the difference $\omega_{\text{LO}}^2 - \omega_{\text{TO}}^2$ is due to the extra restoring force associated with the charges induced by the longitudinal oscillations.

Problem 14.5t. Prove (14.24), (14.25), and (14.26), taking into account the following: The polarization $\mathbf{P}$ is given by

$$\mathbf{P} = \frac{1}{V_p} [q_c e (\mathbf{u}_+ - \mathbf{u}_-) + (\tilde{\alpha}_+ + \tilde{\alpha}_-) \mathbf{E}_l]. \quad (14.28)$$

The equation of motion for the ionic displacements $\mathbf{u}_+$ and $\mathbf{u}_-$ have the form

$$M_1 \ddot{\mathbf{u}}_+ = -\kappa(\mathbf{u}_+ - \mathbf{u}_-) + q_c e \mathbf{E}_l, \quad (14.29)$$

$$M_2 \ddot{\mathbf{u}}_- = -\kappa(\mathbf{u}_- - \mathbf{u}_+) - q_c e \mathbf{E}_l. \quad (14.30)$$

By eliminating $\mathbf{E}_l$, and $\mathbf{u}_+ - \mathbf{u}_-$ with the help of (14.27), (14.29), and (14.30), a linear relation between $\mathbf{P}$ and $\mathbf{E}$ results that gives $\chi_e(\omega)$:

$$\chi_e(\omega) = b_{22} + \frac{b_{12}b_{21}}{-b_{11} - \omega^2}, \quad (14.31)$$

where

$$b_{12} = b_{21} = \frac{q_c e / (MV_p)^{1/2}}{1 - (4\pi/3V_p)(\tilde{\alpha}_+ + \tilde{\alpha}_-)}, \quad (14.32)$$

$$b_{22} = \frac{(\tilde{\alpha}_+ + \tilde{\alpha}_-) / V_p}{1 - (4\pi/3V_p)(\tilde{\alpha}_+ + \tilde{\alpha}_-)}, \quad (14.33)$$

$$b_{11} = -\frac{\kappa}{M} + \frac{(4\pi/3V_p)(q_c^2 e^2 / M)}{1 - (4\pi/3V_p)(\tilde{\alpha}_+ + \tilde{\alpha}_-)}. \quad (14.34)$$

Table 14.7. Comparison of theoretical estimates with experimental data for some ionic solids of the type C^+A^-

		LiF	LiBr	NaCl	RbI	KCl
ω_T (in 10^3 rad/s)	Experiment	5.80	3	3.1	1.4	2.7
q_c	Experiment and (14.25)	0.83	0.86	0.72	0.67	0.7
ε_∞	(14.24)	1.9	3.1	2.3	2.48	2.13
	(14.35)	2.0	2.22	1.77	1.55	1.46
	Experiment	1.9	3.2	2.25	2.6	2.1
ω_L (in 10^3 rad/s)	(14.26) + exp	12.7	7.40	4.73	1.83	3.72
	(14.36) + exp	12.9	6.0	4.96	1.88	3.99
	Experiment	12	6.1	5.00	1.9	4.0
$\varepsilon(0)$	From LST, and exp. for ω_{LO} , ω_{TO} , and ε_∞	8.1	13.2	5.85	4.8	4.6
	Experiment	8.9	13.2	5.9	5.5	4.85

To relate κ with $B(\kappa = 3V_p B/d^2)$ we use the following relations (the second one is valid for the NaCl structure)

$$\kappa = 2f'' + \frac{4f'}{d},$$

$$\frac{E_t}{N_p} = -\frac{q_c^2 e^2 \alpha}{d'} + 6f(d'),$$

where $f(r_{ij})$ is the overlap energy between a pair of anion-cation. (See Born and Huang [AW64], pp. 82–89).

Harrison in his book [SS76], pp. 327–336, follows the second, LCAO band-based, approach to obtain the following relations

$$\chi_{e,\infty} = \frac{4e^2 V_{sp\sigma}^2}{E_g^3 d}, \quad (14.35)$$

$$\omega_L^2 - \omega_T^2 = \frac{4\pi e_T^{*2} e^2}{M V_p \varepsilon_\infty}, \quad (14.36)$$

where $e_T^* = 1 + 4(V_{sp\sigma}/E_g)^2$. In Table 14.7 we compare theoretical estimates with experimental data. The value of q_c is adjusted so as to reproduce the experimental value of ω_{TO} according to (14.25).

14.5 Key Points

- Van der Waals solids are the elemental ones consisting of noble gas atoms and molecular solids made out of nonpolar molecules (such N_2 , O_2 , CO_2 , etc).

- The melting and the boiling points of the noble gas solids/liquids under normal pressure are very close to each other indicating that the binding energy of the liquid state is very close to zero.
- In elemental noble gas solids the attractive force is of the van der Waals type, while the repulsive one is of the overlap type; the Lennard Jones 12/6 potential, characterized by the length σ and the energy ε , is a fair representation of this competition of repulsion/attraction.
- The zero point motion provides a substantial contribution to the cohesive energy, bulk modulus, etc, especially for the lighter elements Ne and Ar. De Boer's parameter, $\Lambda \equiv \hbar/\sigma\sqrt{m_a\varepsilon}$, provides a measure of the importance of the zero point motion.
- The simpler ionic solids are binary compounds of the form $A^{-\zeta}C^{+\zeta}$ with $\zeta = 1$ (the alkali-halides), and $\zeta = 2$ (II-VI compounds); more complicated ionic compounds are quite common. Alkali-halides crystallize in the NaCl structure (when the ionic character is strong) or the CsCl structure (when the ionic character is weaker).
- The mechanical properties of the simpler ionic solids are determined by the competition of the attractive Coulomb forces among ions and the repulsive overlap forces; the latter can be approximated by treating the ions as almost rigid spheres. The ions in an ionic solid are not fully ionized; for alkali-halides the degree of ionization is about 70% (see Table 14.7).
- The most significant optical quantity of ionic solids is the dielectric function, which behaves as in Fig. 14.3 with an approximate analytical expression (for $\hbar\omega < E_g$) as in (7.86), out of which the LST relation follows: $\varepsilon(0) = \varepsilon(\infty)\omega_{LO}^2/\omega_{TO}^2$. In $\varepsilon(0)$ both the ionic motion and the electronic polarization contribute, while in $\varepsilon(\infty)$ (i.e., for $\omega_{LO} \ll \omega < E_g/\hbar$) the time scale of the external force is too fast for the ions to respond.
- Both the local approach (assuming only intraionic electronic rearrangement) and the LCAO band approach allow for a fair estimate of the values of $\varepsilon(\infty)$, $\varepsilon(0)$, ω_{TO} , and ω_{LO} .

14.6 Problems

- 14.1. Prove (14.5) till (14.7).
- 14.2s. Within the Debye model calculate the zero point energy $U_i^{(0)}$, the Debye temperature, and the corrected total energy $E_t \equiv E'_t + U_i^{(0)}$, using the equilibrium value of d as given by (14.5), and the value of B as given by (14.7).
- 14.3. Define $x \equiv \sigma/d'$ and show that the total energy $E_t \equiv E'_t + U_i^{(0)}$ of van der Waals solids including zero point motion is given by

$$\frac{E_t}{N_a\varepsilon} = 24.26x^{12} - 28.91x^6 + 6.96f\Lambda[242.64x^{14} - 86.72x^8]^{1/2}.$$

In the previous expression the bulk modulus entering the expression for $U_i^{(0)}$ has been approximated by $V(\partial^2 E_t'/\partial V^2)$. Plot $E_t/N_a\varepsilon$ and determine graphically the new equilibrium distance d , and the new equilibrium energy E_t . The new bulk modulus B and the new Debye temperature Θ_D can be estimated as in problem (14.2) but with the new value of d . Compare these results for Ne, Ar, Kr, and Xe with the corresponding experimental data and the results of Problem 14.2s.

- 14.4. Assume that He were solid under normal conditions. Calculate the ratio $U_i^{(0)}/E_t'$ taking f to be 0.55, $\sigma = 2.2 \text{ \AA}$, and $\varepsilon = 2 \text{ meV}$. What do you conclude from this result?
- 14.5s. From the phase diagram in the P, T plane and the data of Table 14.1, estimate the temperature and the pressure of the triple point of Ne, Ar, Kr, and Xe.
- 14.6. Write (14.27) in SI.

Further Reading

- Harrison in his book [SS76], pp. 291–337, treats the topics of this chapter in more details.
- In Ashcroft and Mermin book [SS75], mechanical, pp. 398–413, and optical, pp. 534–557, properties of closed-shell solids are studied.
- In the books by Kittel [SS74], pp. 455–474, and especially by Born and Huang [AW64], pp. 82–116, formulas for various optical quantities are derived.

Transition Metals and Compounds

Summary. The lattice structure, the bond length, the cohesive energy, and the bulk modulus across each of the three rows of the transition metals are presented. The role of the Coulomb repulsion vs. the width of the d band is examined and its relation to magnetic properties is pointed out. Band structure calculations are performed usually by the APW or the KKR methods (if accuracy is sought) or by LCAO if simplicity is asked for. Among the important compounds of transition metals are the perovskites, the ceramic high- T_c superconductors, and the oxides.

15.1 Experimental Data for the Transition Metals

By the term *transition metal* we mean usually those composed of atoms having the 3d or 4d or 5d shell partially filled (i.e., those in the box of the periodic table from Sc to Ni, down to Pt and back to La, without the lanthanides). It is not unusual to include in the transition metals the noble ones (i.e., Cu, Ag, Au) and even the Zn, Cd, and Hg.

The transition metals include iron, the most important metal both technologically and historically, which being alloyed with carbon and other transition metals (Mn, Ni, Cr, V, etc.) makes the various types of steel. They include also some of the heaviest, with the highest cohesive energy and highest melting point solids such as Ir (iridium), Os (osmium), W (tungsten), etc. Iron, Co, and Ni exhibit spontaneous magnetization and as a result they find many technological uses.

In Fig. 15.1 the variation of the radius r_a per atom (first row), of the cohesive energy per atom U_c (second row), and of the bulk modulus B (third row) is shown as we move across the 3d row, the 4d row, and the 5d row of the periodic table. Notice that in every row and around its middle the smaller radius r_a , the highest energy U_c , and the highest bulk modulus B appear.

To interpret this behavior keep in mind that the radius R_d of the nd orbital is smaller than the radius R_s of the $(n + 1)$ s orbital by a factor $n^2/(n + 1)^2$ where $n = 3, 4, 5$ for 3d, 4d, and 5d row, respectively; hence, the radius per

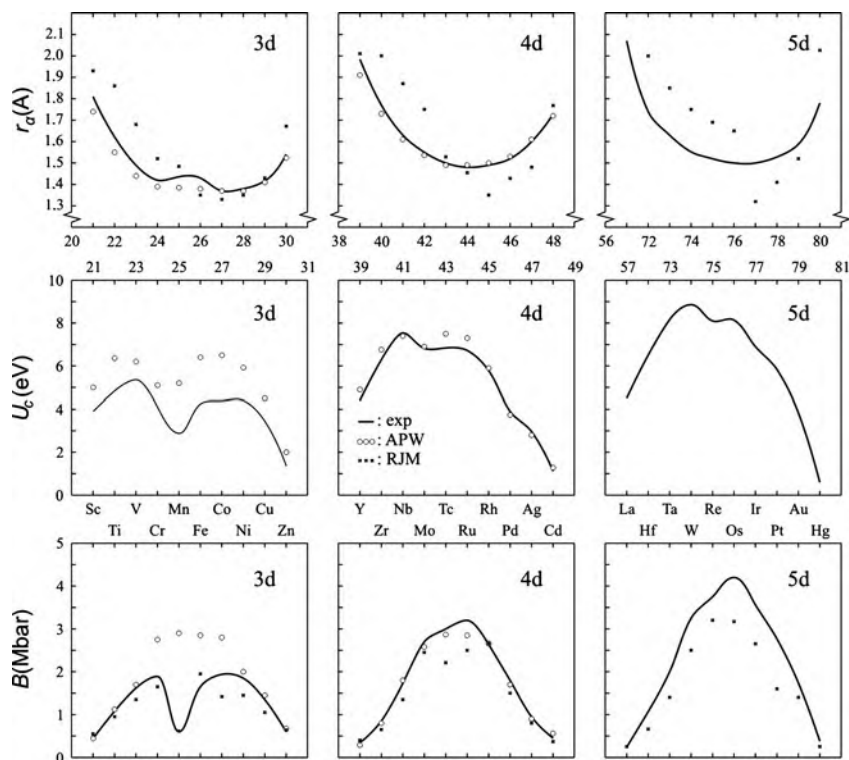


Fig. 15.1. The radius, r_a , per atom, the cohesive energy, U_c , per atom, and the bulk modulus, B , across the three rows of the transition metals. The solid line passes through the experimental data, the open circles are the theoretical results of V. L. Moruzzi *et al.* (Phys. Rev. B **15**, 2854 (1977)) based on the APW method, and solid points are the RJM results for r_a and B (U_c results based on RJM being unreliable are not presented)

atom is determined by R_s . On the other hand, the energy of the $(n+1)$ s orbitals are comparable to the energy of the nd orbitals. For zero or low occupation of the d orbitals the $(n+1)$ s level is lower than the nd energy as indicated by the double occupation of the $(n+1)$ s level; as a result, the screening of the s electrons by the d electrons is nonexistent or weak. As the occupation of the d states increases, the d-level shrinks and the d-electrons screening action becomes more efficient. Thus, as we move from the left end point of each series, the s electrons experience initially the increased effective nuclear charge, and hence, their radius R_s shrinks. Eventually, this tendency is reversed as a result of the more efficient screening by the d electrons. Especially for the 3d row this reversal seems to take place twice: the first time at $Z = 24$ (i.e., Cr) and the second time at $Z = 28$ (i.e., Ni). It is no coincidence that in the Cr atom the electronic configuration becomes $3d^5 4s^1$ vs. $3d^3 4s^2$ in

V indicating a drop of the 3d level below the 4s level and, consequently, a dramatic increase of the screening by the d electrons; similarly, between Ni and Cu the electronic configuration changes from $3d^8 4s^2$ to $3d^{10} 4s^1$.

This non-monotonic variation of R_s as we move across the transition metal series implies a similar variation of r_a (since the $(n+1)$ s orbitals is the most external occupied orbital in the nd series and, as a result, it determines r_a); the quantities U_c and B exhibit also a similar variation (since both U_c and B are inversely proportional to some power of r_a). At this point we must stress the intermediate character of the d levels in the transition elements. As it was pointed out before, the d orbitals are clearly interior to the s orbitals (see also Fig. B.1) but not as close to the nucleus as to be irrelevant to the solid formation. As a result, the d levels develop into bands that, however, are much narrower than the s bands. The ratio W_d/W_s of the d bandwidth to the s bandwidth is expected to be smaller for the 3d series than for the 4d series (which in turn is expected to be smaller than for the 5d series); this is a consequence of the fact that $R_d/R_s \approx n^2/(n+1)^2 = 0.56, 0.64$, and 0.69 for the 3d, 4d, and 5d series.

In addition, we expect the d electrons in these narrow overlapping bands to be correlated. These correlations are stronger, the narrower the bandwidth is and the higher the occupation of these d bands is. In other words, as we move from the left end of each series to the right end and from 5d series to the 3d series, the d electrons become more and more correlated and behave less and less as independent Bloch electrons. According to this argument, the most severe deviations from the picture of independent band electrons are expected toward the right end of the 3d series. Indeed, the last three elements of this series, Fe, Co, and Ni, are the only ones among the elemental transition metals that exhibit ferromagnetic behavior. Furthermore, the two preceding them, Cr and Mn, are antiferromagnets. Ferromagnetism and antiferromagnetism are incompatible with the picture of independent Bloch electrons and require for their existence strong correlations due to increased Coulomb el-el interactions.

Further evidence supporting the expected deviations from the independent electron picture in the 3d series is the observed disagreement (first column in Fig. 14.1) between the experimental data and the theoretical results based on the reliable APW method (reliable within the framework of the independent electron picture). On the contrary, for the 4d series (second column in Fig. 14.1), for which the ordinary band picture is expected to be closer to reality, the agreement between the APW results and the experimental data is quite good.

In conclusion, the d overlapping bands in elemental transition metals and compounds, under weak correlation among their electrons, behave as ordinary bands, while under strong correlation they behave more like being localized (in the sense of developing microscopic magnetic moments and not contributing significantly to the conductivity).

15.2 Calculations I: APW or KKR

Band structure calculations for the elemental transition metals have been performed mostly by the advanced APW and KKR methods. In Figs. 15.2–15.4 the band structure results along the straight line segment ΓM (for the *hcp* lattice), or ΓH (for the *bcc* lattice), or ΓX (for the *fcc* lattice) are plotted for all transition metals. These results provide quantitative support to the qualitative conclusions we reached in Sect. 15.1 following simple physical arguments. Anyway, here are the main points one can extract from Figs. 15.2–15.4:

1. The band structure consists of an almost free-electron branch $E \sim k^2$ and branches involving the five *d* orbitals. The branch $E \sim k^2$ starts from the point Γ_1 and ends up at the point H_{15} (for the *bcc* lattice) or the point X'_4 (for the *fcc* lattice).¹ There is strong hybridization between the $E \sim k^2$ branch and the *d* branches.
2. The total bandwidth of the *d* branches (which is equal to the difference between the point H'_{25} and H_{12} (for the *bcc* lattice) or between the points X_5 and X_1 (for the *fcc* lattice)) is much smaller than the bandwidth of the $E \sim k^2$ branch. As was pointed out in Sect. 15.1, the ratio of these two bandwidths is smaller for the series 3*d* than for the series 4*d* and 5*d*. It becomes also smaller as we move from the left to the right as a result of the shrinking of the *d* bands width. These results support the conclusion that, as we move up and to the right of the transition part of the periodic table, the *d* electrons retain more their atomic localized character.
3. As we move from left to right within each series and for a given lattice structure, the combined composite *d* band sinks more and more relative to the Fermi level (dashed line). For Cu, Zn, Ag, Cd, and Au, the entire *d* band is below the Fermi energy and, as a result, does not participate in the excited states.

In Fig. 15.5 we plot the DOS for nine characteristic transition metals, three from each series. In almost all cases, the *d* bands produce a complicated DOS with four main peaks and further fine structure. The total width of the combination of the *d* bands is in the range between approximately 6 and 12 eV. As we move from left to right in each series, the number of electrons increases, and consequently, the Fermi level runs across the width of the composite *d* band from the lower end until the upper end, passing through deeps and peaks. Thus, the DOS at E_F , exhibits strong fluctuations from metal to metal, as shown in Fig. 15.6 (taken from [SS76], p. 493). Hence, the coefficient of the linear term in the specific heat and the magnetic susceptibility, being proportional to ρ_F , will also exhibit equally strong variations among elemental

¹ The *hcp* lattice has two atoms per primitive cell and, as a result, produces twice as many branches as the *bcc* or the *fcc* lattice structure. For this reason it is not easy to distinguish the branch $E \sim k^2$ from the overlapping ten *d* branches. Zn and Cd are obvious exceptions.

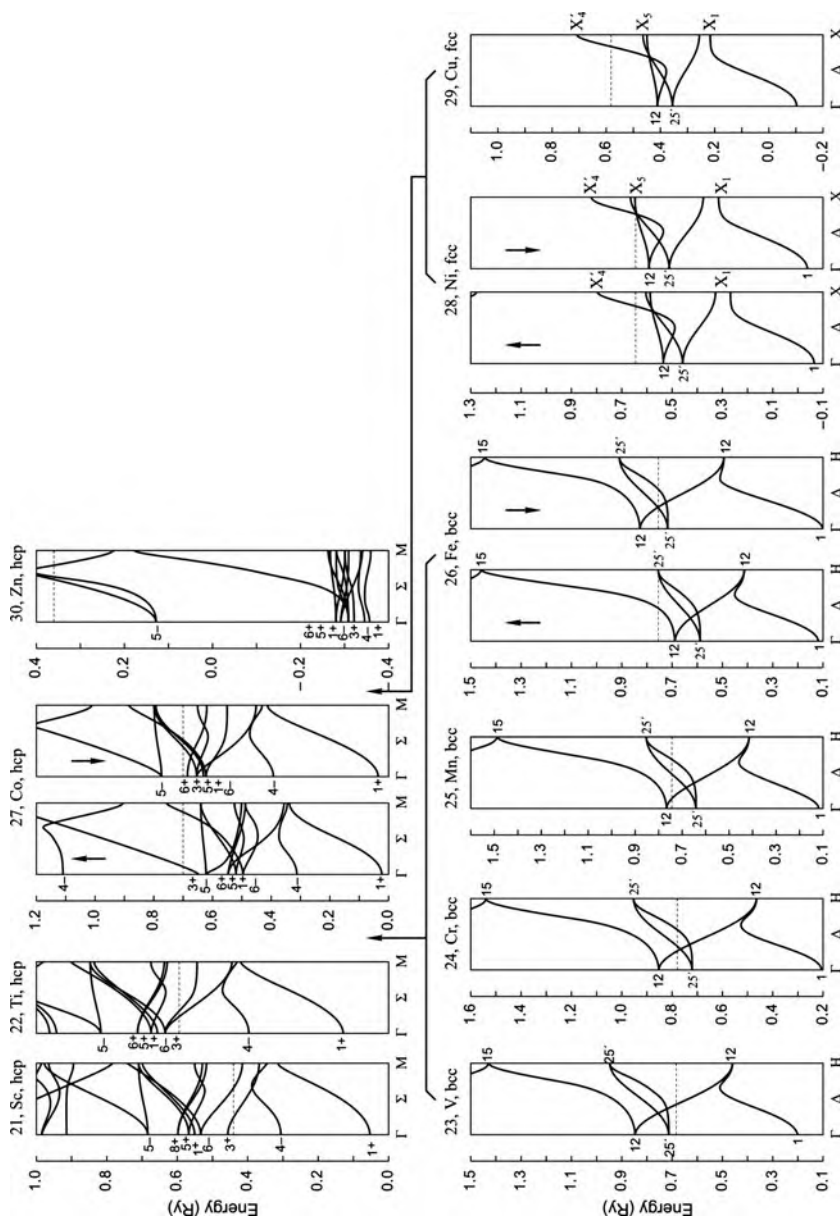


Fig. 15.2. Band structure of the elemental transition metals of the 3d series (after Papaconstantopoulos [SS81], based on the APW method). Within similar lattice structure (*hcp*, *bcc*, or *fcc*) the elements have been arranged according to their atomic number. For the ferromagnetic metals Fe, Co, and Ni both the spin up and the spin down results are shown

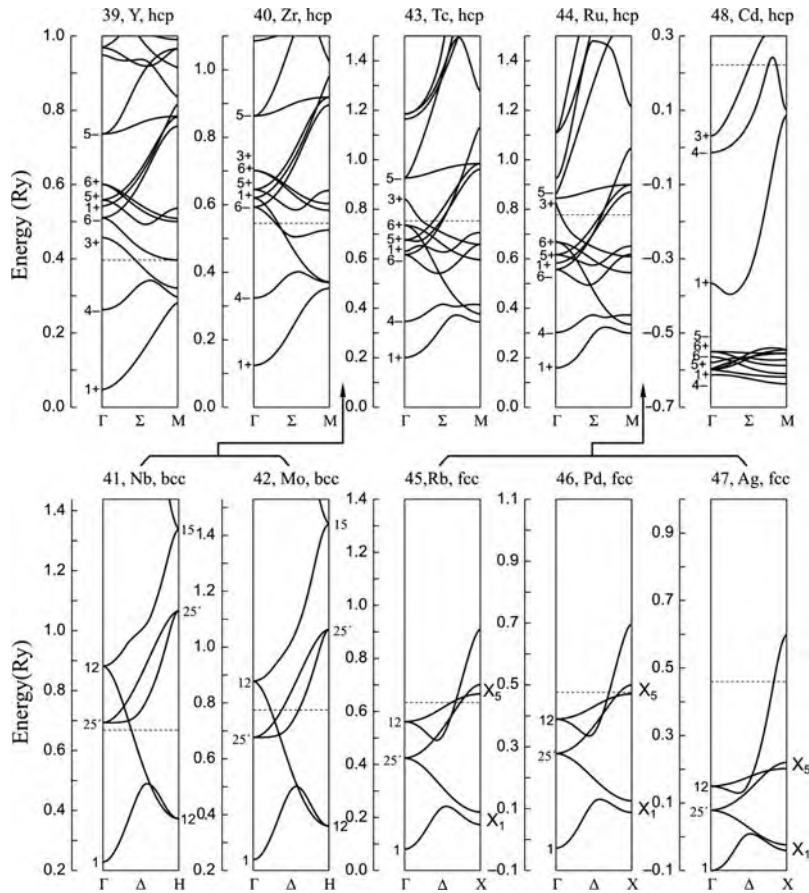


Fig. 15.3. As in Fig. 15.2 but for the 4d series. There are no ferromagnetic metals in this series

transition metals. For example, the ρ_F of Pd is more than six times larger than the ρ_F of W.

The Fermi surface of transition metals, as determined experimentally and theoretically, is in general complicated and it cannot be guessed by transferring to the first BZ the properly modified pieces of it belonging to other BZs. In Fig. 15.7 the proposed Fermi surface of tungsten is shown as an example of a complicated Fermi surface consisting of disjoint pieces.

For such complicated Fermi surfaces, it is possible that two or more different pieces are “parallel” to each other, in the sense that they coincide if translated by the same vector $\mathbf{k}_0$. The occurrence of two or more “parallel” to each other pieces of the Fermi surface is called *nesting*. An example of nesting occurs in Cr and it is shown schematically in Fig. 15.8. Its importance lies in providing many pairs $\{|\mathbf{k}\rangle, |\mathbf{k} + \mathbf{k}_0\rangle\}$ of degenerate states (where $\mathbf{k}$

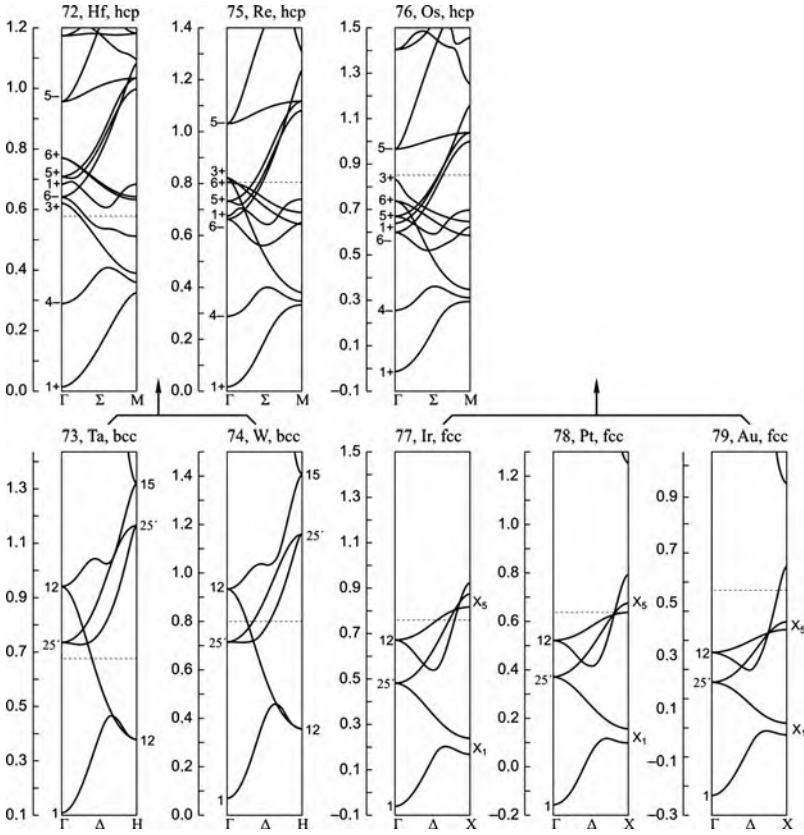


Fig. 15.4. As in Fig. 15.2 but for the 5d series. There are no ferromagnetic metals in this series

belongs to one of the nesting pieces). Thus the appearance of a perturbation of the form $\cos(\mathbf{k}_0 \cdot \mathbf{r} + \phi)$ will couple the two states of each pair creating a level repulsion that will lower the energy of each pair. The total energy will be lowered as well, since the same perturbation will lower the energy of too many pairs as a result of nesting. Thus in the presence of nesting the appearance of a new structure that will introduce a perturbation of the form $\cos(\mathbf{r}_0 \cdot \mathbf{k} + \phi)$ is energetically favorable. This phenomenon is analogous to Peierls instability occurring in 1-D systems (see p. 162). It is the nesting that makes a 3-D system to behave as a one-dimensional one. In Cr the appearance of antiferromagnetic ordering is attributed to the nesting shown in Fig. 15.8.

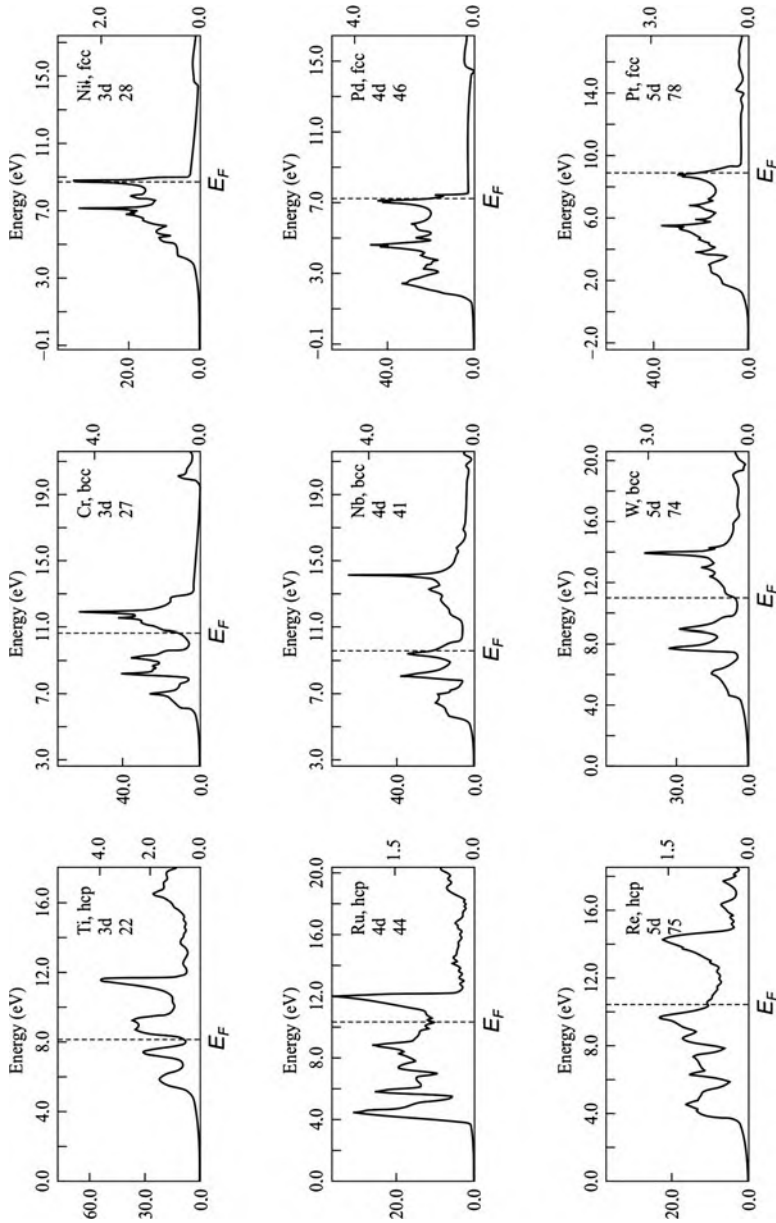


Fig. 15.5. DOS per atom and Ry (left), or eV (right), vs. energy for nine characteristic transition metals, three for each series (in the same row), and three for each lattice structure (in the same column). The atomic number for each of the nine elements is also shown. The low background corresponds to the branch $E \sim k^2$, while the superimposed structure with its peaks and deeps corresponds to the d branches

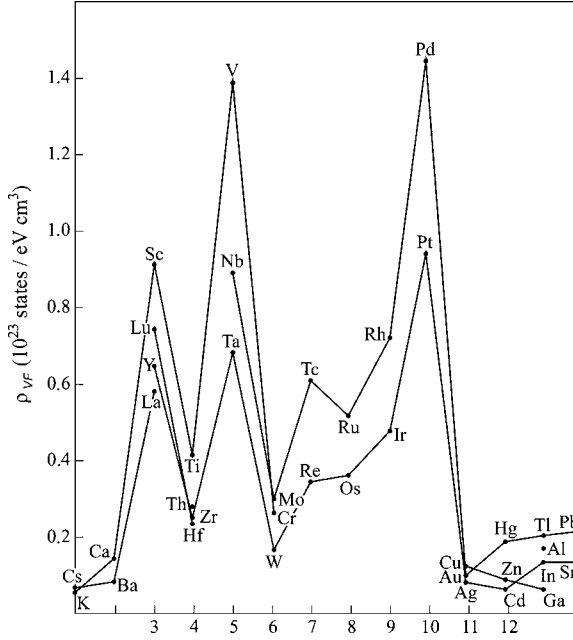


Fig. 15.6. The DOS at E_F , ρ_{VF} , per eV and volume for the transition metals. The horizontal axis is the number of electrons per atom in the s and d external orbitals. The DOS at E_F for alkalis, alkaline earths, noble metals, Zn, Cd, Hg as well as some sp metals are also shown for comparison See Harrison [SS76], p. 493

15.3 Calculations II: LCAO

The simple version of the LCAO, which we employ in Chaps. 6 and 7, has been extended by Harrison [SS76], pp. 479–487, in order to treat the transition metals and their compounds. The simplifying assumptions are the following:

1. Each transition atom has six atomic orbitals, five d and one s.
2. The matrix elements of the Hamiltonian are characterized by three quantities: r_d , k_d , and d , the bond length. The first two are associated and characterize each atom. The length r_d is used for the calculation of the off-diagonal matrix elements as shown in Fig. 15.9. The quantity k_d determines the energy difference, E_d , between the middle, ε_d , of the composite d band and the lower band edge $E_s(0)$ of the s-like branch, according to the formula

$$E_d = \frac{\hbar^2 k_d^2}{2m_s^*}, \quad (15.1)$$

where $m_s^* = m^* [1 + (5r_d^3/\pi r_a^3)]^{-1}$; m^* is usually taken equal to the free electronic mass. In Table 15.1 the Harrison's choices ([SS76], p. 552) for

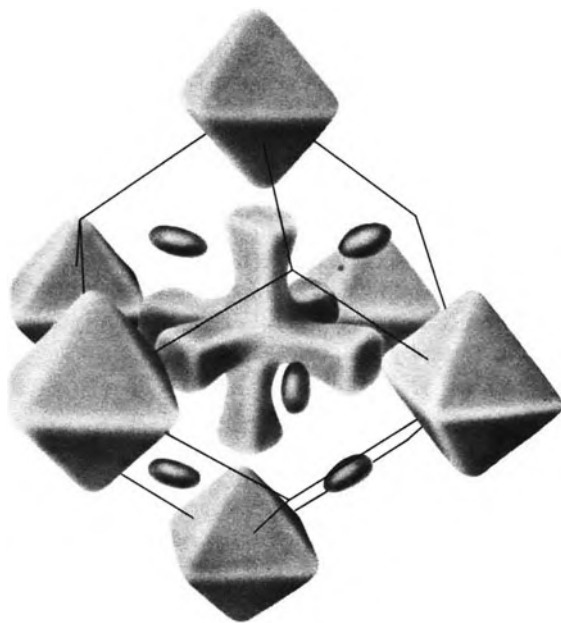


Fig. 15.7. The proposed Fermi surface for tungsten (W), which forms a bcc lattice (see [SS75], p. 306). The six “octahedral” at the corners of the first BZ and the 12 ellipsoids at the faces of the first BZ form closed surfaces in the repeated zone scheme and they enclose empty states. The 3-D cross-like surface at the center of the first BZ encloses occupied states. The volume of one octahedron plus six ellipsoids, equal the volume of the central cross-like shape. Thus tungsten is a compensated metal, $n_e = n_h$, and, consequently, the magnetoresistance grows proportionally to B^2 in all directions (see (10.76))

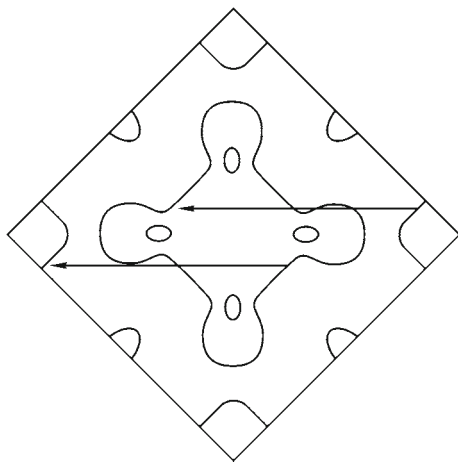


Fig. 15.8. Cross-section of the Fermi surface of Cr by a plane of slightly different orientation than that of (001). The vector connecting “parallel” pieces of the Fermi surface is shown (see [SS76])

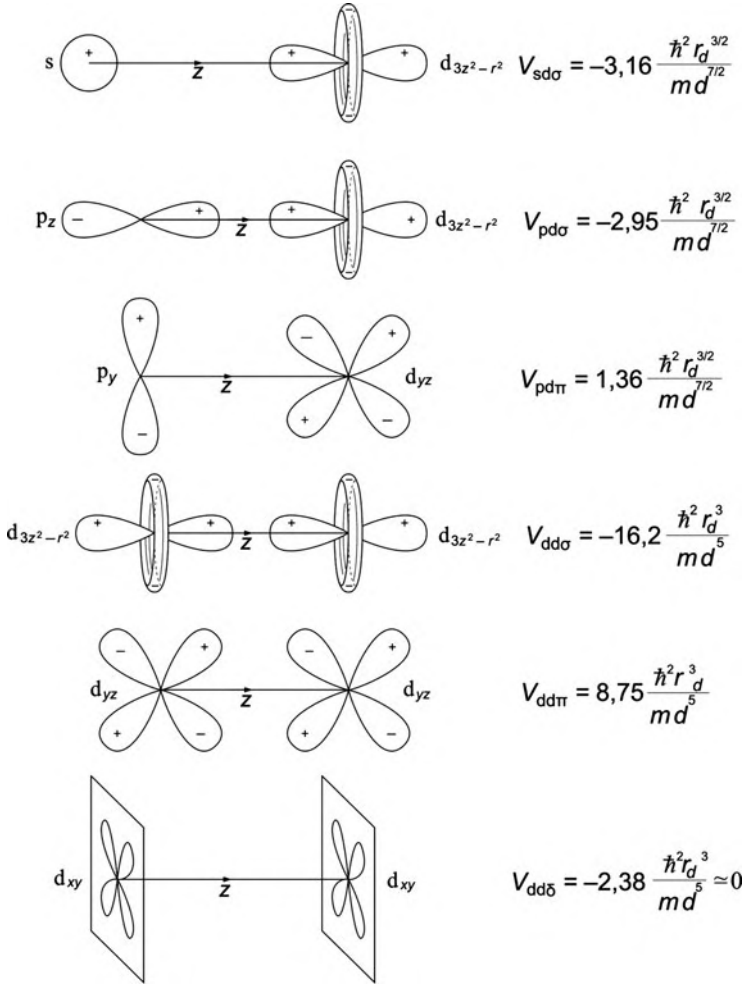


Fig. 15.9. The off-diagonal matrix elements of the Hamiltonian between pairs of s and d , of p and d , and of d and d orbitals belonging to nearest neighbor atoms, according to Harrison's approximation. The vector joining the centers of the two atoms is assumed to be $d(0, 0, 1)$. For the general orientation $d(\ell, m, n)$ of this vector relative to orbitals see the Slater-Koster formulas [15.7] (see p. 481 of Harrison's book)

the quantities r_d and k_d and for each transition element are given. Notice that r_d is decreasing monotonically as we move from left to right in each series.

3. The diagonal matrix element ε_s of the s band is chosen to be equal to ε_d , and the off-diagonal $V_{ss\sigma}$ to satisfy the relation $\varepsilon_s - E_s(0) = \varepsilon_{d0} - E_s(0) = E_d$, which implies (see Problem 10.4s)

Table 15.1. Values of the parameters r_d (in Å) and k_d (in Å⁻¹) for the transition elemental metals according to Harrison

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	
r_d	1.24	1.08	0.98	0.90	0.86	0.80	0.76	0.71	0.67	3d
k_d	1.11	1.17	1.21	1.22	1.24	1.25	1.24	1.22	1.15	
r_d	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	4d
k_d	1.58	1.41	1.28	1.20	1.11	1.05	0.99	0.94	0.89	
r_d	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	5d
k_d	1.58	1.44	1.34	1.27	1.20	1.13	1.08	1.04	1.01	
r_d	1.09	1.12	1.15	1.16	1.15	1.14	1.10	1.07	0.98	

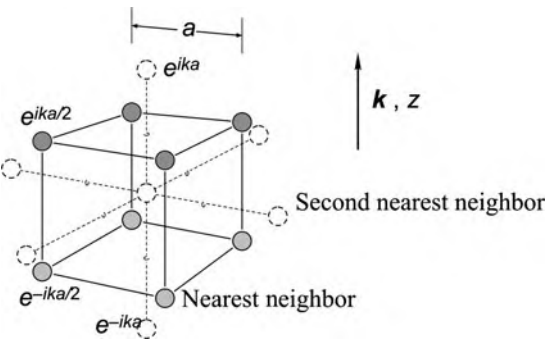


Fig. 15.10. The nearest neighbors and the second nearest neighbors in a bcc direct lattice

$$\begin{aligned} V_{ss\sigma} &= -\frac{E_d}{8} \text{ for bcc,} \\ V_{ss\sigma} &= -\frac{E_d}{12} \text{ for fcc.} \end{aligned} \tag{15.2}$$

As an example of the application of Harrison’s LCAO method in transition metals, we shall calculate the band structure of a bcc metal for $\mathbf{k}$ along the high-symmetry ΓH line segment (to be chosen as the z -direction). The matrix elements $\langle 0, a | H | \mathbf{R}_n, \beta \rangle$ between the atomic orbital a of an atom located at the origin and the atomic orbital β of an atom located at the site $\mathbf{R}_n$ (where $\mathbf{R}_n$ is the site of a nearest neighbor or second nearest neighbor) is obtained for each lattice structure by a combination of Fig. 15.9, and the Slater–Koster table; the case of the bcc lattice is shown in Fig. 15.10.

The next step is to find the matrix elements $H_{a\beta}(\mathbf{k}) = \sum_{\mathbf{R}_n} \exp(i\mathbf{k} \cdot \mathbf{R}_n) \cdot \langle 0, a | \hat{H} | \mathbf{R}_n, \beta \rangle$ (see (6.49) and Problem 6.3t), which by taking advantage of

Bloch's theorem are diagonal in $\mathbf{k}$ (i.e., there is no coupling between $H_{a\beta}(\mathbf{k})$ and $H_{\gamma\delta}(\mathbf{k}')$ for $\mathbf{k}' \neq \mathbf{k}$). Because $\mathbf{k}$ has been chosen along a high symmetry axis several matrix elements $H_{a\beta}(\mathbf{k})$ are immediately zero for all $\mathbf{k}$ s in this direction. If the readers are familiar with applications of group theory, they can determine a priori which matrix elements $H_{a\beta}(\mathbf{k})$ are identically zero. Otherwise, he has to calculate all matrix elements $\langle 0, a | \hat{H} | \mathbf{R}_n, \beta \rangle$ and to do the summations over $\mathbf{R}_n$ in order to find out which $H_{a\beta}(\mathbf{k})$ are zero and which are not. Here we quote the final result for the matrix $H_{a\beta}(\mathbf{k})$, which has the following form

$$\begin{vmatrix} A & 0 \\ 0 & B \end{vmatrix}, \quad (15.3)$$

where A is a 2×2 matrix

$$A = \begin{vmatrix} H_{ss}(\mathbf{k}) & H_{s,3z^2-r^2}(\mathbf{k}) \\ H_{s,3z^2-r^2}(\mathbf{k}) & H_{3z^2-r^2,3z^2-r^2}(\mathbf{k}) \end{vmatrix}, \quad (15.4)$$

and B is a diagonal 4×4 matrix with matrix elements

$$H_{x^2-y^2, x^2-y^2}(\mathbf{k}) = \frac{16}{3}V_{dd\pi} \cos\left(\frac{ka}{2}\right) + 3V_{dd\sigma}^{(2)} + \varepsilon_d, \quad (15.5)$$

$$H_{xy, xy}(\mathbf{k}) = \left[\frac{8}{3}V_{dd\sigma} + \frac{16}{9}V_{dd\pi} \right] \cos\left(\frac{ka}{2}\right) + 4V_{dd\pi}^{(2)} + \varepsilon_d, \quad (15.6)$$

$$H_{zx, zx} = \left[\frac{8}{3}V_{dd\sigma} + \frac{16}{9}V_{dd\pi} \right] \cos\left(\frac{ka}{2}\right) + 2V_{dd\pi}^{(2)} (1 + \cos ka) + \varepsilon_d, \quad (15.7)$$

$$H_{zy, zy} = H_{zx, zx}. \quad (15.8)$$

Furthermore,

$$H_{ss}(\mathbf{k}) = 8V_{ss\sigma} \cos\left(\frac{ka}{2}\right) + \varepsilon_d, \quad (15.9)$$

$$H_{s,3z^2-r^2}(\mathbf{k}) = -4V_{sd\sigma}^{(2)} \sin^2\left(\frac{ka}{2}\right), \quad (15.10)$$

$$H_{3z^2-r^2, 3z^2-r^2}(\mathbf{k}) = \frac{16}{3}V_{dd\pi} \cos\left(\frac{ka}{2}\right) + 2V_{dd\sigma}^{(2)} \left[\cos(ka) + \frac{1}{2} \right] + \varepsilon_d. \quad (15.11)$$

The upper index (2) denotes second nearest neighbor. The matrix elements $V_{dd\delta}$, $V_{dd\delta}^{(2)}$, and $V_{ss\sigma}^{(2)}$ were taken to be zero. The readers are urged to prove (15.3) till (15.11), to calculate explicitly the Mn band structure along ΓH , and to compare with the Mn result in Fig. 15.2.

15.4 Calculations III: The Simple Friedel Model

Our previous analysis shows that there are two parameters that give the gross features of the DOS in transition metals. One is the difference E_d giving the position of the composite d band relative to the lower band edge of the $E \sim k^2$

branch (see (15.1)). The second is the bandwidth W_d of the composite d band. As it was mentioned before this bandwidth is the difference between the point H_{25} and the point H_{12} in Fig. 15.2 for the *bcc* lattice. The point H_{25} is the same as $H_{xy,xy}$ for $ka = 2\pi$ while the point H_{12} is the same as $H_{x^2-y^2, x^2-y^2}$ again for $ka = 2\pi$. From (15.6) and (15.5) in combination with Fig. 15.9 we obtain

$$W_d = 115 \frac{\hbar^2 r_d^3}{m d^5} = 6.83 \frac{\hbar^2 r_d^3}{m r_a^5}. \quad (15.12)$$

The last expression in (15.12) does not involve quantities associated with any specific lattice.

The simplest possible model for the DOS incorporating E_d and W_d is the one proposed by Friedel [15.2]. The branch $E(k) = \hbar^2 k^2 / 2m_s^*$ contributes a DOS per atom and spin of the form

$$\rho_s(E) \simeq \frac{1}{3\pi} \left(\frac{2m_s^* r_a^2}{\hbar^2} \right)^{3/2} E^{1/2}. \quad (15.13)$$

The composite d band DOS $\rho_d(E)$ is replaced by a gross approximation of a constant extending from $E_d - W_d/2$ to $E_d + W_d/2$.

$$\begin{aligned} \rho_d(E) &\simeq \frac{5}{W_d}, & E_d - \frac{W_d}{2} < E < E_d + \frac{W_d}{2} \\ \rho_d(E) &= 0 & \text{Otherwise.} \end{aligned} \quad (15.14)$$

In Fig. 15.11 we plot the gross approximation to the DOS according to Friedel. Using this model DOS, we can determine the Fermi energy, the number of electrons ζ_s in the s band and the number of electrons ζ_d in the composite d band by the relations

$$\zeta_s + \zeta_d = \zeta_{sd}, \quad (15.15)$$

$$\zeta_i = 2 \int^{E_F} \rho_i(E) dE, \quad i = s, d. \quad (15.16)$$

The quantity ζ_{sd} is the total number of electrons in the incomplete shell involving both s and d levels, which is immediately known for each element.

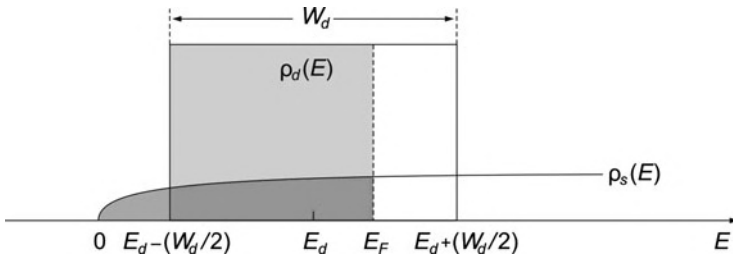


Fig. 15.11. The DOS for a transition metal according to the simple Friedel model

Table 15.2. Calculated values of ζ_d (according to (15.15) and (15.16)) and experimental values of the cohesive energy U_c (in eV per atom) for the elemental transition metals

ζ_{sd} Series	3	4	5	6	7	8	9	10	11	12
3d	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
ζ_d	2.54	3.42	4.31	5.24	6.18	7.16	8.16	9.19	10	10
U_c	3.90	4.85	5.31	4.10	2.92	4.28	4.39	4.44	3.49	1.35
4d	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
ζ_d	2.32	3.38	4.40	5.37	6.32	7.3	8.31	9.27	10	10
U_c	4.37	6.25	7.57	6.82	6.85	6.74	5.75	3.89	2.95	1.16
5d	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
ζ_d	—	—	4.18	5.04	5.96	—	—	—	10	10
U_c	4.47	6.44	8.10	8.90	8.03	8.17	6.94	5.84	3.81	0.67

The highest cohesive energy (in eV per atom) within each series is written in bold to facilitate the checking of the prediction that $U_{c, \max}$ corresponds to ζ_d around 5

Problem 15.1t. Find E_F , ζ_s , and ζ_d for V and Cr.

The simple Friedel model can be used also to find out which metal in each series has the maximum cohesive energy (assuming that this maximum coincides with the maximum of the energy $|U_d|$ associated with the formation of the composite d band). Obviously,

$$U_d = 2 \int_{E_0}^{E_F} dE \rho_d(E) E - \zeta_d E_d, \quad (15.17)$$

where $E_0 = E_d - (W_d/2)$ is the lower edge of the d band.

Problem 15.2t. Show that U_d is equal to

$$U_d = -5W_d \left[\left(\frac{\zeta_d}{10} \right) - \left(\frac{\zeta_d}{10} \right)^2 \right]. \quad (15.18)$$

The lowest value of U_d – and hence, the highest value of the cohesive energy – is obtained when $\zeta_d = 5$. In Table 15.2 the calculated value of ζ_d (according to (15.15) and (15.16)), for each of the elemental transition metals is given together with the experimental value of the cohesive energy per atom in order to test the conclusion that $\zeta_d = 5$ corresponds to the largest cohesive energy.

15.5 Compounds of Transition Elements, I: Perovskites

Perovskites are compounds of the following chemical formula ABD_3 , where D is usually oxygen (although it could be fluorine), B is usually a transition element, and A is usually a simple metal such as an alkali or alkaline earth.

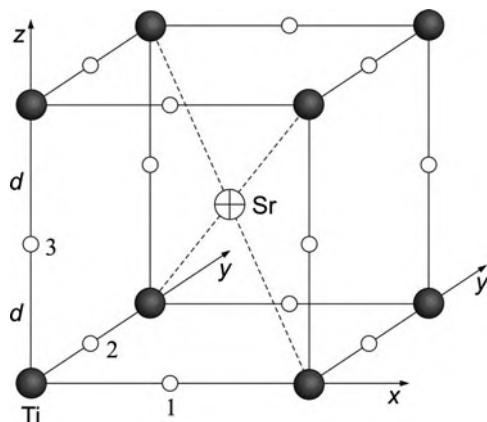


Fig. 15.12. Crystal structure of a typical perovskite: SrTiO_3 . The transition atoms occupy the eight corners of the primitive cubic cell; the simple metal atom the center of the cube, and the oxygen atoms the middle of each of the 12 edges. Thus the primitive cell contains one transition atom ($8/8$), one simple metal atom, and three oxygen atoms ($12/4$); d is the distance between oxygen and transition metal atoms; $a = 2d$

Common perovskites are: SrTiO_3 , KMoO_3 , KTaO_3 , Na_xWO_3 (where x is in the range between 0 and 1), PbTiO_3 , KMnF_3 , KFeF_3 , KCoF_3 , KCuF_3 . There are perovskites that have no transition element, e.g., NaMgF_3 .

The main characteristic of perovskites is their crystal structure, which is shown in Fig. 15.12 with $\text{Sr} \equiv \text{A}$, $\text{Ti} \equiv \text{B}$, and $\text{O} \equiv \text{D}$. In cases such as Na_xWO_3 with $x < 1$, the simple metal atom is missing in some primitive cells. These vacant cells are usually randomly located.

Perovskites exhibit either metallic or insulating behavior. The latter appears when the total number of electrons required for the completion of the p shells of the oxygen atoms (six electrons) or the three fluorine atoms (three electrons) is equal to the number of valence electrons in A and B together. Thus, SrTiO_3 is an insulator since the two valence electrons of Sr plus the four of Ti are just enough to complete the shell of the three oxygen atoms.

When the sum of the valence electrons of A plus B exceeds the ones needed to complete the shells of the three D elements, the perovskite can be either a conductor or an insulator. For example, in KMoO_3 the one electron of K plus the six of Mo exceed the six needed by the three oxygen atoms. The one electron left remains in the composite d band of Mo and it is responsible for the metallic behavior of KMoO_3 . Similarly in the compound PbTiO_3 out of eight electrons offered by Pb and Ti six are used by the three oxygen atoms and the remaining two populate the mixed band of Pb and Ti. On the other hand, in KFeF_3 , the nine electrons offered by the metals (one from K and eight from Fe) only three are needed by F. The remaining six are expected to occupy the s and d bands of iron. However, the behavior of KFeF_3 is *insulating*, which implies that the composite d band of iron in KFeF_3 is exhibiting a strongly

correlated, localized-like behavior. This is not surprising, since iron belongs to the near right end of the 3d series where the correlations are stronger and the independent Bloch electron picture is prone to fail.

A first idea for the electronic structure of perovskites can be obtained by starting with the atomic levels of the constituent atoms and broadening them into bands. In Fig. 15.13 the so estimated bands are compared with APW band calculations in SrTiO_3 . The correspondence is surprisingly satisfactory if one takes into account how simplistic the approach that produced the results of Fig. 15.13a is; only a rough estimate of the off-diagonal matrix elements was needed in order to obtain approximately the width of the bands. Note that the top valence subband consists mainly of 2p oxygen atomic orbitals, while the bottom of the conduction band involves 3d titanium atomic orbitals; many

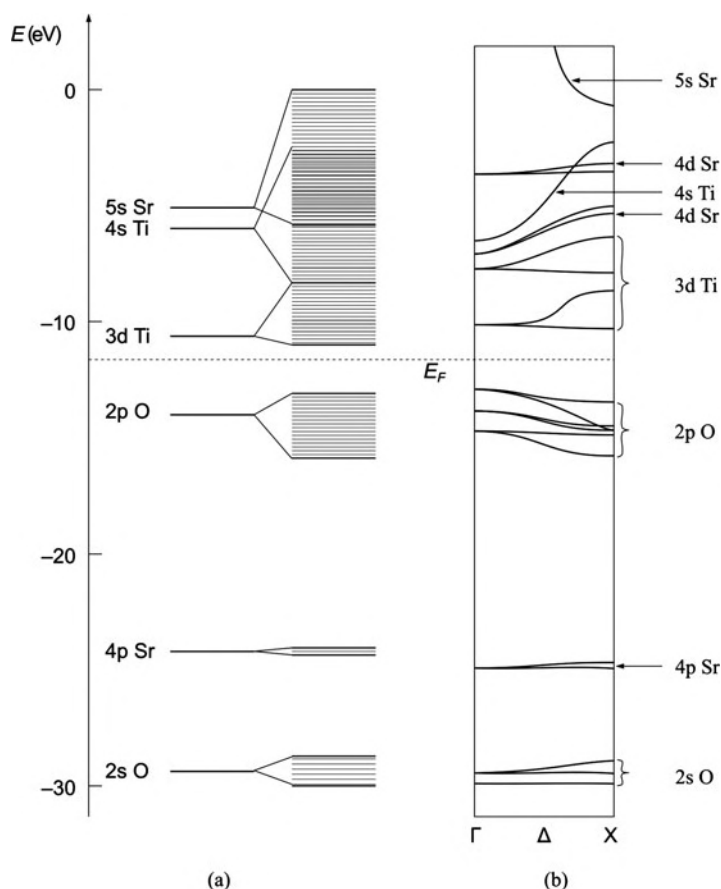


Fig. 15.13. (a) Atomic levels of the elements making up SrTiO_3 and their expected broadening into bands. (b) APW band structure calculation for SrTiO_3 corrected to reproduce the gap which is about 3 eV (L.F. Mattheiss, Phys. Rev. B **6**, 4718 (1972) [15.3])

orbitals (4s of Sr, 4s of Ti, 4d of Sr, 5s of Sr) contribute to the upper part of the conduction band. At first sight, the relatively large width of the deep 2s band of oxygen is surprising. At second thought, one has to take into account the large matrix element $V_{sd\sigma}$ between the 2s orbital of oxygen and the 3d orbital of titanium. This large value (-2.61 eV) is due to the small distance $d \simeq 1.95$ Å and the large coefficient in the corresponding matrix element (-3.16 , see Fig. 15.9).

The readers may wish to go one step further than the simplistic approach that produced the picture shown in Fig. 15.13a and employ LCAO method to produce the band structure of oxygen-based perovskites such as SrTiO_3 . The minimum number of orbitals per primitive cell are 17; 12 orbitals from the three oxygens ($3 \times 4 = 12$) and five d orbitals for titanium. This minimum choice is expected to reproduce the lower part of the conduction band and all the subbands of the valence band (with the exception of the 4p Sr, which is practically uncoupled with the rest of the band structure as indicated by its very narrow bandwidth (see Fig. 15.13b). To further simplify the problem we can choose to obtain the band structure for $\mathbf{k}$ along a high symmetry axis, e.g. the ΓX , which we identify with the z -axis. Then the 17 orbitals of the primitive cell break into groups of different symmetry that have no couplings among them. These groups are the following:

One group of five orbitals, $d_{3z^2-r^2}$, p_{3z} , $\frac{1}{\sqrt{2}}(p_{1z} + p_{2z})$, s_3 , $\frac{1}{\sqrt{2}}(s_1 + s_2)$.

One group of four orbitals, d_{zx} , p_{1x} , p_{2x} , p_{3x} .

Another equivalent group of four orbitals, d_{zy} , p_{1y} , p_{2y} , p_{3y} .

One group of a single orbital, d_{xy} .

And one group of three orbitals $d_{x^2-y^2}$, $\frac{1}{\sqrt{2}}(p_{1z} - p_{2z})$, $\frac{1}{\sqrt{2}}(s_1 - s_2)$.

Thus for the direction ΓX , the 17×17 Hamiltonian matrix breaks down to five independent matrices: one 5×5 , two 4×4 , one 1×1 , and one 3×3 . For more information the reader is referred to the book by Harrison, pp. 441–449.

15.6 Compounds of Transition Elements, II: High T_c Superconducting Materials

It was mentioned in Sect. 8.5.2 that many metals and other materials change from the normal to the superconducting state; the latter is characterized by frictionless flow of DC electric current, and expulsion of the magnetic field (perfect diamagnetism). This transition occurs for low temperatures below a critical one denoted by T_c ; until 1986 the highest T_c was 23 K for the compound Nb_3Ge . Since then a group of compounds has been identified that could be described as generalized perovskites with copper in the place of the transition element; within this group the critical temperature has reached the value of 138 K under normal pressure. Thus, this group of ceramic compounds is known as high- T_c materials. In Table 15.3 we present some of them. In Fig. 15.14 the crystal structure of the compound $\text{YBa}_2\text{Cu}_3\text{O}_7$ is presented; this material,

Table 15.3. Important high- T_c ceramic materials. $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ was the first one to be discovered; $\text{YBa}_2\text{Cu}_3\text{O}_7$ was the first with T_c above the temperature of 77 (at which liquid nitrogen is boiling under normal pressure)

Chemical formula	Abbreviation	Critical temperature (K)
$\text{YBa}_2\text{Cu}_3\text{O}_7$	Y123 or YBCO	92
$\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$	Bi2223 or BSCCO	122
$\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$	Bi2212 or BSCCO	90
$\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$	Tl2223 or TBCCO	127
$\text{Tl}_2\text{Ba}_2\text{Ca}_1\text{Cu}_2\text{O}_8$	Tl2212 or TBCCO	110
$\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$	Hg1223	135

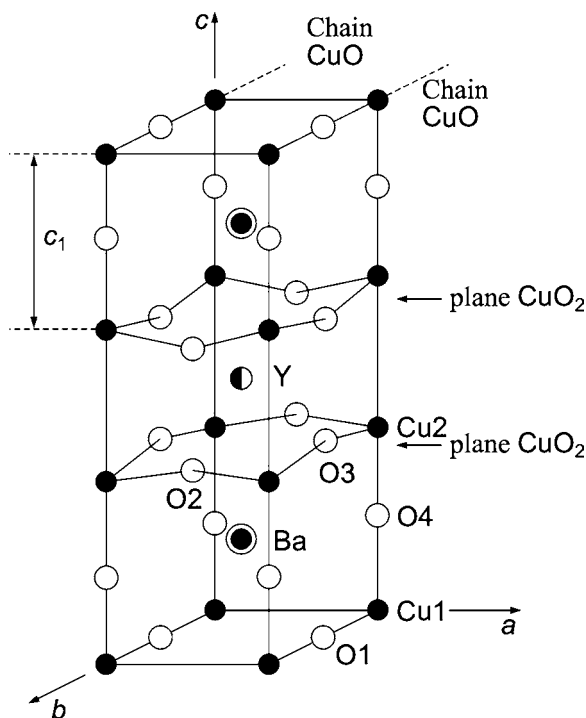


Fig. 15.14. The primitive cell of the compound $\text{YBa}_2\text{Cu}_3\text{O}_7$. In the orthorhombic phase (which is the only one to exhibit superconductivity) the dimensions are: $a = 3.82 \text{ \AA}$, $b = 3.88 \text{ \AA}$, and $c = 11.67 \text{ \AA}$ ($c_1 \simeq 3.7 \text{ \AA}$)

known also as Y123 or YBCO, was the first one to break the barrier of 77 K and thus to allow the use of liquid nitrogen as the cooling agent. As shown in Fig. 15.14, the primitive cell consists of two perovskite-like units (with copper in the place of the transition element and barium in the place of the simple metal) that are connected through the yttrium atom.

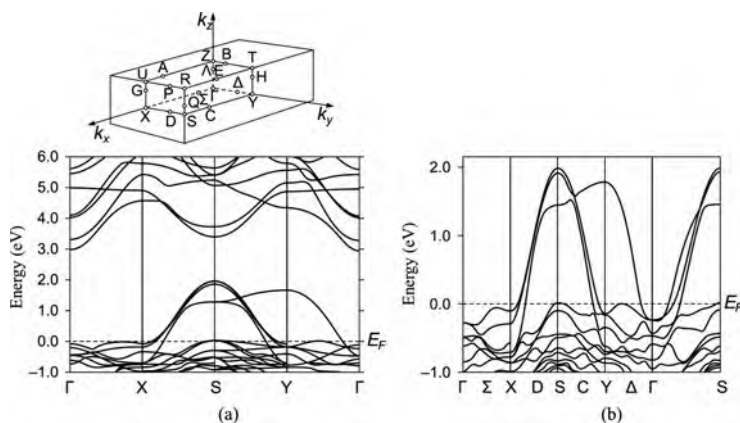


Fig. 15.15. Band structure of $\text{YBa}_2\text{Cu}_3\text{O}_7$. The first BZ is also shown. (a) The top branches of the VB and the bottom branches of the CB^2 are shown. (b) The top branches of the VB^3 in more details. The branches at the top of the VB involve almost 100% the 3d orbitals of Cu and the 2p orbitals of O

Notice that there are no oxygen atoms at the yttrium plane. Also at the base of the lower perovskite-like unit (and at the top of the upper perovskite-like unit) there are no oxygen atoms in the direction of the a -axis. Another difference between the two perovskite-like units and the normal perovskite structure is that the former are not cubic but orthorhombic ($a \neq b \neq c_1$). There are usually oxygen vacancies along the CuO chains so that the chemical formula is actually $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$; if x exceeds about 0.6 the lattice structure becomes tetragonal ($a = b$), with the oxygen atoms to occupy randomly the sites between copper atoms either in the direction a or b . Notice also that the oxygen atoms in the two CuO_2 plane have been slightly off-plane toward the yttrium atom.

Superconductivity in YBCO appears for $0 \lesssim x \lesssim 0.6$ with the maximum value of T_c occurring at $x \simeq 0.15$. In Fig. 15.15 we plot the calculated band structure of $\text{YBa}_2\text{Cu}_3\text{O}_7$ and in Figs. 15.16 and 15.17 the DOS and the Fermi surface as obtained from this band structure. Notice that the Fermi surface, although very complicated as expected for such a complex primitive cell, has an almost-cylindrical shape as a result of the large anisotropy, which makes the electronic motion almost two-dimensional in the a and b planes (if it were exactly 2-D, the projection shown in Fig. 15.17b would be curves of zero width instead of shaded areas). The readers are urged to calculate the band structure of the simplified model presented in Problem 15.4; this model captures the most basic features of the bands shown in Fig. 15.15b.

² W.Y. Ching et al., Phys. Rev. Lett, **59**, 1933 (1987).

³ W. Pickett, Phys.Rev. **B42**, 8764 (1990).

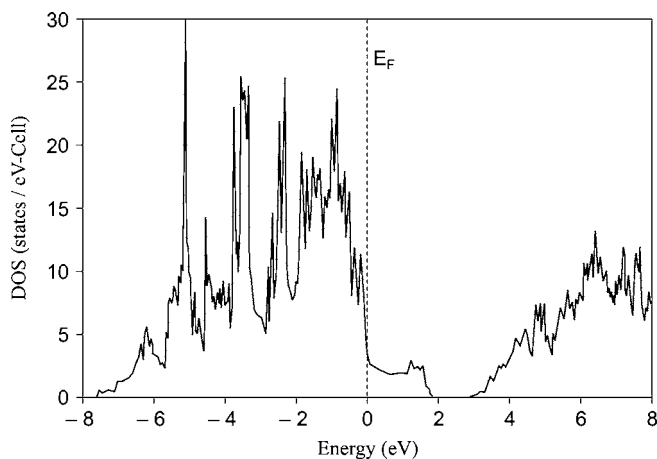


Fig. 15.16. DOS vs. energy for $\text{YBa}_2\text{Cu}_3\text{O}_7^4$

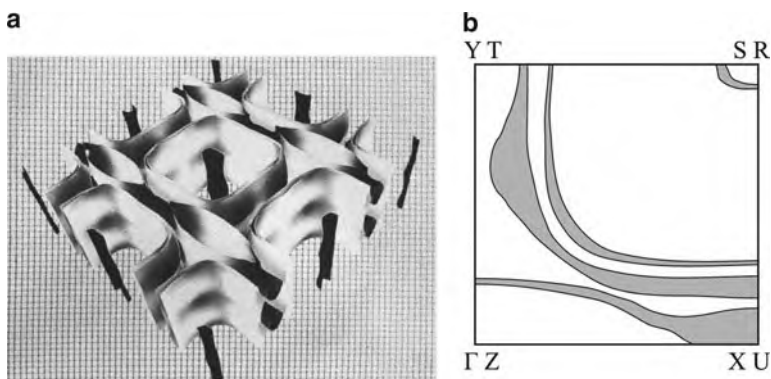


Fig. 15.17. (a) The Fermi surface of $\text{YBa}_2\text{Cu}_3\text{O}_7$ and (b) its projection (shaded area), in the first quadrant of the $k_z = 0$ plane of the first BZ⁵

Besides $\text{YBa}_2\text{Cu}_3\text{O}_7$, there are several other similar materials with even higher T_c , as shown in Table 15.3. Probably the most important technologically among them is the compound $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (with some Bi atoms replaced by Pb atoms), the lattice structure of which is shown in Fig. 15.18.

We shall conclude this section by mentioning another class of materials that, until 1986, were the champions in high T_c . These materials are compounds of Nb or V of the chemical formula Nb_3B or V_3B , where B is Si, or Ge, or Sn, or Al, or Ga. In Table 15.4 the T_c of some of these materials is shown.

⁴ W.Y. Ching et al., Phys. Rev. Lett, **59**, 1933 (1987).

⁵ W. Pickett, Phys.Rev. B**42**, 8764 (1990).

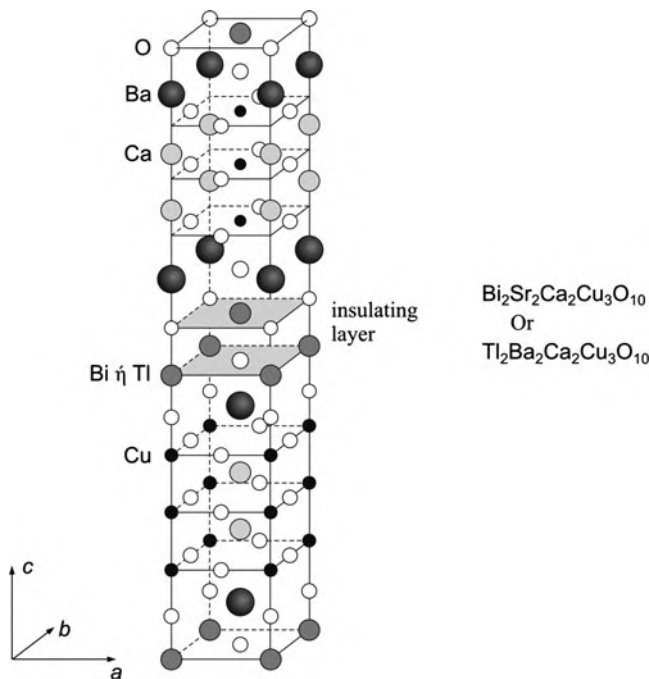


Fig. 15.18. Lattice structure of $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (the $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ has the same structure). In this figure the primitive cell has been displaced normal to the c -axis relative to this in Fig. 15.14 so that the Cu atoms in the CuO_2 planes to be at the center axis of the primitive cell

Table 15.4. Critical superconducting temperature T_c , of some materials, of the type A_3B , and of the so-called A15 type

Material	Nb_3Ge	Nb_3Sn	Nb_3Al	V_3Si	V_3Ge	V_3Ga
T_c (K)	23.2	18.05	17.5	17.1	7	16.5

In Fig. 15.19 the unit cell of the A15 crystal lattice is shown. The atoms B(Si, or Ge, or Al, etc.) occupied the center and the corners of a cube forming a bcc structure, while pairs of atoms A (Nb or V) occupy the faces of the cube along axes of symmetry parallel to the x , y , z axes as shown in Fig. 15.19. In Fig. 15.20 we plot the Nb_3Sn DOS, which is representative of the complexity of this class of materials.

15.7 Compounds of Transition Metals, III: Oxides, etc.

The simplest group of these compounds is the monoxides of the transition metals. For 3d series the first two, TiO and VO are conductors, the monoxides MnO, FeO, CoO, and NiO are antiferromagnetic insulators; the

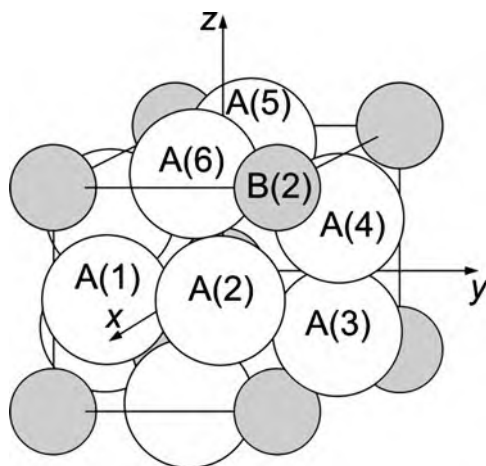


Fig. 15.19. The unit cell of the A15 lattice structure exhibited by compounds of the formula A_3B where A is either Nb or V and B is element of the III B (13) or IV B (14) columns

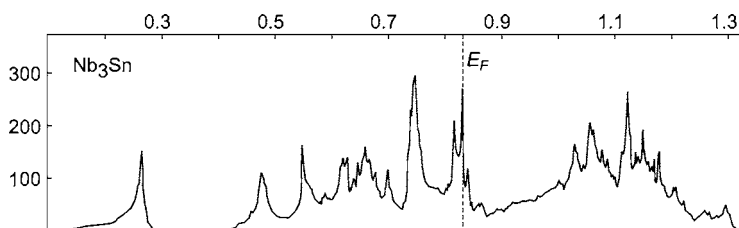


Fig. 15.20. DOS per unit cell for both orientations of spin as a function of energy (in Rydbergs) for Nb_3Sn (D. Papaconstantopoulos, private communications)

copper monoxide CuO shows semiconducting behavior. All these monoxides are strong ionic materials made of doubly charged transition cations and oxygen anions; the latter have completed their shells with two extra electrons offered by the transition atoms. Their lattice structure is that of $NaCl$ (see Fig. 3.17 and Table 3.3), since this structure is energetically favored due to the strong Coulomb attraction among ions.

The band structure of the 3d monoxides is determined by the relative position of the 2p level of oxygen and the 4s and 3d levels of the transition element. Another factor is whether or not the composite 3d band would exhibit a regular Bloch behavior. Since oxygen, being strongly electronegative, has completed all of its 2p levels, it is only natural to place the oxygen 2p band below the transition element 3d band (see also Table B.3); furthermore, the Fermi level is expected to be within the composite d band, since the latter is neither empty nor fully occupied (remember that only two electrons were removed from each transition atom). Finally, the 4s band of the

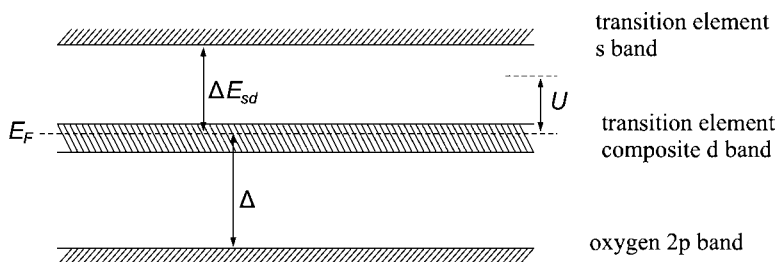


Fig. 15.21. Schematic diagram of the band of transition element monoxides; the quantity ΔE_{sd} can be negative implying overlap of the s and d bands. The effective bandwidth of the d band is W_d

transition element can be either above the 3d or it can overlap with the 3d. Hence, the situation is expected to be as shown schematically in Fig. 15.21. The propagating or localized-like behavior of the composite d band depends on the ratio U/W_d , where U is the effective intra-atomic Coulomb repulsion. If this ratio is much larger than one the transfer of electron between d-levels of neighboring atoms requires an energy U ; hence, the transport within the d band will be semiconducting-like with an effective gap $E_g \simeq U$. In the opposite limit $U \ll W_d$, the composite d band would exhibit Bloch-like conducting behavior.

On the basis of these arguments, we expect a transition element monoxide to be conducting if either ΔE_{sd} is negative or $U \ll W_d$. Otherwise, a semiconducting behavior will be exhibited with E_g being equal approximately with the smallest of the three quantities, Δ , U , ΔE_{sd} . It seems that the ΔE_{sd} is larger than Δ or U at least for the elements to the right end of the 3d row. For example, for CuO we have that $0 < \Delta < U < \Delta E_{sd}$ and, consequently, $E_g \simeq \Delta$ with the VB being the oxygen 2p and the CB the copper 3d. The holes in the VB are mobile, while the electrons in the CB are of very low mobility, since U is not negligible in comparison with W_d . In contrast, at the other end of the 3d row, the TiO 3d band shows a Bloch behavior, since the Coulomb repulsion U is small in comparison with the bandwidth W_d ; furthermore, there is an overlap with the 4s ($\Delta E_{sd} < 0$) that makes the material even more conducting. This analysis is applicable to other oxides and other similar materials. Thus:

- In the oxides V_2O_3 , Ti_2O_3 , Cr_2O_3 and the corresponding halides, the size ordering is as follows:
 $W_d \ll U < \Delta$. Hence, these materials are insulators with $E_g \simeq U$.
- In contrast, in the compounds CuO, $CuCl_2$, $CuBr_2$, $NiCl_2$, $NiBr_2$, NiI_2 we have $0 < \Delta < U$ and, as a result these materials are semiconductors with $E_g \simeq \Delta$.
- The compounds NiO, NiF_2 , CuF_2 have large values of U and Δ with $U \simeq \Delta$. Hence, they are insulators with mobile holes in the p VB and sluggish electrons in the 3d CB.

- The compounds V_2O_3 and Ti_2O_3 at higher temperatures undergo a phase transition to a conducting phase characterized by U being smaller than W_d . Thus, the composite d band at this high-temperature phase exhibits the usual Bloch behavior.
- In the compounds CuS , $CuSe$, and $NiSe$, the transfer of electrons from Cu or Ni to S or Se is clearly less than two, since Se is less electronegative than S, which is much less electronegative than O or F. To quantify this statement notice that $\varepsilon_p = -10.68$ eV for Se, -11.60 eV for S, -16.72 eV for O, and -19.86 eV for F. This partial transfer of electrons from cation to anion suggests that the p band in these compounds may overlap with the 3d band, i.e. that $\Delta \lesssim 0$, which implies metallic conductivity for these materials.

The crystal structures of these oxides, halides, etc. is determined by the competition of two terms: the Coulomb energy $E_c = \frac{1}{2} \sum_{ij} Z_i Z_j e^2 / 4\pi\epsilon_0 r_{ij}$ among the ions (which is attractive) and the overlap energy E_o (which becomes large and positive when there is substantial cation–anion overlap. Quite often E_o is replaced by a hard sphere approximation (i.e. $E_o \simeq 0$, if $r_{ij} > R_a + R_c$ and $E_o = +\infty$, if $r_{ij} < R_a + R_c$, where R_a , R_c are the ionic radii of the anion and the cation, respectively). The Coulomb energy of an ionic compound $A_x C_y$ can be written in terms of the *Madelung constant* α as follows

$$E_c \equiv -\alpha \frac{N_a + N_c}{2} \frac{e^2 |Z_a Z_c|}{4\pi\epsilon_0 d'},$$

where N_a , N_c is the total number of anions, cations in the solid; Z_a , Z_c is the charge of each anion, cation, respectively, and d' is the nearest neighbor distance. Obviously, electrical neutrality requires $xZ_a + yZ_c$ to be zero. Numerical techniques for the calculation of Madelung constant can be found in several textbooks⁶ as well as numerical values for various lattices.⁷ Depending on the values of the parameters x , y , Z_a , Z_c , R_a , R_c various lattice structures are realized. In Fig. 15.22 two of those crystal lattices are shown.

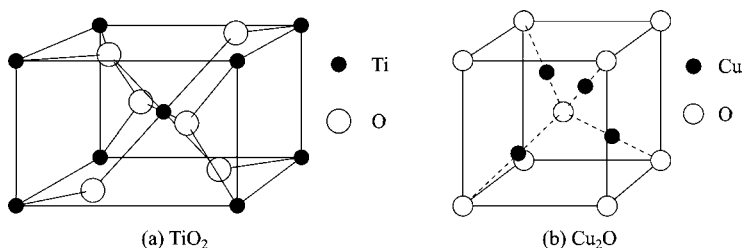


Fig. 15.22. The unit cell of the so-called *rutile* structure (a) and the unit cell of the crystalline compound Cu_2O

⁶ Marder [SS82], pp. 270–274; Kaxiras [SS83], pp. 640–642.

⁷ Harrison [SS76], p. 305.

We have seen that the composite d band in transition metals and transition compound in some cases behaves as an ordinary Bloch band with metallic mobility, while in other cases exhibits atomic-like localized-like behavior of almost zero (or exactly zero) mobility. We attributed this duality to the competition between the effective intra-atomic Coulomb repulsion U and the d bandwidth W_d . If U is much larger than W_d , we expect strong electron-electron correlations and non-metallic mobility; this takes place toward the right end of the 3d series. If $U \sim W_d$, we expect a restoration of the ordinary Bloch behavior, the more complete which is, the smaller the ratio U/W_d is; this happens as we move toward the left end of each row and toward the 5d series.

The strong correlations due to the large ratio U/W_d influence not only the transport properties of the d band electrons but also their magnetic properties, which exhibits a variety of behaviors. For example, the compound CrO_2 is a ferromagnet (up to $T = 386 \text{ K}$), while Cr itself is an antiferromagnet. The compounds, which contain a hematite unit, Fe_2O_3 such as MnOFe_2O_3 , FeOFe_2O_3 , NiOFe_2O_3 , CuOFe_2O_3 , and MgOFe_2O_3 are also ferromagnets (more precisely: ferrites), while the monoxides, MnO , FeO , CoO , and NiO , as well as the compounds MnS , MnTe , MnF_2 , FeF_2 , CoCl_2 , and NiCl_2 are antiferromagnets. Other oxides, such as OsO_2 , are non-magnetic materials.

We shall conclude this chapter by mentioning that elemental rare earth metals and their compounds, having a partially filled f band exhibit similar features with the transition solids, only more extreme. Since, the orbital $(n-1)f$ is of the smallest extent among the three $((n-1)f, nd, (n+1)s)$ which participate in the formation of the rare earth solids (see Fig. B.1 p. 709), the f bandwidth, W_f , is the narrowest and the ratio U_f/W_f is the largest. As a result, we expect that the f bands to be strongly correlated, to exhibit more their atomic rather than the Bloch character, and, hence, to give rise, when partially filled, to magnetic ordering. Indeed, this is the case: some of the strongest permanent magnets are based on rare earths (e.g., Gd, Dy, Eu0). In addition, partially filled f bands produce extremely large effective electronic masses and very high values of the DOS at E_F .

15.8 Key Points

- Elemental transition metals are close-packed solids (forming *hcp*, or *fcc*, or the dense-packed bcc lattice) of small bond length, high cohesive energy, and high elastic constants. Their distinctive features and their complexity stem from the d levels, the energy position of which relative to the corresponding s levels depends on the degree of occupation.
- The largest cohesive energy and elastic constant and the smallest bond length appear around the middle of each series when the d levels are almost half occupied.

- The d bands exhibit Coulomb-driven electron–electron correlations the stronger which are, the larger the ratio U/W_d is; U is the effective intra-atomic Coulomb repulsion and W_d is the width of the composite d band. This ratio becomes in general larger as we move from the 5d to the 4d and finally to the 3d series, and as we move from the left to the right within each series. Large values of U/W_d drastically reduce the mobility of the d electrons and may set up long-range magnetic ordering.
- Ab initio band structure calculations of transition metals are usually performed within the APW or the KKR method. More simplified calculations within the LCAO approach employ either fitted matrix elements or approximate matrix elements expressed in terms of two parameters, r_d and k_d (see Table 15.1) and the bond length. The DOS of the composite d band exhibits four main peaks and weaker fine structure. The Fermi surface is in general quite complicated. A very simplified model of the band structure is that of Friedel (see Fig. 15.11).
- Among the plethora of transition element compound, the perovskites of chemical formula ABD_3 and characteristic lattice structure shown in Fig. 15.12 are physically and technologically important. The perovskite-based ceramic solids known as high- T_c materials have been studied extensively since 1987 because of their extreme superconducting resilience to elevated temperatures. The oxides of transition metals exhibit very rich electric (insulator or conductor) and magnetic (paramagnetic, ferromagnetic, antiferromagnetic) properties.

15.9 Problems

- 15.1 Prove (15.3) till (15.11) (see Harrison [SS76], pp. 478–487).
- 15.2s Calculate the band structure of SrTiO_3 by keeping 17 orbitals ($3 \times 4 = 12$ for the three oxygens and the five d orbitals of Ti). Choose $\mathbf{k}$ along the ΓX direction (z -direction) as to reduce the 17×17 matrix to one 5×5 , two equivalent 4×4 , one 3×3 , and one 1×1 matrices. Find all eigenenergies at the points Γ and X .
- 15.3 Using the results of Problem 15.2s plot roughly the band structure of SrTiO_3 along the ΓX direction. Compare your results with those of Matheiss, Phys. Rev. B **6**, 4718 (1972). See Harrison's book [SS76], p. 449.
- 15.4 Calculate the band structure of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Y123) by employing the following approximations. (a) Assume that each conducting CuO_2 plane shown in Fig. 15.23 is independent from the rest of the structure and forms a two-dimensional square lattice with lattice constant $a = 2d = 3.8 \text{ \AA}$. (b) Assume that each CuO chain as shown in Fig. 15.24 is independent from the rest and forms a one-dimensional periodic system with period $a = 2d = 3.8 \text{ \AA}$. Compare your results with those in Fig. 15.15b (W.A. Harrison, Phys. Rev. B **38**, 270 (1998)).

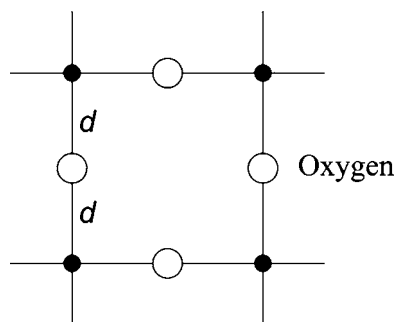


Fig. 15.23. The CuO_2 plane of $\text{YBa}_2\text{Cu}_3\text{O}_7$

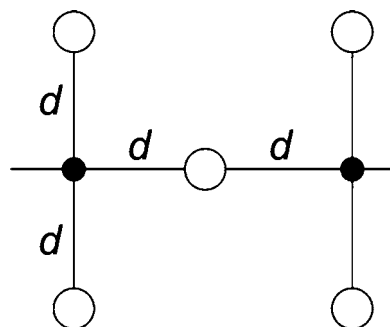


Fig. 15.24. The CuO chain of $\text{YBa}_2\text{Cu}_3\text{O}_7$

15.5 Could you interpret the main features of the DOS shown in Fig. 15.20 by employing the e_s and e_d of Nb?

Further Reading

- References to the books of Ashcroft & Mermin [SS75], Papaconstantopoulos [SS81], and, especially, Harrison [SS76], in connection with specific topics, were given in the text of this chapter.

Artificial Periodic Structures

Summary. There is a large number of different artificial structures that either serve technological requirements (e.g., various solid state devices) or facilitate the physical understanding of certain phenomena by controlling the relevant parameters (or both). These structures may be periodic in one-dimension, two-dimensions, or fully, in three-dimensions. In some cases (e.g., in the so-called photonic and phononic crystals), periodicity is of critical importance, because the existence of the desired features depends on the existence of periodicity. In other cases (e.g., in the Left-handed Metamaterials to be discussed in this chapter), the unit cell already incorporates the core of the desired features and the periodic repetition simply enhances them.

16.1 Semiconductor Superlattices

In Fig. 16.1, we plot the dispersion relation, $E_n(k)$, (thin line), of a model, 1-D, indirect-gap semiconductor resembling that of Si, in the sense that the VB($n = 1$) has its highest energy at $k = 0$, while in the CB($n = 2$) the minimum appears at $k = 0.8(\pi/a)$. By making an artificial periodic structure, the unit cell of which includes five primitive cells of the original semiconductor, the new BZ becomes five times smaller and the original dispersion relation is transferred to the new BZ by appropriate reciprocal vectors $2\pi n/w = 2\pi n/5a$ of the lattice associated with the new periodicity, $w = 5a$. Besides this folding of the original dispersion relation to the new BZ, there is in general a lifting of the degeneracies appearing at $k = 0$ and at $k = \pm\pi/5a$, as a result of the additional potential associated with the imposed periodicity of the superlattice, as shown in Fig. 16.1. It is worthwhile to point out that the construction of the superlattice has transformed an indirect gap semiconductor to a direct gap device; this may improve drastically its optical properties.

The technique of Molecular Beam Epitaxy (MBE) allows the fabrication of other types of superlattices consisting of alternating layers of different semiconductors, e.g., GaAs and $\text{Al}_x\text{Ga}_{1-x}\text{As}$ as shown in Fig. 16.2b. The width of each layer (w_1 and w_2) is usually of the order of a few atomic planes.

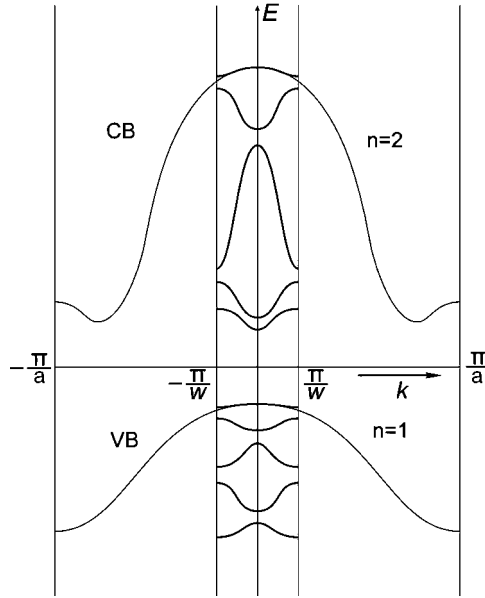


Fig. 16.1. Folding of the original BZ, $(-\pi/a \leq k < \pi/a)$, and the dispersion relations, $E_n(k)$, $n = 1, 2$ (*thin line*) to the interior of the new BZ, $(-\pi/5a \leq k < \pi/5a)$; the new BZ corresponds to an artificial superlattice the unit cell of which, w , consists of five original unit cells. The degeneracies at $k = 0$ and at the edges, $k = \pm\pi/5a$, of the new BZ are lifted and, as a result, five bands (*thick lines*) in both the VB and the CB emerge. Notice that the superlattice became a direct-gap semiconductor

In Fig. 16.2b the bottom of the CB and the top of the VB are changing abruptly as we cross each interface. In Fig. 16.2c, we show the case where the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ layers (only those) have been doped with donors; then the levels E_c , E_v , and E_d within each layer are bent for the following reason: The level E_d in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ is higher than the bottom E_c of the CB in GaAs; as a result, electrons migrate from the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ side to the GaAs side. Thus, a charge density around each interface appears (positive in the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ side and negative in the GaAs side), which in turn creates an electrostatic potential. Hence, the electronic potential energy is lower near the boundaries than in the center of each GaAs layer, while the opposite occurs in the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ layers (see Fig. 17.4 in next chapter). The end result is the bending shown in Fig. 16.2c.

We shall point out two significant advantages of the structure shown in Fig. 16.2. The first one has to do with basic physics. Indeed, if the potential energy minimum at point A (and at each equivalent point) is deep enough, a bound state in the z -direction will be formed essentially localized in the immediate vicinity of the interface. The electrons trapped in this bound state (along z) are free to move in the $x-y$ plane, i.e., along the interface (assuming

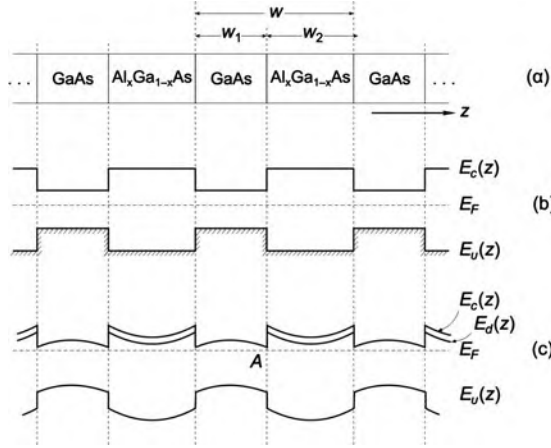


Fig. 16.2. (a) Alternating layers of GaAs ($E_g = 1.42$ eV) and $\text{Al}_x\text{Ga}_{1-x}\text{As}$ ($E_g \simeq 1.92$ eV for $x = 0.4$ and $T = 300$ K) create the superlattice. (b) The variation of the bottom, $E_c(z)$, of the CB and the top, $E_v(z)$, of the VB, as the distance z measured from the substrate increases, entering one or the other of the undoped semiconductors. (c) The same as (b) but with the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ layers doped with donor atoms; $E_d(z)$ is the donor level

that the interface is smooth enough). Thus, a 2-D electron “gas” is created, which allows for experimental tests of various theoretical predictions regarding the behavior of the interacting particles in reduced dimensions.

The other advantage, besides the one from the point of view of physics, is the opening up of technological possibilities related to the very high electronic mobility in the x, y directions, and hence, high-speed electronic devices. The reason for the high mobility is that the carriers (electrons in the CB of the GaAs) are spatially separated from the donor atoms (which are at the side of $\text{Al}_x\text{Ga}_{1-x}\text{As}$), and as a result, they undergo reduced scattering.

We shall conclude this section by mentioning the so-called nipi superlattice. Its unit cell in the z -direction consists of four layers: the first is n-doped semiconductor, the second is the same semiconductor undoped (i.e., intrinsic), the third is p-doped (still the same semiconductor), and the fourth is again undoped (i.e., intrinsic). This type of structure is made in an MBE chamber by depositing either the intrinsic semiconductor (for the i layers) or simultaneously the semiconductor atoms and the dopant atoms (donor type for n layer and acceptor type for the p layer). More about semiconductor superlattices can be found in the book by Burns, [SS77], p. 724–736.

16.2 Photonic Crystals: An Overview

In the study of electronic motion in a crystalline solid, bands and gaps are ever present and of central importance. This alternation of allowed and forbidden energy regions is usually (but not always) the result of the wavy character of

the electronic motion in combination with the periodic feature of the forces acting on the electrons.

In contrast, bands and gaps rarely, if at all, appear for electromagnetic (EM) waves propagating in natural materials.¹ In the next section we shall provide an explanation for this striking difference. Here we shall mention that in the late eighties the question was raised of designing and constructing an artificial medium such that the propagation of electromagnetic waves of certain frequency region(s) through this medium was prohibited. There were two motivations leading to this development: One was the quest for more efficient lasers [16.1] and the other was the need to clarify the role of disorder in wave propagation [16.2] (the so-called localization problem; see Chap. 18 and [16.3, 16.4]) under *controlled* conditions. Once such artificial composite materials were designed and constructed in the GHz range [16.5] and the propagation of EM waves in various lattices was studied theoretically [16.6, 16.7, 16.8, 16.9, 16.10], there was rapid progress [16.11, 16.12] toward design, fabrication, and measurements [16.13, 16.14, 16.15, 16.16, 16.17, 16.18, 16.19, 16.20, 16.21, 16.22, 16.23]. Thus, a new field emerged, that of the so-called photonic crystals (*PhCs*), which found additional technological applications (other than the original motivations) and forced us to reconsider the problem of wave propagation in periodic media.

Photonic Crystals (PhCs) are artificial periodic structures (of period size ranging from one (or even less than one) micron to a cm or more) exhibiting spectral gaps (or pseudogaps) in the photonic density of states (DOS), due to strong scattering and destructive interference of EM waves. Usually, the PhCs consist of two dielectrics (one of them can be air). The periodicity can be in all the three spatial directions, or in two of them, or in one [PC122].

In Figs. 16.3–16.6, some of the successful 3-D designs for PhCs are shown.

Besides 3-D PhCs, 2-D PhCs have been fabricated usually by “drilling” [16.18], in a dielectric, parallel air cylinders arranged in a 2-D periodic lattice. Such 2-D PhCs have several current and future applications in microfabricated optical fibers (see Fig. 16.7) [16.24, 16.25, 16.26], beam splitters and beam switches (see Fig. 16.8) [16.27, 16.28], microwave planar antennas [16.29, 16.30] (where emission in the back half-space is prevented by the presence of a PhC), photonic integrated circuits (where PhCs guide the photonic beam through narrow channels forcing it to make sharp turns where is needed), etc. The existence of a photonic gap permits the creation of a single-mode photon trapped around a local defect in the PhC with an eigenfrequency in the photonic gap (see Fig. 16.9 [16.31]); this is an analog to the impurity-bound electronic states in semiconductors. As we shall see shortly, an attractive impurity electronic potential corresponds to a local defect with excessive dielectric; such

¹ Bands and *pseudogaps* at visible frequencies are responsible for the iridescent colors of butterfly wings. The pseudogaps (i.e., frequency region of very low DOS) appear because of the periodic structure of the wings at a scale of submicron. (see [16.65]).

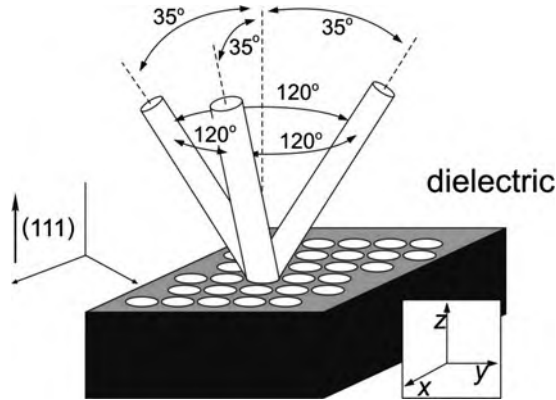


Fig. 16.3. The so-called Yablonovite. Identical circles arranged in a periodic triangular array on the flat surface of a dielectric are drawn. Three holes through each circle area are drilled in the directions shown. For lattice constant of 11.5 mm and circle diameter 5.4 mm, the gap is in the range from 13 to 16 GHz [16.11]

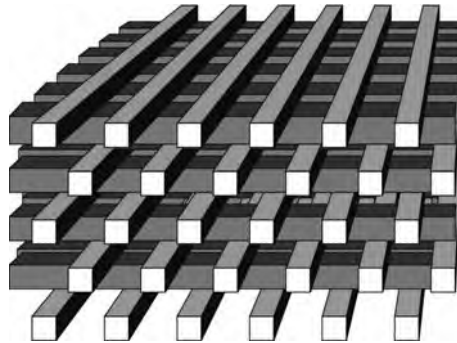


Fig. 16.4. The layer-by-layer structure invented by the Iowa group [16.12] has a period of four layers as shown. With this structure a photonic gap around 200 THz ($\lambda \simeq 1.5 \mu\text{m}$) was obtained [16.15]

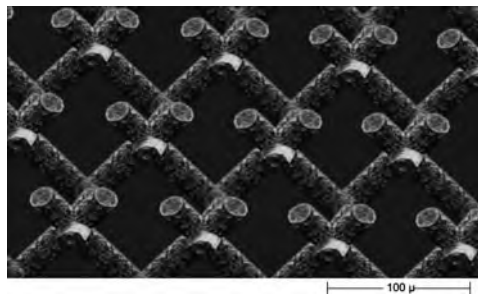


Fig. 16.5. This structure is the negative of the Yablonovite, in the sense that air and dielectric are interchanged. It serves as a mould for the fabrications of small period Yablonovites ($a < 0.1 \text{ mm}$) [16.14]

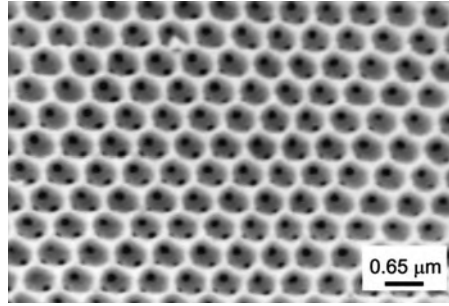


Fig. 16.6. The 111 surface of a PhC consisting of air spheres in a titanium oxide matrix. The lattice constant is $a = 910$ nm. Both the air spheres and the matrix form a singly connected network [16.16]

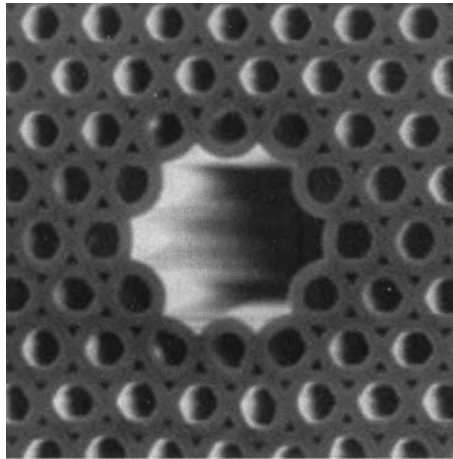


Fig. 16.7. The cross section of a microfabricated optical fiber as proposed by Ph. St. J. Russell [16.24,16.25]. The EM wave propagates along the central hole allowing thus higher photonic energy flow with minimum absorption; this is achieved because the small holes in the surrounding dielectric act as a 2-D PhC preventing the lateral spreading of the EM beam out of the central hole and into the dielectric

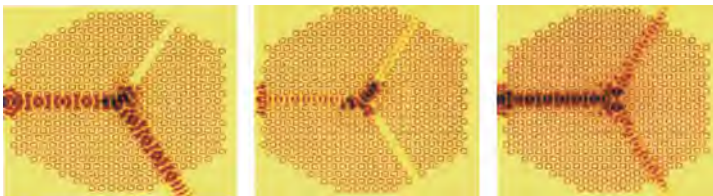


Fig. 16.8. Top view of a 2-D PhC in which Y shaped channels have been formed by proper removal and rearrangement of some of the dielectric cylinders forming the PhC. Depending on the frequency (within the gap) of the incoming EM wave, the latter can go to the right channel, or to the left channel, or to both directions [16.27,16.28]

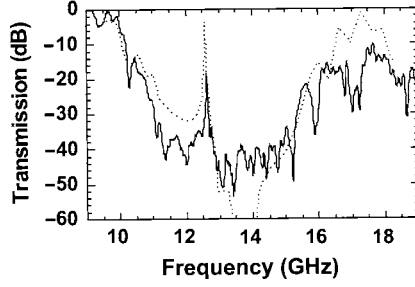


Fig. 16.9. Transmission coefficient vs. frequency revealing the local photonic mode (at eigenfrequency 12.6 GHz) bound around a local defect in a PhC with a frequency gap extending from 11 to 16 GHz [16.31]; the finite width of the peak and the rest of the fine structure are due to the finiteness of the PhC. The continuous line shows the experimental data and the dotted line the theoretical results obtained by the transfer matrix approach

excessive dielectric-defect pulls one or more bound photonic states out of the upper band and into the photonic gap (the volume of the excess dielectric must exceed a critical value for the first bound photonic state to appear in the gap). In contrast, air-defects (corresponding to missing dielectric locally) push (if large enough) one or more photonic modes out of the lower band and into the photonic gap. The existence of bound local photonic modes led to the fabrication of low-threshold tiny lasers and single-mode light emitting diodes (LEDs).

Concluding this section, we shall mention that the fabrication of 3-D PhCs with small period of one micron or less is a challenging problem both from the material point of view and from the design point of view. An example of the latter is the layer-by-layer design shown in Fig. 16.4, while an example of the former is the recent synthesis [16.32] of colloidal photonic crystals (exhibiting pseudogaps) consisting of small (10 nm) magnetite particles coated with charged polymer; by an external magnetic field the distance among clusters of colloidal particles can be controlled, leading to an easily tunable pseudogap. The exploitation of an external magnetic field as well as gyromagnetic properties in connection with PhCs is examined in [16.34] and [16.33] respectively.

16.3 Photonic Crystals: Theoretical Considerations

We start this section by comparing the familiar Schrödinger equation with the classical wave equations (EM, acoustic, elastic) in the rather unfamiliar case where the parameters in the latter are functions of the position vector $\mathbf{r}$. We shall write Schrödinger's equation by introducing the difference $\delta\mathcal{V}(\mathbf{r}) \equiv \mathcal{V}(\mathbf{r}) - \mathcal{V}_m$, where $\mathcal{V}_m$ is the maximum value of $\mathcal{V}(\mathbf{r})$.

$$\nabla^2 \psi + \frac{2m}{\hbar^2} (E - \mathcal{V}_m) \psi - \frac{2m}{\hbar^2} \delta \mathcal{V} \psi = 0. \quad (16.1)$$

Maxwell's equations in the case where the relative permittivity $\varepsilon_r \equiv \varepsilon/\varepsilon_o$ and the relative permeability $\mu_r \equiv \mu/\mu_o$ are both functions of $\mathbf{r}$ can be reduced to the following set of two equations (in what follows we drop the subscript r from ε_r and μ_r , and we assume a time dependence of the form $\exp(-i\omega t)$, and the absence of external charges and currents within the medium under consideration):

$$\nabla \times \left(\frac{1}{\epsilon} \nabla \times \mathbf{H} \right) = \frac{\omega^2}{c^2} \mu \mathbf{H}, \quad \frac{1}{c^2} = \varepsilon_o \mu_o, \quad (16.2)$$

$$\nabla \cdot (\mu \mathbf{H}) = 0. \quad (16.3)$$

Equation (16.2) is obtained by dividing the fourth Maxwell equation by ε , taking into account that $\mathbf{D}/\varepsilon = \mathbf{E}$ (in SI $\mathbf{D}/\varepsilon\varepsilon_o = \mathbf{E}$, see Problem 16.2), acting on it by the curl operator, and replacing $\nabla \times \mathbf{E}$ from the second Maxwell equation. Instead of (16.2) and (16.3), involving only the $\mathbf{H}$ field, we can write equivalently the following two equations involving only the vector $\mathbf{E}$:

$$\nabla \times \left(\frac{1}{\mu} \nabla \times \mathbf{E} \right) = \frac{\omega^2 \varepsilon}{c^2} \mathbf{E}, \quad (16.4)$$

$$\nabla \cdot (\varepsilon \mathbf{E}) = 0. \quad (16.5)$$

The elastic wave equation (E.15) in the case where all parameters ρ_M , λ , μ_s are functions of the position vector $\mathbf{r}$, can be generalized as follows:

$$\frac{1}{\rho_M} \left\{ \frac{\partial}{\partial x_i} \left(\lambda \frac{\partial u_l}{\partial x_l} \right) + \frac{\partial}{\partial x_l} \left[\mu_s \left(\frac{\partial u_i}{\partial x_l} + \frac{\partial u_l}{\partial x_i} \right) \right] \right\} + \omega^2 u_i = 0. \quad (16.6)$$

Summation over repeated Cartesian coordinates is implied. Equation (16.6) is obtained by replacing in (E.6) $\mathbf{f}$ from (E.9) and (E.14) and taking into account (E.1). (See Problem 16.3). Equation (16.6) is simplified for a liquid medium, where $\mu_s = 0$. In this case, it is more convenient to introduce the pressure exercised by the body, $p(\mathbf{r})$ (a scalar), instead of the displacement vector, $\mathbf{u}(\mathbf{r})$; their relation follows immediately from (E.14), since $T_{\nu\mu} = -p\delta_{\nu\mu}$ (in view of $\mu_s = 0$):

$$p = -\lambda \nabla \cdot \mathbf{u}. \quad (16.7)$$

By taking the div of (E.6) after dividing by ρ_M , and employing (E.9) and $T_{\nu\mu} = -p\delta_{\nu\mu}$, we obtain:

$$\omega^2 p + \lambda \nabla \cdot \left(\frac{1}{\rho_M} \nabla p \right) = 0. \quad (16.8)$$

Furthermore, if ρ_M does not depend on $\mathbf{r}$, (16.8) reduces to the ordinary wave equation with a position dependent velocity $c_o(\mathbf{r}) = \sqrt{\lambda/\rho_M}$:

$$\nabla^2 p + \frac{\omega^2}{c_o^2} p = 0. \quad (16.9)$$

In (16.9), we introduce the difference $(1/c_{\text{om}}^2) - (1/c_o^2)$ and we have

$$\nabla^2 p + \frac{\omega^2}{c_{\text{om}}^2} p - \omega^2 \left[\frac{1}{c_{\text{om}}^2} - \frac{1}{c_o^2} \right] p = 0, \quad (16.10)$$

where c_{om} is the maximum value of the velocity. By comparing (16.1) with (16.10), we see that the classical wave problem corresponds always to E in the Schrödinger case being larger than the maximum value of the potential, since ω^2/c_{om}^2 is always positive. Furthermore, $(2m/\hbar^2) \delta\mathcal{V}$ corresponds to $\omega^2 [c_{\text{om}}^{-2} - c_o^{-2}]$, which implies that (a) any fluctuation in c_o is multiplied by ω^2 and tends to disappear² as $\omega^2 \rightarrow 0$, and (b) the potential wells in $\mathcal{V}(\mathbf{r})$ correspond to the regions of low velocity c_o . These observations provide a clue to the question of why it is difficult to obtain photonic gaps: The latter, obviously, correspond to gaps in the electronic case located above the maximum of the potential (and not well below it as in the case of electrons in solids). Furthermore, for small ω^2 , the scattering cross section for (16.10) goes to zero proportionally to ω^4 . To be more specific, consider a muffin-tin electronic problem where the potential inside each muffin-tin sphere, $\mathcal{V}_{\text{MT}}$, is constant and negative, while outside the muffin-tin spheres it is zero. The equivalent (16.10) classical problem consists of identical spherical particles placed periodically in a matrix the sound velocity of which is c_m ; the sound-velocity inside the spherical particles is a constant $c_o < c_m$. Notice the correspondences $(2m/\hbar^2) E \Leftrightarrow \omega^2/c_m^2$, $(2m/\hbar^2) \mathcal{V}_{\text{MT}} \Leftrightarrow \omega^2 [c_m^{-2} - c_o^{-2}]$, from which it follows that as ω^2 increases from zero, both E and $\mathcal{V}_{\text{MT}}$ in the corresponding electronic problem change proportionally to ω^2 , following in the $\mathcal{V}_{\text{MT}}, E$ plane a straight line the slope $E/\mathcal{V}_{\text{MT}}$ of which is given by

$$\frac{E}{\mathcal{V}_{\text{MT}}} = - \frac{1}{(c_m/c_o)^2 - 1}. \quad (16.11)$$

Thus, the frequency square axis of the classical wave problem is mapped to the straight line (16.11) in the electronic muffin-tin problem [16.4]. For the latter, one can determine for each value of $\mathcal{V}_{\text{MT}}$ the energy gaps. The gap edges, as $\mathcal{V}_{\text{MT}}$ changes, follow a nonmonotonic line, shown as dotted contours in Fig. 16.10 (only the positive- E -part of these contours is shown, because only this part is relevant to the corresponding classical wave problem); the shaded areas bounded by these contours correspond to gaps. The intersections (if any) of the straight line representing the ω^2 axis with the shaded areas show the frequency regions where the corresponding classical wave problem develops gaps.

² Since the scattering cross section (in the low $\delta\mathcal{V}$ limit) is proportional to $\langle \delta\mathcal{V}^2 \rangle$, it follows by the equivalence of (16.1) and (16.10) that the scalar classical wave scattering cross section is proportional to ω^4 as $\omega \rightarrow 0$ (Rayleigh formula).

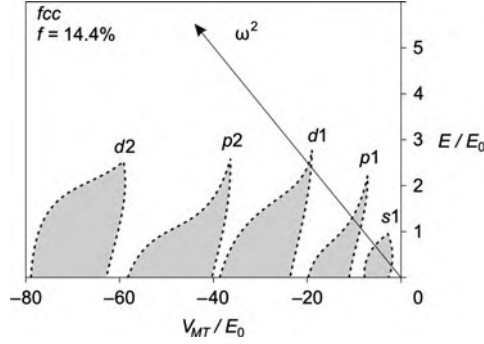


Fig. 16.10. In the plane $E, \mathcal{V}_{\text{MT}}$ (where $\mathcal{V}_{\text{MT}}$ is the potential inside the muffin-tin spheres), the grey areas correspond to the electronic, positive E , gaps. The quantity f is the volume fraction occupied by the muffin-tin spheres and $E_0 = \hbar^2/2mr^2$, where r is the radius of each muffin-tin sphere. Outside the muffin-tin spheres, the potential is taken as zero. The straight line corresponds to the frequency-square axis of the equivalent classical wave problem for a ratio of sound velocities $c_m/c_o = 3$ (the subscripts m and o denote outside and inside the muffin-tin respectively). The value of ω^2 at each point on the ω^2 -axis is inversely proportional to r^2 and it is given by $\omega^2 = (E/E_0)(c_m^2/r^2)$. Classical wave-gaps appear at the regions where the ω^2 -axis passes through the gray areas. The strong non monotonic dependence of the gap contours on the depth of the potential wells is due to Mie resonances. For each spherical harmonic, s, p, d , there are infinitely many such resonances ($s1, s2, \dots, p1, p2, \dots, d1, d2, \dots$) which for a single sphere and in the limit $E \rightarrow 0$ are given by the roots of spherical Bessel functions $j_{\ell-1}(x_{\ell n}) = 0$. The corresponding critical values of $\mathcal{V}_{\text{MT}}$ are given by $|\mathcal{V}_{\text{MT}}| = x_{\ell n}^2 E_0$. Notice that there are no electronic gaps in this muffin-tin model for $E > 3E_0$.

It is important to keep in mind that the electromagnetic equations (16.2) and (16.3) are considerably more complicated than the simple scalar classical equation (16.9), which is equivalent to the Schrödinger equation. Thus, the conclusions we reached before may not be valid for the EM case. Explicit solutions may be needed, which can be obtained by plane wave expansion. In the usual case where $\mu = 1$, it is more convenient to start with (16.2) and (16.3). By writing

$$\frac{1}{\varepsilon(\mathbf{r})} = \sum_{\mathbf{G}'} a_{\mathbf{G}'} e^{i \mathbf{G}' \cdot \mathbf{r}}, \quad (16.12)$$

$$\mathbf{H}(\mathbf{r}) = \sum_{\mathbf{G}} \mathbf{H}_{\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}}, \quad (16.13)$$

$$\mathbf{K}' \equiv \mathbf{k} + \mathbf{G}', \quad \mathbf{K} \equiv \mathbf{k} + \mathbf{G} + \mathbf{G}', \quad (16.14)$$

equations (16.2) and (16.3) become respectively

$$\sum_{\mathbf{K}'} a_{\mathbf{K}-\mathbf{K}'} \mathbf{K} \times (\mathbf{K}' \times \mathbf{H}_{\mathbf{K}'}) = -\frac{\omega^2}{c^2} \mathbf{H}_{\mathbf{K}}, \quad (16.15)$$

$$\mathbf{L} \cdot \mathbf{H}_{\mathbf{L}} = 0, \quad \mathbf{L} = \mathbf{K}, \mathbf{K}'. \quad (16.16)$$

Because of (16.16), $\mathbf{H}_{\mathbf{L}}$ has components only along the unit vectors $\mathbf{x}_{\mathbf{L}}$ and $\mathbf{y}_{\mathbf{L}}$ where $\mathbf{x}_{\mathbf{L}} \cdot \mathbf{y}_{\mathbf{L}} = 0$ and $\mathbf{x}_{\mathbf{L}} \cdot \mathbf{L} = \mathbf{y}_{\mathbf{L}} \cdot \mathbf{L} = 0$:

$$\mathbf{H}_{\mathbf{L}} = H_{Lx} \mathbf{x}_{\mathbf{L}} + H_{Ly} \mathbf{y}_{\mathbf{L}}, \quad \mathbf{L} = \mathbf{K}, \mathbf{K}'. \quad (16.17)$$

Problem 16.1t. Prove that

$$\sum_{\mathbf{K}'} M_{\mathbf{K}\mathbf{K}'} H_{\mathbf{K}'} = \frac{\omega^2}{c^2} H_{\mathbf{K}}, \quad (16.18)$$

where $H_{\mathbf{L}}$, $\mathbf{L} = \mathbf{K}, \mathbf{K}'$, is a two-component column matrix with elements H_{Lx} and H_{Ly} and $M_{\mathbf{K}\mathbf{K}'}$ is a 2×2 matrix of the form

$$M_{\mathbf{K}\mathbf{K}'} = |\mathbf{K}| |\mathbf{K}'| a_{\mathbf{K}-\mathbf{K}'} \begin{vmatrix} \mathbf{y}_{\mathbf{K}} \cdot \mathbf{y}_{\mathbf{K}'} & -\mathbf{y}_{\mathbf{K}} \cdot \mathbf{x}_{\mathbf{K}'} \\ -\mathbf{x}_{\mathbf{K}} \cdot \mathbf{y}_{\mathbf{K}'} & \mathbf{x}_{\mathbf{K}} \cdot \mathbf{x}_{\mathbf{K}'} \end{vmatrix}. \quad (16.19)$$

Keeping a finite number of reciprocal vectors $\mathbf{G}$ and $\mathbf{G}'$ and solving the linear system (16.18), we determine the eigenfrequencies $\omega_{\mathbf{k}}$ and the corresponding eigenmodes $\mathbf{H}_{\mathbf{k}}$. In Fig. 16.11 we plot the results for $\omega_{\mathbf{k}}$ of the first calculation based on (16.18), which exhibited a complete photonic gap in a periodic system of overlapping air spheres the centers of which formed a diamond lattice [16.6].

We conclude this section by summarizing the role of the various parameters in promoting the appearance of gaps for classical waves.

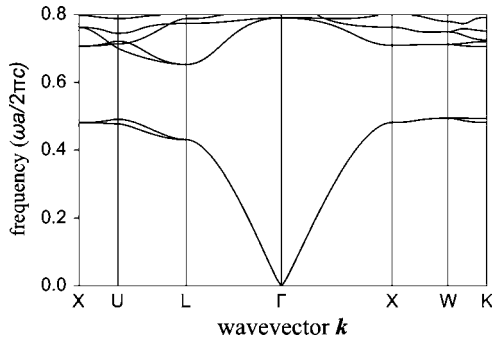


Fig. 16.11. Calculated photonic band structure for a system of overlapping air spheres embedded in a dielectric of $\varepsilon = 13$ ($n = \sqrt{13} \simeq 3.61$) and forming a diamond lattice. The volume fraction of spheres is 81% and that of dielectric 19%; a is the lattice constant (the sphere diameter equals $0.65a$, and the distance between centers of the nearest neighbor spheres is $\sqrt{3}a/4 \simeq 0.43a$) [After Ho, Chan, Soukoulis, Phys. Rev. Lett., **65**, 3152 (1990).]

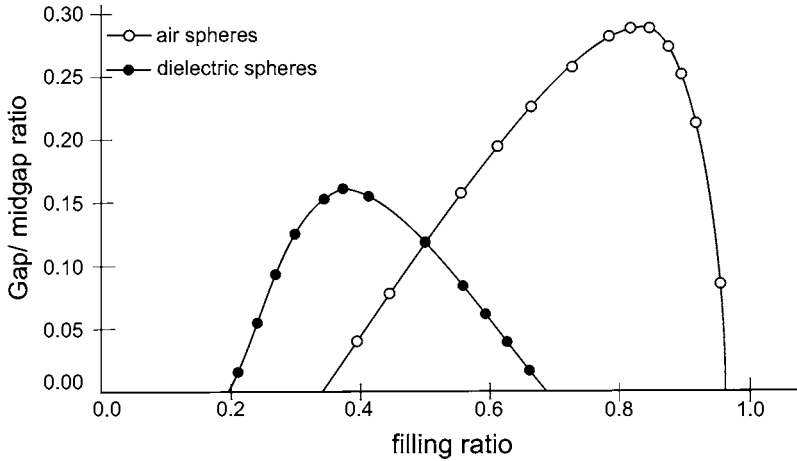


Fig. 16.12. The size of the gap over the midgap frequency vs. the volume fraction of the dielectric (the scattering material) for EM waves propagating in a system of dielectric spheres in air (cermet topology, curve to the left) or air spheres in the same dielectric (network topology, curve to the right). The centers of the spheres in both cases form a diamond lattice (after [16.6])

1. *Topology*: The most common configuration is that of the *cermet*³ topology, where the scattering material (i.e., the one with the low phase velocity) consists of isolated particles completely surrounded by the material of the matrix (the matrix being the high velocity material). The other common topology is that of the *network* type, where the scattering material forms a singly connected continuous network (so does the matrix material). The network topology favors gap formation in the case of EM waves as shown in Fig. 16.12. On the other hand, the cermet topology favors gap formation in the case of the scalar classical waves, as well as in the case of elastic waves. This is shown in Fig. 16.13.
2. *Lattice symmetry*: It is reasonable to expect that the cubic symmetry in general and the **fcc** in particular would be the most favorable for gap formation. The argument is as follows: Since there are always gaps for a *particular direction* of propagation, the spherical symmetry, if it were feasible, would transform them to complete gaps, i.e., common gaps in every direction; **fcc**, being as close as possible to the spherical symmetry, is expected to be the most favorable for gap formation. Indeed, this is the case for Schrödinger waves, for acoustic waves, and for elastic waves. However, diamond symmetry, against expectations, turned out to be the preferable one for gap formation in the EM case.
3. *Volume fraction of the scatterers*: To have gaps, we need strong individual scattering (achieved under resonance conditions) and destructive

³ The name “cermet” is combined from “ceramic” and “metal”.

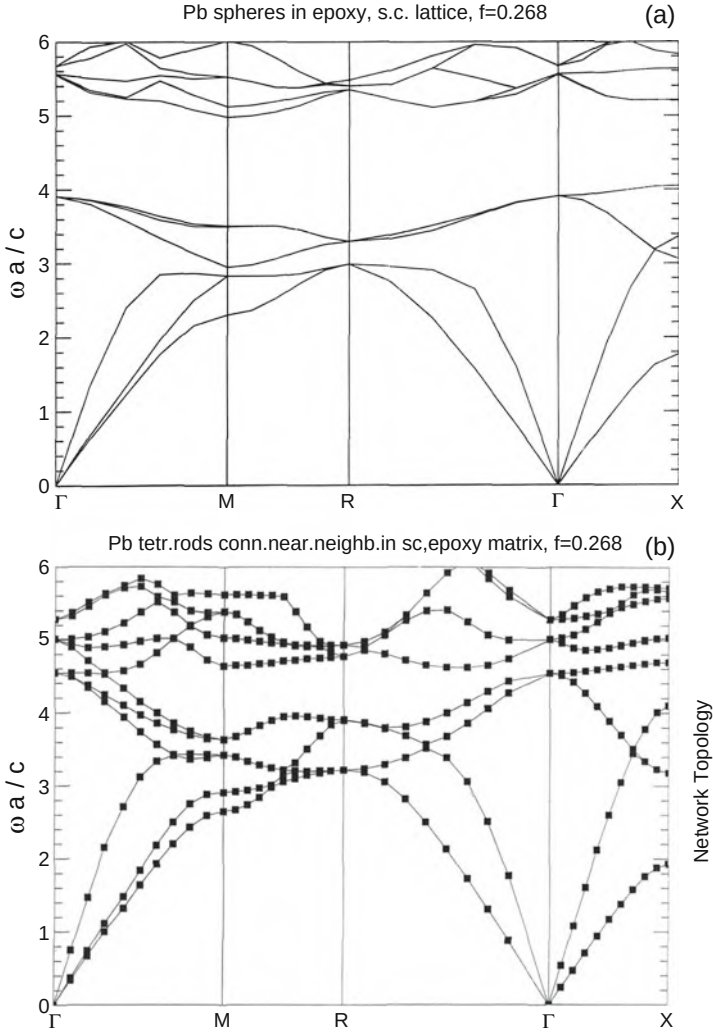


Fig. 16.13. Band structure of elastic waves propagating in a periodic system consisting of lead spheres in epoxy (a, cermet topology), or of connected lead rods in epoxy (b, network topology). In both cases the lattice is simple cubic. (see also [PC126], pp. 148 and 150.)

interference of the scattered waves. The first condition of resonance is realized usually when the wavelength λ (within the scatterer) satisfies (approximately) the relation $n\lambda/2 \simeq 2r$, where n is an integer and $2r$ is the diameter of the individual scatterer (Mie resonance). The second condition for destructive interference implies that $(2n' - 1)\lambda_o/2 \simeq 2d \sin \theta$, where λ_o is the wavelength in the matrix material and d is the nearest neighbor distance. Comparing these two relations, we obtain roughly that $d/r \approx 3$, which means that the scatterers volume fraction must be about

20% or less for optimum gap formation. This estimate is consistent with detailed numerical calculations (see, e.g., Fig. 16.12).

4. *Scale of the unit cell*: The previous arguments imply that both the size of each individual scatterer and the lattice constant are required to be comparable to the wavelength for a gap to appear around this wavelength. For example, for telecommunication wavelength ($\lambda \simeq 1.5 \mu\text{m}$), the scale of the unit cell must be of the order of $1 \mu\text{m}$. This conclusion is valid if the resonance is geometric, as in the Mie case, but it is invalid if the resonance is due to some physical property of the scattering material.
5. *Dielectric contrast*: The larger the ratio $\varepsilon_s/\varepsilon_m$ of the dielectric constants of the scatterer and the matrix, the more favorable the conditions for gap formation (at least for the scalar wave equation). This is clear from Fig. 16.10, since a larger ratio $\varepsilon_s/\varepsilon_m$ implies a larger ratio of c_m/c_s , and hence, a smaller slope (in absolute value) of the ω^2 -axis (see (16.11)). Figure 16.10 also shows that there is a lower threshold for the ratio $\varepsilon_s/\varepsilon_m$. Below this threshold, the slope of the ω^2 -axis is so close to the vertical axis that there is no intersection with the shaded (gap) areas. For EM waves the lowest threshold is $\varepsilon_s/\eta_m \simeq 4$.

16.4 Phononic Crystals

In full analogy with the photonic crystals, phononic crystals are periodic structures consisting of at least two media and exhibiting spectral gaps (or pseudogaps) in the phononic DOS, due to strong scattering and destructive interference of acoustic or elastic waves [16.35, 16.36, 16.37, 16.38, 16.39, 16.40]. These gaps appear usually at frequencies of the order of $\pi c_o/a$, where c_o is a typical sound velocity and a is the lattice constant of the composite structure (a is usually in the range from mm to a few cm); in any case, these gap frequencies are seven or eight orders of magnitude smaller than the typical ionic frequency. Natural systems such as colloidal suspensions or colloidal crystals, where the structural units are microspheres of silicon dioxide or polymer spheres (typical size between 10 nm and $1 \mu\text{m}$), exhibit pseudogaps (at frequencies in the GHz range) and they can be considered as phononic pseudocrystals. As we shall see, there are cases where we can escape from the confinement of the rough geometric relations $\lambda \approx 2r \approx a$ connecting the wavelength (at which strong scattering and interference are expected) with the size of the scatterer and the lattice constant. This can be achieved if the scatterer exhibits a strong nongeometric resonance associated with its material characteristics.

Phononic crystals are of practical value, because they allow us to manipulate the flow of sound waves. Furthermore, they have theoretical interest because of the full vector character of the elastic waves and the richness of the relevant parameters (besides the transverse and the longitudinal sound velocities, the mass density offers an extra opportunity for gap creation).

Table 16.1. The dependence of the size of the phononic gap $\Delta\omega$ (over the midgap frequency, ω_g) on the ratios of the material parameters of the scatterer to the material parameters of the matrix

Scatterers/matrix materials	$\frac{\rho_s}{\rho}$	$\frac{c_{ls}}{c_l}$	$\frac{c_{ts}}{c_t}$	$\max\left(\frac{\Delta\omega}{\omega_g}\right)$
W/epoxy	15.85	2.04	2.44	0.75
Ni/epoxy	7.6	2.33	2.78	0.55
Fe/epoxy	6.66	2.38	2.86	0.50
Cu/epoxy	7.6	1.85	2.00	0.50
Steel/epoxy	6.61	2.33	2.78	0.50
Ag/epoxy	8.77	1.49	1.69	0.50
Au/Si	8.36	0.38	0.23	0.055
Pb/Si	4.88	0.24	0.16	0.033

The phononic band structure in a periodic medium can be calculated by the plane wave method. The parameters ρ_M , λ , μ_s are expanded in Fourier series and the displacement vector, $\mathbf{u}$, is written as

$$\mathbf{u}(\mathbf{r}) = \sum_{\mathbf{G}} \mathbf{w}_{\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}, \quad (16.20)$$

according to Bloch's theorem [16.39,16.40]. Results based on the plane-wave method have already been presented in Fig. 16.13, showing that full gaps (and quite wide ones) do appear by appropriate selections of the materials and the various other parameters (volume fraction, lattice structure, etc.). In Table 16.1, we show the largest gap $\Delta\omega$ (over midgap frequency) obtained for different combinations of scatterer/matrix under optimum conditions of topology (cermet), lattice structure (fcc), and volume fraction.

The results shown in Table 16.1 [16.36] make clear that a large mass-ratio combined with a *large* sound-velocity ratio of scatterer over matrix produces large gaps $\Delta\omega/\omega_g$. On the contrary, large mass ratio combined with *small* sound velocity ratio is unfavorable for large gaps. This behavior is in contrast to what happens in the scalar classical wave equation and in the electromagnetic case where *small* values of the ratio c_s/c_m (corresponding to potential wells in the Schrödinger case) are very favorable for gap formation. A possible interpretation of this unexpected result can be obtained by considering the scattering cross-section of an elastic wave by a single sphere embedded in the matrix material. In Fig. 16.14a we plot the scattering cross-section

$$\sigma = \int d\Omega \left[|f_l|^2 + |f_t|^2 \right], \quad (16.21)$$

vs. frequency by a steel sphere embedded in an epoxy matrix; f_l is the scattering amplitude for a longitudinal elastic wave and f_t is the scattering amplitude for a transverse elastic wave. In Fig. 16.14b we plot the scattering cross-section by a single *rigid* sphere of the same radius as the steel sphere

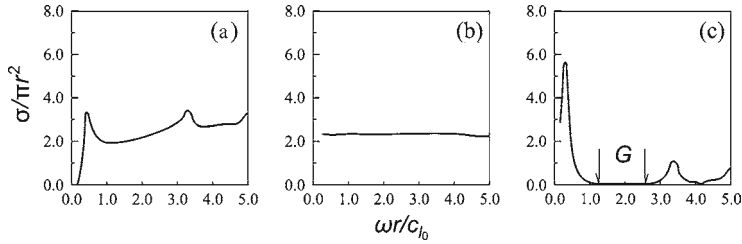


Fig. 16.14. (a) The dimensionless total scattering cross-section $\sigma/\pi r^2$ of a longitudinal elastic wave propagating in an epoxy matrix and scattered by a single steel sphere of radius r vs. the reduced frequency $\omega r/c_{10}$; c_{10} is the longitudinal sound velocity in epoxy. (b) As in (a) but for a rigid sphere of the same radius. (c) The dimensionless cross-section resulting from the difference of the scattering amplitudes of cases (a) and (b); the arrows and the letter G denote the expected gap in a phononic crystal of steel spheres in epoxy [16.37]

embedded in the same matrix; a rigid sphere is one for which ρ , λ , μ are infinite and $c_l = c_t = 0$, so that the displacement field $\mathbf{u}$ inside this sphere is exactly zero. Finally, in Fig. 16.14c we plot a cross-section, σ' , resulting from the difference of the scattering amplitudes of the steel and rigid spheres:

$$\sigma' = \int d\Omega \left[\left| f_l - f_l^{(r)} \right|^2 + \left| f_t - f_t^{(r)} \right|^2 \right]. \quad (16.22)$$

Subtracting the purely geometrical component (due to the rigid sphere and shown in Fig. 16.14b) from the scattering amplitude, we are left with the resonances due to the physical characteristic of the material epoxy/steel combination (Fig. 16.14c). It is worthwhile to point out that the presence of rigid spheres forces the wave to propagate only through the matrix, since inside the rigid spheres the field is zero. On the contrary, the presence of material spheres (steel spheres in the present case) opens up another channel of propagation (besides that of using exclusively the matrix). This second channel employs the resonances shown in Fig. 16.14c to transfer the wave from scatterer to scatterer in analogy with the LCAO where electrons are transferred from atom to atom by employing the atomic orbitals. In the current case the resonances (which are approximate eigenmodes) are the analogs of the atomic orbitals. To obtain a gap, both channels of propagation must be blocked. The blocking of the first one (i.e., the one through the matrix only) is favored when the scattering cross-section by a single rigid sphere is large enough; the deactivation of the second one is achieved if we are in a frequency region far enough from the nearest resonance. According to these arguments, the frequency region in Fig. 16.14c denoted by G and located between the two arrows is expected to become a frequency gap for the elastic wave propagating in a periodic system (e.g., **fcc**) consisting of steel spheres in a matrix of epoxy. Indeed, for this frequency region the first channel of propagation can be blocked (since σ_r is large) and the second is absent. Of course, to really block the first channel,

the concentration n of these spheres must be large enough; we can estimate its magnitude by the condition that the mean free path⁴ $\ell = 1/n\sigma_r$ should be approximately equal to the nearest neighbor distance $d = a/\sqrt{2}$, where a is the **fcc** lattice constant. This condition leads to the following relation for the volume fraction f occupied by the spheres:

$$f \simeq \frac{0.63}{(\sigma/\pi r^2)^{3/2}} \simeq 20\%. \quad (16.23)$$

To obtain the numerical value of 20%, the $\sigma_r/\pi r^2 \simeq 2.1$ result shown in Fig. 16.14b was used.

The analysis shown in Fig. 16.14 provides an explanation of why small values of c_s/c_m are unfavorable for gap formation in the elastic wave case. It turns out that small values of c_s/c_m create strong but *close-spaced* resonances. As a result, it is difficult to find frequency regions where the second channel of propagation (i.e., the one from resonance to resonance) is absent.

We conclude this section by examining briefly two cases of phononic propagation in composite media where there is one or more strong non geometric resonances, i.e., resonances occurring at frequencies such that the corresponding wavelength is quite different from the size of each scatterer.

The first case is that of air bubbles in water. A strong resonance at low frequency, called *Minnaert frequency*, appears; the resonance is so strong that a gap is opened up even in the absence of periodic order. The Minnaert frequency is given by the formula

$$\frac{\omega_M r}{c_i} = \sqrt{\frac{3\rho_i}{\rho_o}}, \quad (16.24)$$

or

$$\nu_M = \frac{\omega_M}{2\pi} = \frac{3,274}{r} \text{Hz}, \quad (16.25)$$

where c_i is the velocity of sound in air, ρ_i and ρ_o are the air and water densities respectively, and r is the bubble radius. Equation (16.25) is valid for pure water and a temperature of 15 °C, with r expressed in mm; (16.25) implies that the resonance wavelength, λ_i , in the bubble is equal to $107r$, i.e., much larger than the radius of the bubble. Actually, the Minnaert resonance is an isotropic (i.e., s-wave) oscillation of the radius of the bubble, where the kinetic energy of an average mass of water equal to ρ_o Sr is balanced by the potential energy of the isotropic deformation of the air in the bubble ($S = 4\pi r^2$).

Problem 16.2t. Following the aforementioned physical description, prove (16.24).

Hint: Take into account that the additional pressure δP on the air equals to $(P_i/V_i)\delta V_i$ where P_i , V_i are the equilibrium pressure and volume of the air respectively. Furthermore, $c_i^2 = B_i/\rho_i$ and $B_i = P_i$.

⁴ We remind the reader that the relation $\ell = 1/n\sigma$ ignores the multi-scattering effects.

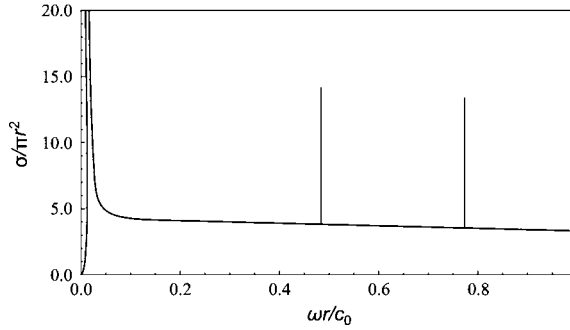


Fig. 16.15. Dimensionless cross-section $\sigma/\pi r^2$ vs. $\omega r/c_o$ of an acoustic wave propagating in water and scattered by a single spherical bubble of air. The low-frequency isotropic Minnaert resonance is shown, as well as other much weaker resonances; r is the radius of the bubble and c_o the sound velocity in the water

Problem 16.3t. Calculate the scattering cross-section of a sound wave propagating in water and scattered by an air bubble, using (16.8), expansion (11.74), and the appropriate boundary conditions. Find the Minnaert and the other resonances.

Hint: The dimensionless scattering cross-section, $\sigma/\pi r^2$, has the following form:

$$\sigma/\pi r^2 = (4/q_o^2) \sum_{\ell=0}^{\infty} (2\ell + 1) |b_{\ell}|^2, \quad q_o = \omega r/c_o.$$

In Fig. 16.15, we plot the dimensionless cross-section $\sigma/\pi r^2$ vs. $\omega r/c_o$ where c_o is the sound velocity in water. Notice the strong low frequency Minnaert resonance and the large background ($\sigma_r/\pi r^2 \simeq 4$).

In Fig. 16.16, we plot the results of acoustic propagation in bubbly water where the volume fraction occupied by the bubbles is 1%. In Fig. 16.16a, the band structure for the periodic case is shown. Notice the very low sound velocity as $\omega \rightarrow 0$ ($c \simeq 90 \text{ ms}^{-1}$), much lower than that of air, and the large gap extending from about the Minnaert frequency to $\omega r/c_o \simeq 0.2$, in spite of the bubble volume fraction being only 1%. This low sound velocity can be explained by the formula $c = (B/\rho)^{1/2}$ where B is that of air (because it is the air bubbles that control the compressibility of the composite system) and $\rho \simeq \rho_o f$ where ρ_o is the density of water and f is the volume fraction of water that participates in the kinetic energy and offers the required inertia. In Fig. 16.16b the relative transmission coefficient through a finite composite system containing $7 \times 7 \times 3$ bubbles is shown; the continuous line refers to the periodic placement of the bubbles, while the other two incorporate randomness. Notice the practically zero transmission in the frequency range corresponding to the gap, which confirms the consistency of these calculations. In the current case of strong scattering the incorporation of multiple scattering effects is absolutely necessary. This is demonstrated in Fig. 16.16c

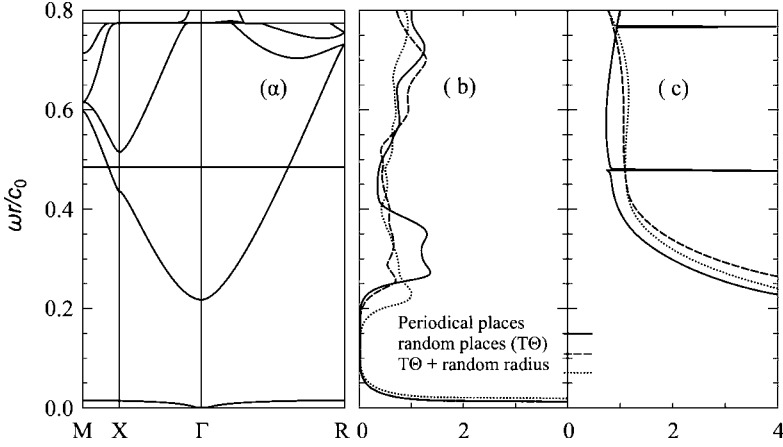


Fig. 16.16. (a) Band structure of sound propagation in bubbly water with the bubbles of volume fraction $f = 1\%$ been placed periodically (in **sc** lattice). (b) Relative transmission coefficient through a finite box of bubbly water containing $7 \times 7 \times 3$ bubbles, placed either periodically (*continuous line*) or randomly (*dashed line*); the *dotted line* corresponds to randomness in both the placement of the bubbles as well as in their radius r' ($0.75 \leq r'/r \leq 1.25$; $r = \langle r' \rangle$); the volume fraction is again 1%. Notice that the gap survives almost intact in the presence of the positional randomness, while tends to shrink from the top edge because of the randomness in the radius. (c). The same as in (b) but with multiscattering effect ignored [16.38]

where the transmission coefficient has been calculated by ignoring the multiple scattering effects; as a result of this, the calculation fails completely, since in the region of the gap produces large transmission!

The other example of nongeometric resonance, appearing at wavelengths much larger than the size of the scatterer or the lattice constant, was proposed a few years ago ([16.41], Liu et al., *Science*, **289**, 1734 (2000)). The matrix is an epoxy cube of linear size 12.4 cm in the interior of which $8 \times 8 \times 8$ coated lead spheres (*radius* 0.5 cm plus 0.25 the thickness of coating) have been placed periodically in a **sc** lattice. The coating material is *soft* (silicone rubber). The lowest resonance appears at $\nu = \omega/2\pi = 386$ Hz corresponding to a wavelength in air of about 1 m; this resonance is associated with the lead sphere, as an almost rigid body, pressing against the epoxy wall with the soft rubber material exercising the restoring force (very weak leading to this very low resonance). There is another resonance at 1,333 Hz. Both resonances create gaps, the first one between 300 and 600 Hz and the second in the range from 1,200 to 1,600 Hz.

16.5 Left-Handed Metamaterials (LHMs)

By the term metamaterials we denote composite (usually artificial) systems exhibiting, as a result of their structure, novel properties that are absent in each one of their constituents. For example, we may have a system of metallic wires behaving as a dielectric (except at a narrow frequency range) [16.42]; or a system of nonmagnetic metallic rings exhibiting strong diamagnetism above a certain frequency [16.43, 16.44]. Photonic and phononic crystals can also be classified as metamaterials [16.45, 16.46, 16.47, 16.48, 16.49, 16.50, 16.51, 16.52].

Most of the work on metamaterials is focused on designing artificial structures exhibiting novel *electromagnetic* properties [16.53]. This is only natural, since the interaction of EM waves with matter is indispensable in emitting, receiving, storing, handling, and retrieving both information and energy. However, metamaterials aiming in other directions, such as novel acoustic or elastic properties, are also pursued.

The most common and extensively employed electromagnetic properties of metamaterials are the relative dielectric function $\varepsilon(\omega)$ and the relative permeability,⁵ $\mu(\omega)$. As we have seen, in most materials μ is very close to one, while $\varepsilon(\omega)$ can be both positive (in dielectrics) and negative (in metals and for $1/\tau \ll \omega < \omega_p$). When both $\varepsilon(\omega)$ and $\mu(\omega)$ are positive, the index of refraction $n(\omega) = \sqrt{\varepsilon(\omega)\mu(\omega)}$ is positive and the EM waves propagate with a velocity $c/n(\omega)$. When one of them is negative and the other positive, the index of refraction is imaginary and the EM waves cannot propagate in such materials. What happens if both $\varepsilon(\omega)$ and $\mu(\omega)$ are negative? This question was not asked until 1967 [16.54]; apparently, the reason was that there is no natural material⁶ having both $\varepsilon(\omega)$ and $\mu(\omega)$ negative over a common frequency range. Nevertheless, we shall examine here, following Veselago work [16.54], this case of both $\varepsilon(\omega)$ and $\mu(\omega)$ being negative. By writing $\mathbf{E}(\mathbf{r}, t) = \frac{1}{\sqrt{2}} \mathbf{E}_0 \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)] + \text{c.c.}$ and a similar expression for $\mathbf{H}(\mathbf{r}, t)$, where c.c. means complex conjugate, the second and the fourth Maxwell equations for a plane EM wave have the form

$$\mathbf{k} \times \mathbf{E} = \frac{\mu\omega}{c} \mathbf{H}, \text{ G-CGS}, \quad (16.26)$$

$$\mathbf{k} \times \mathbf{H} = -\frac{\varepsilon\omega}{c} \mathbf{E}, \text{ G-CGS}. \quad (16.27)$$

(In SI, replace μ/c and ε/c by $\mu\mu_0$ and $\varepsilon\varepsilon_0$ respectively). Equations (16.26) and (16.27) lead to the well-known equation for the phase velocity $v^2 \equiv \omega^2/k^2$:

$$v^2 = \frac{c^2}{\varepsilon\mu}, \quad (16.28)$$

⁵ For the sake of simplicity and for the time being we shall ignore the imaginary part of these quantities.

⁶ Ferromagnetic metals have a frequency range in the GHz range where $\mu(\omega)$ can become negative; however, in this frequency range (where $\text{Re } \varepsilon(\omega)$ is negative too) the $\text{Im } \varepsilon(\omega)$ dominates over the real part, $\text{Re } \varepsilon(\omega)$.

which implies a real value of $v = c/|n|$, and hence, free propagation. However, while in the ordinary case of both ε and μ being positive, the triad $\mathbf{k}$, $\mathbf{E}$, $\mathbf{H}$ is right-handed, in the case $\varepsilon < 0$ and $\mu < 0$ it is left-handed; this follows immediately from either (16.26) or (16.27). By cross-multiplying (16.26) by $\mathbf{E} \times$ and (16.27) by $\mathbf{H} \times$ and taking the time average, we obtain

$$\mathbf{k} = \frac{\mu\omega}{cE_o^2} \mathbf{E}_o \times \mathbf{H}_o = \frac{\varepsilon\omega}{cH_o^2} \mathbf{E}_o \times \mathbf{H}_o, \text{ G-CGS.} \quad (16.29)$$

(In SI, replace μ/c and ε/c by $\mu\mu_o$ and $\varepsilon\varepsilon_o$ respectively). It follows that

$$\frac{E_o^2}{\mu\mu_o} = \frac{H_o^2}{\varepsilon\varepsilon_o}, \text{ SI} \quad \text{or} \quad \frac{E_o^2}{\mu} = \frac{H_o^2}{\varepsilon}, \text{ G-CGS.} \quad (16.30)$$

The time-averaged energy flux density, $\mathbf{S}$, is given either by the general formula $u\mathbf{v}_g$, where u is the time-averaged energy density and $\mathbf{v}_g = \partial\omega/\partial\mathbf{k}$ is the group velocity, or by the time-averaged Poynting vector $(c/4\pi)(\mathbf{E}_o \times \mathbf{H}_o)$ (where $\mathbf{E}_o$ and $\mathbf{H}_o$ are the *rms* electric and magnetic field vectors; in SI set $c/4\pi = 1$):

$$\mathbf{S} = u\mathbf{v}_g = \frac{c}{4\pi} \mathbf{E}_o \times \mathbf{H}_o, \text{ G-CGS.} \quad (16.31)$$

By combining (16.29) and (16.31), we have

$$\mathbf{k} = \frac{4\pi\omega}{c^2} \frac{\mu}{E_o^2} \mathbf{S} = \frac{4\pi\omega}{c^2} \frac{\varepsilon}{H_o^2} \mathbf{S}, \text{ G-CGS,} \quad (16.32)$$

$$\mathbf{k} = \frac{4\pi\omega u}{c^2} \frac{\mu}{E_o^2} \mathbf{v}_g = \frac{4\pi\omega u}{c^2} \frac{\varepsilon}{H_o^2} \mathbf{v}_g, \text{ G-CGS.} \quad (16.33)$$

(In SI, replace $4\pi\mu/c^2$ and $4\pi\varepsilon/c^2$ by $\mu\mu_o$ and $\varepsilon\varepsilon_o$ respectively). Equations (16.32) and (16.33) show that in a medium where both ε and μ are negative, the direction of the propagation of the phase, as determined by the wavevector, $\mathbf{k}$, is opposite to the direction of propagation of the energy, as determined by the Poynting vector, or the group velocity; furthermore, the phase velocity, $\mathbf{v} = c\mathbf{k}/|nk|$, is opposite to the group velocity, $\mathbf{v}_g = \partial\omega/\partial\mathbf{k}$. An immediate physical consequence of this is that the refraction of EM waves at the plane interface of a regular right-handed material (RHM) and a left-handed material (LHM) would be “negative” in the sense shown in Fig. 16.17. Thus, Snell’s law is obeyed at the interface of a RHM and a LHM, provided that n is taken as negative.

$$n = -\sqrt{\varepsilon\mu}. \quad (16.34)$$

That the negative square root of the relation $n^2 = \varepsilon\mu$ must be chosen in the case where both ε and μ are negative can be proved also by introducing small imaginary parts $\text{Im}\varepsilon$ and $\text{Im}\mu$ (both of which must be necessarily positive in a passive medium) and taking into account then that $\text{Im}n$ ought to be positive as well.

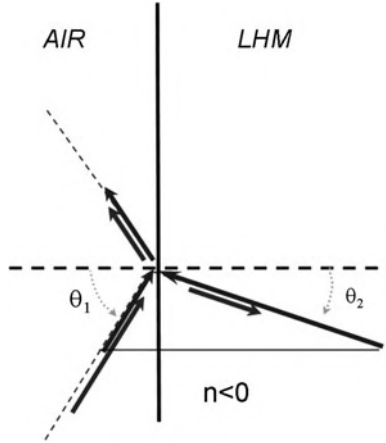


Fig. 16.17. Reflection and refraction of a plane EM wave at the interface of a RHM (air in the present case with $n \simeq 1$) and a LHM. The parallel component of $\mathbf{k}$ of the incident, the reflected, and the refracted wave must be equal; furthermore the energy flux density vector $\mathbf{S}$ of the refracted wave (which is opposite to $\mathbf{k}$) must be directed away from the interface. The only way to satisfy these conditions in view of the fact that $\omega = ck/|n|$, in the LHM, and $\omega = ck$ in the air, is to obey the Snell relation, $n \sin \theta_2 = \sin \theta_1$, with θ_2 to be *negative*⁶ and n to be *negative* too

Problem 16.4t. Show that the group velocity, $\mathbf{v}_g = \partial\omega/\partial\mathbf{k}$, is given in terms of the phase velocity, $\mathbf{v} = c\mathbf{k}/|n\mathbf{k}|$, as follows:

$$\mathbf{v}_g = \frac{\mathbf{v}}{1 + (\omega/n) (\partial n / \partial \omega)}. \quad (16.35)$$

Hint: Take into account that

$$\frac{\partial}{\partial \mathbf{k}} \left(\frac{1}{|n|} \right) = -\frac{1}{n^2} \frac{\partial |n|}{\partial \omega} \frac{\partial \omega}{\partial \mathbf{k}}.$$

Problem 16.5t. Show that the time-averaged energy density, u , is given by

$$u = \frac{1}{8\pi} \left[\frac{\partial(\omega\epsilon)}{\partial\omega} E_o^2 + \frac{\partial(\omega\mu)}{\partial\omega} H_o^2 \right], \text{ G-CGS}, \quad (16.36)$$

(In SI, replace $\epsilon/4\pi$ and $\mu/4\pi$ by $\epsilon\epsilon_o$ and $\mu\mu_o$ respectively) where E_o^2 and H_o^2 are the time-averaged of the squares of the electric and magnetic fields respectively.

Hint: Start with (16.33), take into account that $\mathbf{v}/v_g = (1+x)$ as given by (16.35) and that $k/v = \omega n^2/c^2$. Show that $2n^2(1+x) = [\epsilon\mu + \omega\mu(\partial\epsilon/\partial\omega)] + [\epsilon\mu + \omega\epsilon(\partial\mu/\partial\omega)]$. If ϵ and μ are frequency independent, (16.36) reduces to

⁶ By convention θ_2 is positive, if it results by counterclockwise rotation of the normal.

the usual expression for the energy density. For an alternative proof of (16.36), see the Landau and Lifshitz book [E15], pp. 272–276.

There are also other unexpected properties in the propagation of EM waves in a medium where both ε and μ are negative:

- (a) *Opposite Doppler effect*: Consider a source of EM waves moving away from a detector; both the source and detector are immersed in a LHM. The wavevector, $\mathbf{k}$, at the detector site would be opposite to $\mathbf{S}$, and hence, in the same direction as the velocity, $\mathbf{v}$, of the source. However, when $\mathbf{k} \cdot \mathbf{v} > 0$, the detector would measure a positive frequency shift (as if the medium were right-handed and the source were approaching) i.e., a blue shift. For the same reason, the detector would measure a red shift if the source is approaching.
- (b) *Opposite Cerenkov radiation*: As it was mentioned in Appendix D., a fast-moving charged particle of velocity $\mathbf{v}$ exceeding the velocity of light $c' = c/|n|$ in the medium excites resonantly EM waves; their wavevector $\mathbf{k}$ makes an angle θ with the velocity of the charged particle such that $\cos \theta = c'/v$. If the medium is LHM, the energy flow will be in the direction $-\mathbf{k}$, i.e., in the opposite direction of the usual case.
- (c) *Opposite radiation pressure*: The time-averaged momentum density, $\mathbf{p}$, of an EM wave in a LHM is related to the time-averaged energy density, u , by the standard relativistic equation, $u = cp$, where in the current case c must be replaced by the phase velocity, $c/|n| = \omega/k$. Thus,

$$\mathbf{p} = \frac{u}{\omega} \mathbf{k}. \quad (16.37)$$

Problem 16.6t. Show that (16.37) is equivalent to

$$\mathbf{p} = \frac{\varepsilon\mu}{c^2} \mathbf{S} + \frac{\mathbf{k}}{8\pi} \left[\frac{\partial \varepsilon}{\partial \omega} E_o^2 + \frac{\partial \mu}{\partial \omega} H_o^2 \right], \text{ G-CGS.} \quad (16.38)$$

(In SI, replace $\varepsilon/4\pi$ and $\mu/4\pi$ by $\varepsilon\varepsilon_o$ and $\mu\mu_o$.) *Hint*: Take into account that according to (16.32)

$$\mathbf{S} = \frac{c^2}{8\pi\omega} \mathbf{k} \left(\frac{E_o^2}{\mu} + \frac{H_o^2}{\varepsilon} \right), \text{ G-CGS.} \quad (16.39)$$

(In SI, $c^2/4\pi\mu$ and $c^2/4\pi\varepsilon$ must be replaced by $1/\mu\mu_o$ and $1/\varepsilon\varepsilon_o$ respectively)

The radiation pressure, P , of a plane electromagnetic wave propagating with a wavevector $\mathbf{k}$ in a LHM can be found by the momentum change due to reflection, $2\mathbf{p}dV$, where $dV = S dz$ and $dz = v dt$, divided by the time dt and the surface S :

$$\mathbf{P} = 2pv\mathbf{k}_o = 2u\mathbf{k}_o; \quad \mathbf{k}_o = \mathbf{k}/|\mathbf{k}|. \quad (16.40)$$

- (d) *Flat lenses*: As a result of the negative refraction, we can focus by flat slabs (flat lenses), as shown in Fig. 16.18.

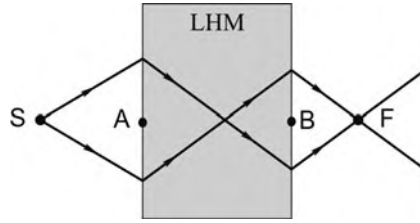


Fig. 16.18. A slab of LHM with flat surfaces can focus both inside and outside it, as shown by the ray diagram

- (e) *Perfect lenses:* Pendry [16.55] suggested that LHMs can act as perfect lenses in principle reproducing images of an object with unlimited details. To see why, consider an object emitting EM waves of frequency ω . In the vacuum, the electric field of such a wave can be analyzed in Fourier components:

$$\mathbf{E}(\mathbf{r}, t) = \sum_{\mathbf{q}, \sigma} E_{\sigma, \mathbf{q}} e^{i \mathbf{q} \cdot \mathbf{R} + i k_z z - i \omega t}, \quad (16.41)$$

where $\mathbf{q} = q_x \mathbf{i} + q_y \mathbf{j}$, $\mathbf{R} = x \mathbf{i} + y \mathbf{j}$; $k_z = \sqrt{(\omega^2/c^2) - q^2}$ and σ is the polarization of the EM wave. To retain the full information about the object, we need all the values of $\mathbf{q}$ and σ . However, for $cq > \omega$, k_z becomes imaginary and $\exp(ik_z z) = \exp(-|k_z|z)$. Thus, as we go away from the object along the z direction, the wave components with $q > q_0 \equiv \omega/c$ (the so-called evanescent waves) decay, and as a result, the information they carry tends to disappear. Hence, at the far-field, where $\exp(-|k_z|z) \simeq 0$, the spatial resolution, δ , cannot be better than about $2\pi/q_0 = 2\pi c/\omega = \lambda$. This limitation is independent of the geometrical features of any lens made of a RHM, since such a lens may change the phase but it cannot influence the amplitude of the evanescent waves. On the other hand, inside a lens made of a LHM, the direction of k_z is opposite to that of $\mathbf{S}$, i.e., opposite to the direction of k_z in a RHM. Thus, it is reasonable to expect that, instead of a decaying wave for $q > q_0 = \omega/c$, we shall have a growing wave of the form $\exp(+|k_z|z)$. If this is true, the presence of a lens made of a LHM in the path of an EM wave propagating along the z -direction cancels to some degree the decay of the evanescent waves in the RHM; in particular, if the LHM has $\varepsilon = \mu = n = -1$ and the thickness d of this flat LH lens is equal to the distance traveled in air between the source and the focus ($d = SA + BF$, see Fig. 16.18), then the decay of the evanescent waves in air will be canceled exactly by their amplification in the LHM and the components with $q > \omega/c$ will reach the focal point, F , without any decay. In this ideal case, a perfect lens will be achieved. Of course, in practice, several factors, including losses, would impose some limits to a perfect resolution, although without excluding the possibility of a *superlens*, i.e., one achieving subdiffraction-limit imaging in the near-field. Detailed calculation (see J. Pendry [16.55]) and experiments using surface plasmons to amplify

evanescent waves [16.56] confirm the realization of this possibility. The readers may wonder, in view of the conservation of energy, how it is possible for a passive medium to amplify the evanescent EM waves. Actually, at the interface and in the bulk of a LHM (or any other strongly scattering medium) the steady state evanescent wave is gradually set up through the interference of strongly multiscattered individual waves. This transient process takes a relatively long time until a steady state is established [16.46]. The stronger the total scattering, the longer this time, leading to more accumulation of energy ([E16], pp. 497–500), which in turn in the steady state appears as a gradually increasing energy density along the thickness of such a medium. In other words, what we gain in energy density we lose in time delay, so that energy conservation is obeyed.

- (f) *Invisibility cloaking*: Suppose that an object is coated by an optically inhomogeneous material such that it deflects the rays, guides them around the object, and release them with the same direction, phase, and amplitude as they would have if the coated object would not be there. If such a coating were available, the system object/coating would be invisible and the coating would act as an invisibility cloak.

In principle, we can make a coordinate transformation $\mathbf{r} \rightarrow \mathbf{r}' = f(\mathbf{r})$ such that the field $\mathbf{E}(\mathbf{r})$ in the absence of the coated object becomes zero within the volume occupied by the coated object itself and remains invariant outside this volume. Such a coordinate transformation would in general change the dielectric function and the relative permeability to tensors dependent on $\mathbf{r}'$: $\varepsilon \rightarrow \varepsilon'(\mathbf{r}')$ and $\mu \rightarrow \mu'(\mathbf{r}')$, while the form of Maxwell's equations would remain invariant in the new coordinate system. It follows that a coating with dielectric tensor $\varepsilon'(\mathbf{r}')$ and relative permeability tensor $\mu'(\mathbf{r}')$ would satisfy all the conditions for acting as an invisibility cloaking system. D. Schurig et al. [16.57], by using cylindrical layers of appropriately designed LHM around a metallic cylinder, managed to make it approximately invisible at an operating frequency of 8.5 GHz. An alternative but equivalent way to examine the question of invisibility cloaking is to surround the object by multiple coatings designed to cancel the dipole, the quadrupole, and the other scatterings; for a review of this approach see [16.58].

16.6 Designing, Fabricating, and Measuring LHMs

To make a periodic, *homogeneous-like* LHM, its unit cell must exhibit a nongeometric magnetic resonance. By nongeometric we mean that the corresponding wavelength λ_m in the medium ought to be much larger than the lattice constant, a ; we have already encountered examples of such resonances in the phononic crystals. The inequality $\lambda_m \gg a$ is necessary in order for the LHM to behave as a homogeneous medium. The resonance is also necessary, since the magnetic response (as measured by the magnetic susceptibility) is for most

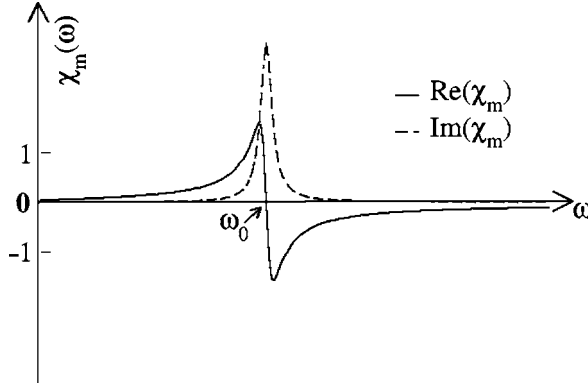


Fig. 16.19. The magnetic susceptibility χ_m vs. frequency ω . At around the resonance, $\omega \simeq \omega_0$, χ_m exhibits a behavior (shown above) typical for any response function

materials very small, of the order of 10^{-4} – 10^{-6} . This is so because magnetism is a relativistic effect of the order of v^2/c^2 , where v is a typical velocity of valence electrons. It takes a collective effect (as in ferromagnets) or a strong resonance to overcome the v^2/c^2 factor. Furthermore, just above a magnetic resonance frequency, the magnetic susceptibility, χ_m , would become negative, as shown in Fig. 16.19. If the resonance is strong enough, $\text{Re } \chi_m$ may become negative enough to drive the permeability, $\mu = 1 + \chi_{m,\text{SI}}$, to negative values over a finite frequency range. A negative value of μ means that the induced magnetic field is opposite to the external field and of larger magnitude. Besides a strong, nongeometric, magnetic resonance to produce a negative μ , we also need a negative ε over a frequency range overlapping with that of negative μ . This, according to what was mentioned before, can be obtained by metallic elements. In Fig. 16.20, we show some of the designs for the unit cell of LHMs. Most of them employ continuous metallic elements running across unit cells along the $\mathbf{E}$ direction, forming thus a set of infinite parallel metallic wires. The dielectric function of this set of parallel, periodically placed, infinite metallic wires is Drude-like:

$$\varepsilon(\omega) = \varepsilon^{(o)} \left(1 - \frac{\omega_p^2}{\omega^2 + i\omega/\tau} \right), \quad (16.42)$$

where $\varepsilon^{(o)}$ is slightly larger than one and the plasma frequency, ω_p , is given by (apart from a numerical factor of the order of one):

$$\omega_p^2 \simeq \frac{c^2}{a^2} \frac{4\pi}{\ln(a^2/s_o)}, \quad (16.43)$$

a^2 is the area per wire normal to the wire and s_o is its geometrical cross-section.

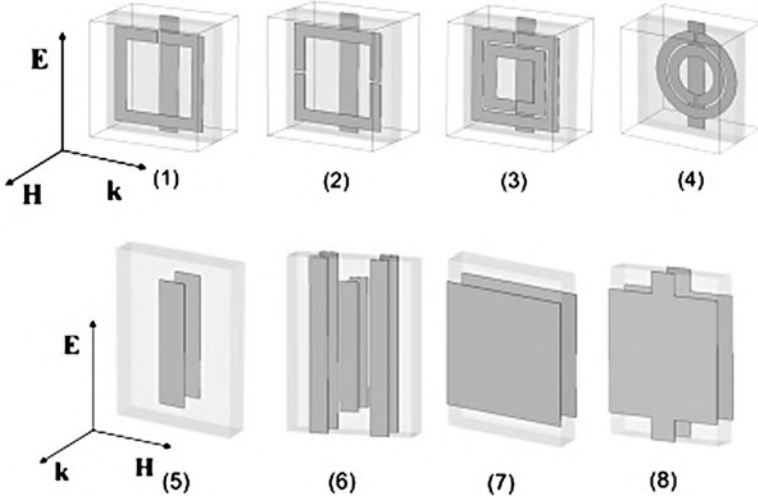


Fig. 16.20. Various designs of the unit cell of LHMs. All of them combine a dielectric slab on both sides of which various metallic elements have been deposited. The designs (1)–(4) utilize various versions of the split ring resonators (SRRs) for the magnetic resonance and a continuous wire for negative ε . The designs (5)–(8) are symmetric with respect to the center plane of the dielectric; the magnetic resonance is associated with an antisymmetric current distribution in the two metallic slabs creating a strong resonant magnetic field in the dielectric [16.59]

Problem 16.7t. Prove (16.43) by equating the electrostatic energy per wire with the magnetic energy per wire. The kinetic energy of the electrons associated with the current, I , is omitted, because usually it is very small (unless the dimensions a and s_o are in the nanoregime).

In designs (5)–(8), there are in each unit cell parallel, metallic slabs of *finite length*. The finite length induces in the dielectric function a resonant frequency ω_r as in the third term in (D.34) of Appendix D.

$$\varepsilon(\omega) = \varepsilon^{(o)} \left(1 - \frac{\omega_p^2}{\omega^2 - \omega_r^2 + i\omega/\tau} \right). \quad (16.44)$$

Finally, in all the designs shown in Fig. 16.20, the magnetic field is oriented in such a way as to produce an alternating magnetic flux, which induces an electromotive force driving a current; the latter gives rise to an induced magnetic field that near the resonance frequency is sufficiently large. In designs (1)–(4), we have metallic rings with one or more cuts, which are known as split ring resonators (SRRs). In designs (5)–(8), the magnetic field induces opposite-running currents in the slabs facing each other; these currents accumulate opposite charges near the ends of the slabs of finite length. Thus, there is a back-and-forth oscillation between the magnetic energy (due to the current) and the electrostatic energy (due to the charge).

This oscillation is equivalent to an effective inductor/capacitor (LC) circuit. The SRRs of the various types are also characterized by a self-inductance L , and a capacitance C , (mainly due to the cut or cuts) and hence, exhibit a resonance frequency $\omega_m = 1/\sqrt{LC}$. If, for a given design of the primitive cell, all lengths are proportional to the lattice constant, a , then both L and C are proportional to a . It follows then that

$$\omega_m \sim 1/a. \quad (16.45)$$

Equation (16.45) implies that to push the region of negative magnetic permeability, μ , to higher frequencies, we need to reduce the size of the unit cell. To reach optical frequencies, both simulations and calculations of the effective L and C indicate that the size of the unit cell must be in the range of a few tens of nanometer. As we approach such length scales, two obstacles appear: First, (16.45) breaks down; the resonance frequency, $f_m = \omega_m/2\pi$, is no more proportional to $1/a$, but it seems to saturate to values that, fortunately, can possibly reach up to 500 THz, i.e., well within the visible spectrum. Second, the magnetic resonance becomes weaker and eventually it fails to produce a negative μ ; this seems to happen around $a \approx 70$ nm, which corresponds to the red end of the spectrum. Thus, these two obstacles, although appreciable, do not seem insurmountable. What is more serious is the problem of ohmic losses in the metallic elements. These losses become more significant as the lattice constant is reduced to sizes of the order of 100 nm or less. As a result of these losses, the so-called *figure of merit*, $FOM = |\text{Re } n|/\text{Im } n$, has not surpassed until now (2007) a number around 3; n is the effective index of refraction.

Problem 16.8t. Consider a square SRR as in Fig. 16.20(1) with the following geometrical dimensions: side length ℓ , width w , metal thickness t , and gap distance d . Show that its self inductance L is given by the following approximate relation:

$$L \simeq \frac{\mu_o \ell'}{2\pi} \left[\ln \frac{8\ell'}{2\pi b} - 1.75 \right] + \frac{\mu_o \ell'}{8\pi}, \quad \text{SI}, \quad (16.46)$$

where $\ell' = 4(\ell - w) - d$ and $\pi b^2 = wt$ (In G-CGS μ_o in (16.46) must be replaced by 4π .) To the magnetic energy, $\frac{1}{2}LI^2$ (in SI; in G-CGS the magnetic energy is $LI^2/2c^2$), we must add the kinetic energy $\frac{1}{2}N_e m_e v^2 \equiv \frac{1}{2}L'I^2$ of the electrons in the metallic SRR. Taking into account that $I = vnes'$, show that the equivalent kinetic inductance is

$$L' = \frac{\ell'}{\varepsilon_o \omega_p^2 s'}, \quad (16.47)$$

where ω_p^2 is the square of the plasma frequency $\omega_p^2 = e^2 n / \varepsilon_o m$ and $s' = \gamma wt$, γ being a numerical factor close to one. If all lengths scale with the lattice constant, a , then $L' \sim 1/a$, which explains the saturation of ω_m as $a \rightarrow 0$. (Find out when L' becomes comparable to L).

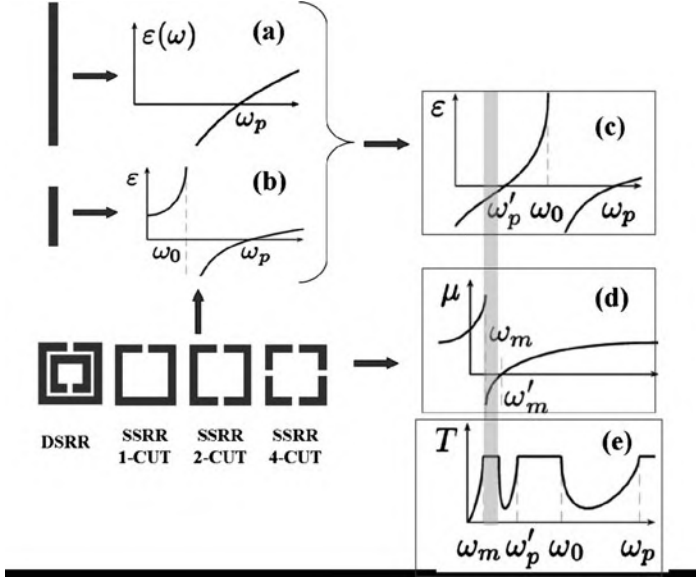


Fig. 16.21. (a) The ε vs. ω dependence for a set of parallel, infinite, periodically placed, metallic wires (see (16.42)) for $\tau \rightarrow \infty$; (b) as in (a) but for wires of finite length; SRRs behave electrically as in (b); (c) the combination of infinite wires and wires of finite length (or SRRs) produce an ε vs. ω as in (c); (d) the μ vs. ω dependence for SRRs (e). In the frequency region where both ε and μ are negative a LH peak appears in the transmission coefficient T ; high transmission appears also when both ε and μ are positive, while in the regions where $\varepsilon\mu < 0$ the transmission coefficient is very small. A LH peak is unequivocally identified by its disappearance when the cut in the SRRs is closed and the magnetic resonance is eliminated

We conclude this section dealing with the fast developing field of LHMs, by mentioning two typical kinds of measurements documenting the existence of the left-handed behavior. The first one is a prism transmission showing negative refraction [16.60, 16.61, 16.62].

The second one is based on measuring transmission of the EM waves through a flat slab of LHM. The expected frequency dependence of the transmission coefficient is shown schematically and explained in Fig. 16.21e. In Fig. 16.22, we show experimental data and the corresponding theoretical results for the transmission coefficient through a slab containing in its unit cell one of the following elements: (a) Only wire; in this case $\mu \simeq 1$ and ε is negative below ω_p as in Fig. 16.21a; hence, a strong drop in the transmission is expected that indeed occurs at 7.9 GHz (dashed line in Figs. 16.22(a) and (b)). (b) Only SRR; then the permeability is as in Fig. 16.21d with negative values of μ , which result in a sharp dip in the transmission at $\omega/2\pi \simeq 3.8$ GHz. (thin continuous line in Figs. 16.22). (c) Both wires and SRR; then the transmission coefficient is as in Fig. 16.21e with the sharp dip at 3.8 GHz transformed to

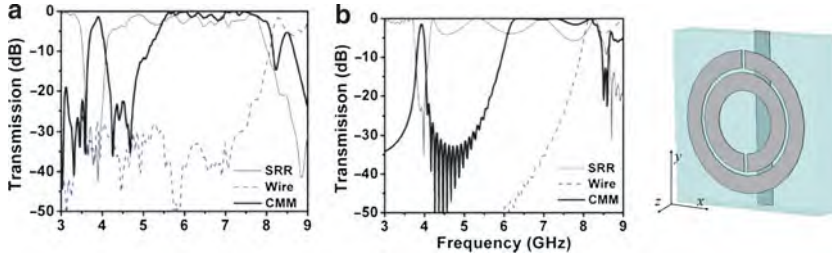


Fig. 16.22. Comparison of experimental data (panel (a)) and theoretical results (panel (b)) for the transmission coefficient (*heavy continuous line*) through a LHM (its unit cell is shown). Thin continuous line is the transmission in the presence of the SRRs only. *Dash-lines* show the transmission in the presence of the infinite wires only [16.63]. Notice the excellent agreement between theory and experiment. Compare with Fig. 16.21a–e

a sharp peak (Figs. 16.22). This peak disappears, if the SRR is replaced by a continuous ring (without a split) of the same size as the SRR.

16.7 Key Points

- Superlattices are artificial periodic structures, the period of which in 1-D consists of several layers of the same or of different materials. The thickness of each layer is of the order of a few atomic distances.
- Superlattices serve various technological and basic physics purposes.
- Photonic crystals (PhCs) are 1-D, or 2-D, or 3-D periodic structures (of period ranging from submicron to a cm or so) consisting usually of two different dielectrics (one of them can be air) and exhibiting spectral gaps (or pseudogaps) in the photonic DOS due to strong scattering and destructive interference of the EM waves [16.64].
- Fabrication of 3-D PhCs with submicron period has been achieved.
- PhCs manipulate the flow of EM waves, blocking their propagation, forcing them to make sharp turns, splitting them, etc.; they may create bound EM modes in the gap and they may inhibit the decay of excited molecular levels of molecules enclosed into them.
- Maxwell's equations in a photonic crystal are reduced to the following equations:

$$\begin{aligned}\nabla \times \left[\frac{1}{\varepsilon} \nabla \times \mathbf{H} \right] &= \frac{\omega^2}{c^2} \mu \mathbf{H}, \\ \nabla \cdot (\mu \mathbf{H}) &= 0,\end{aligned}$$

where usually $\varepsilon = \varepsilon_i$ in the dielectric i ($i = 1, 2, \dots$) and the time dependence is of the form $\exp(-i\omega t)$. The solutions to these equations are obtained by Fourier analyzing ε^{-1} and using Bloch theorem for $\mathbf{H}(\mathbf{r})$.

- Classical waves (scalar, EM, elastic) correspond to $E > \mathcal{V}_{\max}$ in the Schrödinger case; furthermore, fluctuations $\delta\mathcal{V}$ in the potential $\mathcal{V}(\mathbf{r})$ correspond to fluctuations $\delta(c^{-2})$ in the propagation velocity, $c(\mathbf{r})$, *multiplied* by ω^2 , so that the scattering at low frequencies goes as ω^4 (Rayleigh law).
- The classical scalar wave equation with spherical inclusions of wave velocity c_s in a matrix of velocity c_m can be mapped to a straight line of slope

$$\frac{E}{\mathcal{V}_{\text{MT}}} = -\frac{1}{(c_m/c_s)^2 - 1},$$

in the E vs. $\mathcal{V}_{\text{MT}}$ plane, where E is the eigenenergy and $\mathcal{V}_{\text{MT}}$ is the depth of the muffin-tin potential in the Schrödinger case.

- Favorable conditions for EM gaps are the following: Network topology; diamond-type lattice symmetry; volume fraction of about 20% of the low-velocity dielectric; large value of the ratio $\varepsilon_s/\varepsilon_m$ with a threshold value of about 4.
- Phononic crystals are periodic structures in 1-D, 2-D and 3-D consisting of at least two materials; phononic crystals are capable of creating band gaps in the propagation of elastic waves. Each material is characterized by at least two elastic constants (λ, μ_s) and by its density, ρ_M . The equation governing elastic wave propagation is the following

$$\frac{1}{\rho_M} \left\{ \frac{\partial}{\partial x_i} \left(\lambda \frac{\partial u_i}{\partial x_1} \right) + \frac{\partial}{\partial x_1} \left[\mu_s \left(\frac{\partial u_i}{\partial x_1} + \frac{\partial u_1}{\partial x_i} \right) \right] \right\} + \omega^2 u_i = 0,$$

where ρ_M, λ, μ_s are periodic functions of the position vector $\mathbf{r}$.

- In the case of fluids, where $\mu_s = 0$, this equation can be expressed in terms of the pressure, p , as follows:

$$\omega^2 p + \lambda \nabla \cdot \left(\frac{1}{\rho_M} \nabla p \right) = 0.$$

If the density, ρ_M , is constant, this equation reduces to

$$\nabla^2 p + \frac{\omega^2}{c^2} p = 0.$$

- Gaps in the elastic wave spectrum are favored by the cermet topology, by a combination of heavy metal inclusions in a light matrix such as epoxy, and by a velocity ratio c_s/c_m larger than one. The appearance or not of gaps can be understood by subtracting from the scattering amplitude due to a single inclusion, the scattering amplitude by a single rigid inclusion of the same shape and size as the actual inclusion.
- In a bubbly liquid, a strong low-frequency resonance appears, called *Minnaert resonance*, of frequency

$$\omega_M = \frac{c_i}{r} \sqrt{\frac{3\rho_i}{\rho_o}},$$

where r is the radius of the bubble, the subscript i refers to the air, and ρ_o is the density of the liquid. The Minnaert resonance through strong multiple scattering dominates the low-frequency propagation of sound in bubbly liquids.

- Left-handed materials (LHMs) are composite structures exhibiting over a common frequency range negative permittivity, negative permeability, and negative index of refraction. As a result, they exhibit unexpected and important EM properties such as amplification of evanescent waves, etc.
- Usually the creation of negative permittivity relies on the presence of continuous metallic wires, while the negative permeability employs resonant loop-like charge flow, obtained, e.g., through split rings resonators (or other designs); the combination of the two, acts as a LC circuit.

16.8 Problems

- 16.1 Plot schematically the charge density, $\rho(z)$, the electrostatic potential, $\phi(z)$, the bottom of the CB, $E_c(z)$, and the impurity level $E_d(z)$ vs. the distance z at the vicinity of the interface GaAs/Al_xGa_{1-x}As. (see Fig. 17.4 in next chapter).
- 16.2 Derive (16.2) and (16.4) in the SI.
- 16.3 Prove (16.6).
- 16.4 Consider the 3-D equation (16.9) with $c_o(\mathbf{r}) = c_s$ for $|\mathbf{r}| < a$ and $c_o(\mathbf{r}) = c_m$ for $|\mathbf{r}| > a$. Write the scattering solution as follows: $p(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r}) + p_s(\mathbf{r})$; for $\exp(i\mathbf{k} \cdot \mathbf{r})$, the expansion (11.74) must be employed and $p_s(\mathbf{r})$ must be written as a sum of spherical harmonics multiplied by spherical Bessel functions (see Table H.18 at the end of the book); employ the boundary conditions of the continuity of $p(\mathbf{r})$ and $\nabla p(\mathbf{r})$ at $|\mathbf{r}| = a$. Determine the solution $p(\mathbf{r})$, identify the *Mie* resonances, and obtain the scattering cross section. Compare your results with those of the equivalent Schrödinger's problem and check the validity of (16.11).
- 16.5 Prove (16.15).
- 16.6 Justify the estimate (16.23).
- 16.7 Prove (16.29).

Further Reading

- For Photonic and Phononic Crystals see the books [PC122]-[PC130], especially the book by Joannopoulos et al. [PC122]. See also the book by Markos and Soukoulis [AW63].
- For Left-handed Metamaterials, see the references in the text of Ch. 16.

Deviations from Periodicity

Surfaces and Interfaces

Summary. The preparation of clean surfaces requires special techniques and ultra-high vacuum. In such surfaces, ions undergo relaxation and reconstruction. Surfaces and interfaces reflect and refract Bloch waves; in addition, bound states may appear in their vicinity. These so-called surface states may refer to individual electrons or to collective oscillations such as surface phonons or surface plasmons. As the size of the devices is entering deeper into the nanoregime, the importance of the latter is rapidly increasing. The concept of the work function is introduced and methods for its measurement are presented together with a simple approximate formula for its calculation. The p–n homojunction in the absence or in the presence of an external voltage is examined in some details. This junction can act as a rectifier and as a light-emitting diode; under illumination it acts as a battery. The metal–semiconductor junction called Schottky barrier behaves in a similar way as the p–n junction. The field effect transistor is briefly presented.

17.1 Surface Preparation

As it was mentioned in Sect. 8.5.1, surfaces are easily covered by adsorbed molecules (N_2 and O_2). From kinetic theory of gases, one can calculate how many molecules hit a unit surface per unit time when the pressure is P and the temperature is $T = 300 \text{ K}$. Knowing the sticking coefficient S , i.e., the probability of adsorption of an impinging molecule of molecular weight M , we can estimate the time, τ , required for the formation of a monolayer of adsorbed molecules.

Problem 17.1t. Show that

$$\tau \simeq \left(\frac{2Mk_{\text{B}}T}{\pi} \right)^{1/2} \frac{1}{r^2 P \cdot S} \simeq \frac{4.5 \times 10^{-9}}{P \cdot S}. \quad (17.1)$$

In the last relation, r/a_{B} was taken as three and P is in bars and τ in seconds.

Equation (17.1) implies that in order to have $1/10$ of a monolayer in a period of 1 h, we need a pressure of about 10^{-13} bar $\simeq 10^{-10}$ torr assuming a sticking coefficient close to one.

The surfaces of solids, which crystallize in open structures with directed bonds such as the tetrahedral semiconductors, are usually perpendicular to preferred directions of the crystal. For example, in tetrahedral semiconductors, surfaces perpendicular to the (111) direction (and the other seven equivalent to it) are quite common and they can be created by cleaving. In contrast, plane surfaces of other orientations may require a rather complicated procedure (involving cutting, grinding, sputtering by noble gas ions in a vacuum chamber, and annealing) for their creation. The reason for this difference is the fact that the energy of partitioning a solid in two pieces along a plane surface depends on the orientation of this surface relative to the crystalline axes. This surface creation energy can be reasonably assumed to be proportional to the number of bonds per unit area broken in the process of partitioning the solid into two pieces. In problem (17.1s), the readers are asked to show that for the diamond structure the minimum number of bonds per unit area is $4/\sqrt{3}a^2$, $4/a^2$, and $2\sqrt{2}/a^2$ for planes normal to the directions (111), (001), and (110), respectively, where a is the lattice constant. Hence, we expect the partitioning energies E_{111} , E_{001} , and E_{110} along the surfaces (111), (001), and (110) (and their equivalents) to be proportional to 2.309, 4, and 2.828, respectively. This argument suggests that the preferred shape of a diamond lattice crystal ought to be a regular octahedron (the surface of which consists of eight triangular faces that are normal to the eight equivalent low-energy directions (111), ($\bar{1}\bar{1}\bar{1}$), ($\bar{1}11$), ($1\bar{1}\bar{1}$), ($11\bar{1}$), ($\bar{1}11$), ($11\bar{1}$), and ($\bar{1}\bar{1}1$)). This argument is not complete, since the surface energy has to be minimized *under constant volume*. If we truncate the regular octahedron by planes normal to the lines connecting its center to the six vertices and of equal distance from them, we reduce the surface area (under equal volume). However, at the same time, we increase the energy per unit area in the six squares (along the directions (001), ($00\bar{1}$), (010), ($0\bar{1}0$), (100), and ($\bar{1}00$)), produced by the truncation. It turns out that, for $E_{100} \geq \sqrt{3}E_{111}$, the regular octahedron has lower or equal surface energy than that of the truncated octahedron of equal volume. For $E_{100} < \sqrt{3}E_{111}$, a properly truncated octahedron has a lower surface energy than the regular one of equal volume. In reality, both shapes appear in nature indicating that E_{100}/E_{111} is not far from $\sqrt{3}$. Actually, the question of surface energy is more complicated than what these arguments imply, because surfaces undergo relaxation and reconstruction.

17.2 Relaxation and Reconstruction

Let us consider a perfect plane surface. The question is whether the atoms belonging to the outer atomic layer (and to the two or three layers below) occupy the sites dictated by the 3-D bulk lattice or they have been displaced

Table 17.1. The quantity $(z_1 - z_2)/d\%$ showing the relative normal displacement of the outer surface layer minus the displacement of the second atomic layer for various lattice structures, various surfaces, and various metals (after Kittel [SS74]).

Lattice structure	Surface orientation	Metals $[(z_1 - z_2)/d\%]$
hcp	(0001)	Re $[-5\%]$, Sc $[-2\%]$, Ti $[-2\%]$, Zr $[-1\%]$
fcc	(111)	Al $[+1\%]$, Ag $[0\%]$, Cu $[-0.7\%]$, Pt $[+1\%]$, Rh $[0\%]$
bcc	(110)	Fe $[+0.5\%]$, Na $[0\%]$, V $[-0.3\%]$, W $[0\%]$
fcc	(100)	Al $[0\%]$, Cu $[-1\%]$, Rb $[0\%]$
bcc	(100)	Fe $[-5\%]$, Mo $[-9.5\%]$, Ta $[-11\%]$, V $[-7\%]$, W $[-8\%]$
fcc	(110)	Ni $[-8.5\%]$, Al $[-8.5\%]$, Ag $[-8\%]$, Cu $[-8.5\%]$, Pb $[-16\%]$, Rb $[-5\%]$
bcc	(211)	Fe $[-10\%]$, W $[-12\%]$
bcc	(310)	Fe $[-16\%]$
bcc	(111)	Fe $[-17\%]$
bcc	(210)	Fe $[-22\%]$
fcc	(311)	Al $[-13\%]$, Ni $[-16\%]$, Cu $[-5\%]$
fcc	(210)	Al $[-15.5\%]$

from these sites. The answer is that the surface atoms have moved to new positions. The simpler arrangement of this kind is known as *relaxation*; according to it all the atoms of the i layer ($i = 1$ is the outer surface layer) have been displaced by z_i along the direction normal to the surface; z_i is practically zero for $i = 4$ and beyond. Relaxation is quite common in metals. In Table 17.1, we show the quantity $(z_1 - z_2)/d$ where d would be the distance between the outer atomic surface layer and the one just below it, if no relaxation occurred. Notice that the relaxation can be positive (meaning displacement away from the bulk) or negative (meaning displacement toward the bulk); the latter is by far the more frequent, indicating that as we bring back together from infinity the two separated pieces of the metal, the force on each surface is in most cases attractive in the sense that the displacement of each surface is toward each other so that the final (equilibrium) value d is larger than the initial value $d + z_1 - z_2$ and, hence, $z_1 - z_2 < 0$.

In tetrahedral semiconductors and in other open structures with directed bonds, the creation of a surface leads to the creation of unsaturated (dangling) bonds. This situation is energetically unfavorable. To remedy this, the atoms in the outer atomic layer would be displaced both in the normal and in the parallel to the surface direction as to allow at least some saturation of the

dangling bonds among themselves. The parallel to the surface displacement is not uniform (a uniform displacement will not facilitate saturation of the dangling bonds). This non-uniform displacement is called *reconstruction* and it produces a modified 2D surface lattice characterized by basic vectors $\mathbf{c}_1$, $\mathbf{c}_2$ where $\mathbf{c}_1$, $\mathbf{c}_2$ are different from the undisplaced 2D lattice vectors $\mathbf{a}_1$, $\mathbf{a}_2$. The most general relation between $\mathbf{c}_1$ and $\mathbf{c}_2$ and $\mathbf{a}_1$ and $\mathbf{a}_2$ is of the form

$$\begin{pmatrix} \mathbf{c}_1 \\ \mathbf{c}_2 \end{pmatrix} = \begin{pmatrix} p_{11} & p_{12} \\ p_{21} & p_{22} \end{pmatrix} \begin{pmatrix} \mathbf{a}_1 \\ \mathbf{a}_2 \end{pmatrix}. \quad (17.2)$$

If the angle between $\mathbf{c}_1$ and $\mathbf{c}_2$ is the same as that between $\mathbf{a}_1$ and $\mathbf{a}_2$ the reconstruction is denoted as

$$\left(\frac{|\mathbf{c}_1|}{|\mathbf{a}_1|} \times \frac{|\mathbf{c}_2|}{|\mathbf{a}_2|} \right) R\phi,$$

where ϕ is the angle between $\mathbf{c}_1$ and $\mathbf{a}_1$ (or $\mathbf{c}_2$ and $\mathbf{a}_2$). A notation $(p_1 \times p_2)$ means that $\mathbf{c}_1$ is parallel to $\mathbf{a}_1$, $\mathbf{c}_2$ parallel to $\mathbf{a}_2$, $|\mathbf{c}_1|/|\mathbf{a}_1| = p_1$, and $|\mathbf{c}_2|/|\mathbf{a}_2| = p_2$. The reconstruction depends, in general, on the type of solid, the orientation of the surface, the chemical cleanness of the surface, the temperature, etc. For example, the (111) surface of Si, which has been studied extensively for obvious reasons, exhibits the following reconstructions. Cleaving under $T \simeq 300$ K produces 2×1 reconstruction; by heating the sample to over 675 K the reconstruction becomes 7×7 , which remains unchanged when the sample is cooled down to room temperature. Similarly, Ge (111) surface shows different reconstructions, depending mainly on the temperature: cleaving at 4.2 K shows no reconstruction; cleaving at 77 K produces a 2×1 reconstruction. Heating to room temperature stabilizes the (111) surface structure to a new 2×8 reconstruction. One way to avoid reconstruction is to provide atomic hydrogen or chloride, which passivate the dangling bonds eliminating thus the cause for reconstruction. The reliable theoretical study of reconstruction requires very sophisticated and accurate calculational techniques along the lines presented in Sect. 8.4. The challenge of the broken periodicity implied by the mere presence of a surface or an interface is met by adding reflected and refracted waves to the Bloch waves and by the incorporation of individual electronic surface states. In the book by Harrison [SS76] (pp. 233–249), a more physical approach to the question of reconstruction is attempted based on the LCAO method.

17.3 Surface States

The presence of surfaces or interfaces modifies the Bloch waves by adding reflected and refracted waves to them. These are the analog of the scattered wave in the case of a single impurity. The analog of a bound state in the latter is the appearance of surface states, i.e., states that decay (usually exponentially) as the distance from the surface (or the interface) increases.

There are individual electronic surface states as well as collective surface states such as surface phonons, surface plasmons, etc. Individual surface states are not always feasible; for example, a potential of the form $\mathcal{V}(\mathbf{r}) = 0$ for $z > 0$ and $\mathcal{V}(\mathbf{r}) = -V_0$ for $z < 0$, where the z -axis is normal to the plane surface $z = 0$, cannot sustain a bound state. On the other hand, a periodic potential in the $x - y$ plane for $z < 0$ can, under certain conditions,¹ give rise to an electronic surface eigenstate of the form

$$\begin{aligned}\psi(\mathbf{r}) &= e^{-pz} e^{i\mathbf{K} \cdot \mathbf{R}}, \quad z > 0, \\ &= e^{qz} e^{i\mathbf{K} \cdot \mathbf{R}} e^{ik_0 z} (c_{\mathbf{k}} + c_{\mathbf{k}-\mathbf{G}} e^{-iGz}), \quad z < 0,\end{aligned}\tag{17.3}$$

where $\mathbf{K}$ and $\mathbf{R}$ are parallel to the surface, $\mathbf{k} = \mathbf{K} + \mathbf{z}_0(k_0 - iq)$, and $\mathbf{G}$ is a vector of the bulk reciprocal lattice perpendicular to the surface.² In Fig. 17.1, we show theoretical results of the electronic charge redistribution near the surface 001 of Na, as well as near the surface of the JM.

An example of a surface phononic state within the simple Debye model characterized by uniform mass density, ρ , and sound velocities c_ℓ and c_t (for $z < 0$) and $\rho = c_\ell = c_t = 0$ (i.e., the vacuum, for $z > 0$) is the following expression, known as *Rayleigh wave*:

$$\begin{aligned}u_x &= [a k_t e^{k_t z} + b k e^{k_l z}] e^{i(kx - \omega t)} + \text{cc}, \quad z < 0 \\ u_z &= -i [a k e^{k_t z} + b k_l e^{k_l z}] e^{i(kx - \omega t)} + \text{cc}, \quad z < 0 \\ u_y &= 0, \quad z < 0\end{aligned}\tag{17.4}$$

and of course $\mathbf{u} = 0$ for $z > 0$. In the aforementioned equations, $\mathbf{u}(\mathbf{r}, t)$ is the displacement from equilibrium, cc mean complex conjugate, the propagation direction $\mathbf{k}$ parallel to the surface has been chosen as the x -axis, k is the wave vector parallel to the surface, t and l denote transverse and longitudinal wave, and

$$k_j = \left(k^2 - \frac{\omega^2}{c_j^2} \right)^{1/2}, \quad j = t, \ell.\tag{17.5}$$

From the boundary conditions, one obtains³ the following relation between ω and k

$$\omega = \xi c_t k,\tag{17.6}$$

where the dimensionless quantity ξ satisfies the equation

$$\xi^6 - 8\xi^4 + 8\xi^2 \left(3 - 2 \frac{c_t^2}{c_\ell^2} \right) - 16 \left(1 - \frac{c_t^2}{c_\ell^2} \right) = 0.\tag{17.7}$$

The quantity ξ varies from 0.874 to 0.955 as c_t/c_ℓ varies from $1/\sqrt{2}$ to 0. The constants a and b are related as follows

¹ See the book by Ashcroft and Mermin [SS75] p. 369.

² For simplicity, we have assumed that there is only one $\mathbf{G}$ such that $|\mathbf{k}| \simeq |\mathbf{k} - \mathbf{G}|$.

³ See the book by Landau and Lifshitz [AW60], Sect. 24.

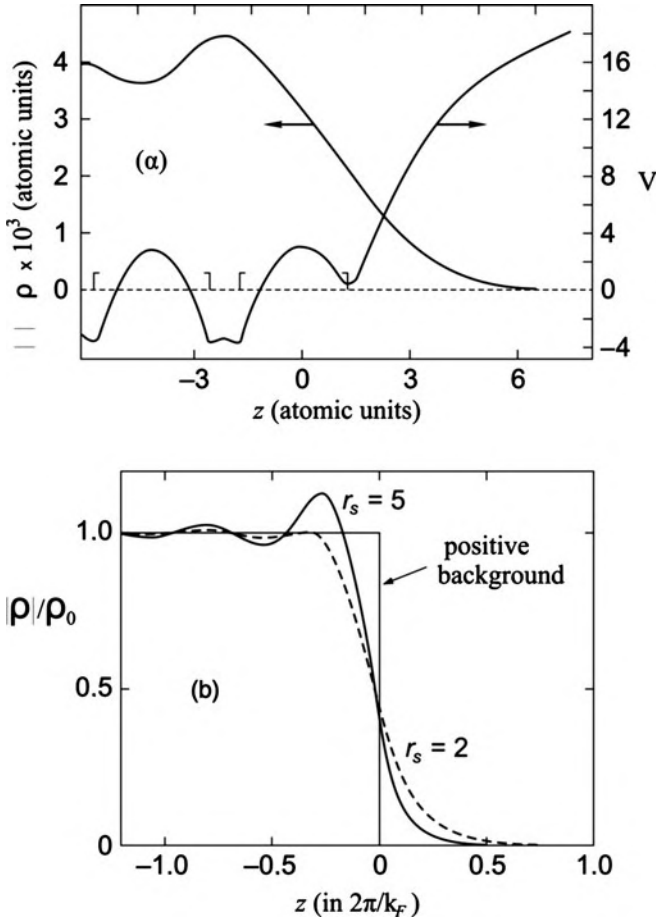


Fig. 17.1. (a) Averaged value $|\bar{\rho}(z)|$ (with respect to the x and y coordinates parallel to the (001) surface of sodium) vs. the distance z from the center of the outer monolayer of this surface. The *brackets* indicated the position and extent of the last two atomic layers. (b) The electronic charge density $|\bar{\rho}(z)|$ near the sharp surface of the JM; ρ_0 is the positive background charge density

$$2a(1 - \xi^2)^{1/2} + (2 - \xi^2)b = 0. \quad (17.8)$$

We shall conclude this section by examining the surface collective oscillations of electrons known as *surface plasmons*. Surface plasmons are strongly coupled to the EM field, being actually composite entities partly collective surface charge oscillations and partly photons (or virtual photons). Their importance has grown – to the level of constituting a new field called *plasmonics* [17.1–17.4] and continues to grow dramatically as our devices continue to shrink from the micro- to the nanoscale. The main reason is that the wavelength of these oscillations depends on the geometry and it can be much

smaller than the wavelength in the vacuum (for the same frequency), allowing thus the EM field to be transmitted through nanoscale channels [17.5–17.9] or to be concentrated around nanoparticles [17.10–17.13]. The applications include “subwavelength” surface plasmon waveguides [17.5–17.7], plasmonic circuits [17.4–17.9] and [17.14], enhanced LEDs [17.15], possibly LEDs based on silicon, detection of single molecule [17.16], even the possibility of cancer treatment by photo-thermal heating through properly designed nanoparticles [17.17] (see Scientific American [17.1]).

Surface plasmons appear at the interface (or the interfaces) between a metal and a dielectric (the latter can be air or even the vacuum). In their classical (i.e., non-quantum) version, they are solutions to Maxwell’s equations, in the presence of material surfaces, or interfaces and in the absence of external sources or incident EM waves. In addition, surface plasmons satisfy the condition $\nabla \cdot \mathbf{E} = 0$ in the interior of each material, while the normal to each interface component of $\mathbf{E}$ is not zero. The first condition, $\nabla \cdot \mathbf{E} = 0$, excludes the possibility of charge fluctuations in the bulk (which are associated with bulk plasmons), while the second, $E_\perp \neq 0$, allows the possibility of surface charge fluctuations (responsible for surface plasmons). For plane and spherical interfaces the surface eigensolutions can be grouped in two categories: the electric solutions (also called transverse magnetic (TM) or P-waves) for which $\hat{H}_\perp = 0$, while $E_\perp \neq 0$, and the magnetic solutions (also called transverse electric (TE) or S-waves) for which $E_\perp = 0$, while $\hat{H}_\perp \neq 0$. Whenever the geometry allows such classification, the surface plasmons belong to the first group (i.e., to the P-waves).

For one (or more parallel to each other) *plane interfaces* with the normal to the interfaces chosen as the z -axis and the propagation direction as the x -axis, the solution within each material n is of the form

$$E_z = F_n(z)e^{i(kx - \omega t)} + cc, \quad (17.9)$$

$$E_x = \left(\frac{i}{k}\right) \left(\frac{dF_n}{dz}\right) e^{i(kx - \omega t)} + cc, \quad (17.10)$$

$$H_y = -\frac{\varepsilon_n \omega}{ck} E_z, \quad \text{G-CGS},^4 \quad (17.11)$$

with all the other component equal to zero and

$$\frac{d^2 F_n}{dz^2} = K_n^2 F_n, \quad (17.12)$$

where

$$K_n^2 = k^2 - \frac{\omega^2 \varepsilon_n \mu_n}{c^2}, \quad \text{Re } K_n \geq 0, \quad (17.13)$$

and ε_n , μ_n are the dielectric function and the relative magnetic permeability. The general solution to (17.12) is a linear combination of $\exp(K_n z)$ and

⁴ In SI, $H_y = -(\varepsilon_0 \varepsilon_n \omega / k) E_z$.

$\exp(-K_n z)$. The boundary conditions are continuity of E_x and H_y at each interface and E_z , E_x , $H_y \rightarrow 0$, as $z \rightarrow \pm\infty$.

For a *single plane interface* between a metal (m) and a dielectric (d), the eigenfrequency of the surface plasmons is given by the equation

$$R \equiv \frac{(K/\varepsilon)_m}{(K/\varepsilon)_d} = -1, \quad (17.14)$$

while the field amplitudes satisfy the relation

$$\frac{F(0)_m}{F(0)_d} = \frac{\varepsilon_d}{\varepsilon_m}. \quad (17.15)$$

In the electrostatic limit, $c \rightarrow \infty$ (valid when $k^2 \gg \omega^2 \varepsilon_n \mu_n / c^2$, $n = m, d$), (17.14), in view of (17.13), becomes

$$\varepsilon_m = -\varepsilon_d. \quad (17.16)$$

Equation (17.16) can be easily obtained by remembering the image method in solving the electrostatic problem of two materials of dielectric functions ε_d and ε_m , respectively, their interface being an infinite plane and a charge q placed in the material of ε_d . The electrostatic potential can be obtained by introducing fictitious image charges $q' = \frac{\varepsilon_d - \varepsilon_m}{\varepsilon_m + \varepsilon_d} q$ and $q'' = \frac{\varepsilon_d}{\varepsilon_m + \varepsilon_d} q$. We see immediately that a non-zero field could exist in the absence of q ($q = 0$), if $\varepsilon_m + \varepsilon_d = 0$; the latter coincides with (17.16).

If we take the dielectric function ε_m of a metal to be of the form shown in Fig. 5.1 and ε_d to be frequency independent, we have from (17.16) that the eigenfrequency of the surface plasmon for $c \rightarrow \infty$ is given by

$$\omega_{sp} = \frac{\omega_p}{\sqrt{1 + (\varepsilon_d/\varepsilon_b)}}. \quad (17.17)$$

If the dielectric is air and $\varepsilon_b = 1$, then $\omega_{sp} = \omega_p/\sqrt{2}$.

If we have a dielectric film of thickness d between two identical semiinfinite metals, the surface plasmon eigenfrequencies are given as solutions to the following equation:

$$R^2 - 2R \coth(K_d d) + 1 = 0, \quad (17.18)$$

where R is defined in (17.14) and K_d in (17.13). For more complicated geometries, see [17.18, 17.19].

For metallic sphere of radius r_0 and dielectric function ε_m surrounded by a dielectric constant ε_d , the eigenfrequencies depend on the spherical harmonics index ℓ and are given in terms of the spherical Bessel, j_ℓ , and Hankel, $h_\ell^{(2)}$, functions as follows:

$$\frac{[x_m j_\ell(x_m)]'}{\varepsilon_m j_\ell(x_m)} = \frac{[x_d h_\ell^{(2)}(x_d)]'}{\varepsilon_d h_\ell^{(2)}(x_d)}, \quad (17.19)$$

where $x_i^2 = \omega^2 \varepsilon_i r_0^2 / c^2$, $i = m, d$, and the prime denotes differentiation with respect to x_m or x_d , respectively. In the electrostatic limit, $c \rightarrow \infty$, (17.19) reduces to

$$\frac{\varepsilon_m}{\varepsilon_d} = -\frac{\ell + 1}{\ell}. \quad (17.20)$$

For $\varepsilon_m = \varepsilon_b \left[1 - \left(\frac{\omega_p}{\omega}\right)^2\right]$, (17.20) gives

$$\omega = \omega_{sp} = \omega_p \sqrt{\frac{\varepsilon_b \ell}{\varepsilon_b \ell + \varepsilon_d (\ell + 1)}}. \quad (17.21)$$

In the limit $\ell \rightarrow \infty$, (17.21) is reduced to (17.17) as it should, while in the case $\ell = 1$ and $\varepsilon_b = \varepsilon_d$, we have $\omega_{sp} = \omega_p / \sqrt{3}$.

17.4 Work Function

The work function, W , is the minimum energy required to transfer an electron (of initial energy E_F) from the interior of a material to an external point close to one of its bounding surfaces. By close we mean at a distance much larger than the lattice constant but much smaller than the linear extent of this surface. The work function can be written as the sum of two contributions.

$$W = W_B + W_s, \quad (17.22)$$

where $W_B \equiv V_B(\infty) - E_F$ and $V_B(\infty)$ is the potential energy at infinite distance from the material under the assumption that the presence of the surfaces produces no modification whatsoever of the ionic positions and no rearrangement of the electronic charge density. Actually, as we have seen, ions undergo relaxation and the electronic charge extends beyond the outer monolayer as shown in Fig. 17.1. Thus, a double layer (of surface charge density σ) is set up, as shown in Fig. 17.2, which was ignored in the definition of W_B . To correct this omission, we add the quantity W_s , which is the energy for the electron to pass through the double layer. Simple electrostatics leads to the following result:

$$W_s = \frac{4\pi |\varepsilon \sigma d'|}{4\pi \varepsilon_0}, \quad (17.23)$$

Notice that the quantity W_s depends not only on the material but also on the orientation of the surface, since both the surface charge density, σ , and the width, d' , depend on this orientation (see Sect. 17.2). We can estimate the magnitude of W_s from Fig. 17.1 to be around 1 eV or lower. We shall choose as representative value $W_s \simeq 0.7$ eV (although smaller values of r_s would produce larger values of W_s).

The quantity W_B for the *simple* JM can be easily obtained. For this model, $V_B(\infty) = 0$, since the total charge density is everywhere zero. Hence, $W_B = -E_F$, but $E_F = (\partial U / \partial N_e)_V$, which in view of (4.39) and (4.44) gives

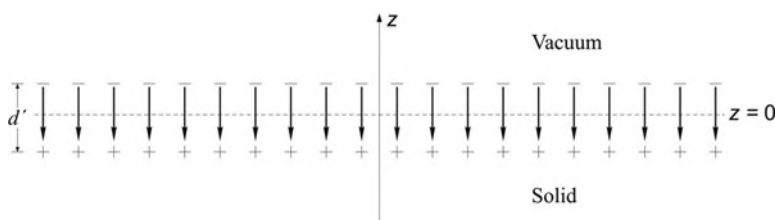


Fig. 17.2. In the surface of a solid a double layer associated with dipole moments is created, since the electronic density extends slightly to the “vacuum” side

Table 17.2. Work function (in eV) of polycrystalline materials, as well as of monocrystalline for various orientation of the surfaces (*CRC Handbook of Chemistry and Physics*, 73rd ed.). In the last column, theoretical results according to the approximate formula (17.25) are presented

Elemental solid	Polycrystalline	Monocrystalline				(17.25)
		(100)	(110)	(111)	(0001)	
Ag	4.26	4.64	4.52	4.74	—	4.15
Al	4.28	4.41	4.06	4.24	—	4.27
Au	5.1	5.47	5.37	5.31	—	4.47
Cu	4.65	4.59	4.48	4.94	—	4.57
Ge	5.0	—	—	4.8	—	—
K	2.30	—	—	—	—	2.37
Na	2.75	—	—	—	—	2.71
Ni	5.15	5.22	5.04	5.35	—	4.93
Si — n	4.85	—	—	—	—	4.50
Si — p	—	4.91	—	4.60	—	4.50
Fe	4.5	4.67	—	4.81	—	4.82
W	4.55	4.63	5.25	4.47	—	5.41
Zn	4.33	—	—	—	4.9	4.24
Cs	2.14	—	—	—	—	2.16

$$\bar{E}_F = \left(\frac{5}{3} \frac{a}{\bar{r}_a^2} - \frac{4}{3} \frac{\gamma}{\bar{r}_a} \right) \frac{dN_a}{dN_e} = -\frac{1}{2} \frac{\gamma}{\bar{r}_a} \frac{1}{\zeta}. \quad (17.24)$$

For γ , we shall use the value $0.56 \zeta^{4/3}$ appropriate for the simple JM (for which the $V_B(\infty) = 0$ is valid).

Combining these relations, we have for W (in eV)

$$W \simeq -E_F + W_S \simeq \frac{7.62 \zeta^{1/3}}{\bar{r}_a} + 0.7 \text{ eV}. \quad (17.25)$$

In Table 17.2, we compare the results of (17.25) with the corresponding experimental data.

17.5 Measuring the Work Function

The most reliable method for measuring the work function is that of *contact potential*. Its drawback is that it determines the difference $W_1 - W_2$ between the work functions of two different metals (conductors in general). This difference is equal to $-e(\phi_1 - \phi_2)$, where $\Delta\phi \equiv \phi_1 - \phi_2$ is established when the two conductors are connected electrically. Indeed, the connection implies that electrons will be transferred from the material with higher Fermi energy to that of the lower until the new Fermi energies E_{F1} and E_{F2} will be equal; according to (5.107), $E_{F1} = E'_{F1} - e\phi_1$ and $E_{F2} = E'_{F2} - e\phi_2$, where E'_{F1} and E'_{F2} are the Fermi energies before the connection. If the minimum energy level outside the two materials before their connection is E'_0 , we have by definition

$$\begin{aligned} W_1 - W_2 &= (E'_0 - E'_{F1}) - (E'_0 - E'_{F2}) = E'_{F2} - E'_{F1} \\ &= (E_{F2} + e\phi_2) - (E_{F1} + e\phi_1) = -e(\phi_1 - \phi_2). \end{aligned}$$

To measure the difference $\phi_1 - \phi_2$, we introduce in the wire connecting the two conductors a variable voltage source (of opposite polarity than $\Delta\phi$) and an ampere meter. Then we adjust the variable voltage until no current flows, which implies that $V + \Delta\phi = 0$. Since this last relation is valid for any distance between the surfaces of the two conductors, we do not actually need the ampere meter. Simply, $\Delta\phi = -V$, where V is the voltage that remains invariant as we change the distance between the two surfaces.

The work function, W , of a conductor can be determined (less accurately than by the contact potential method) by measuring the electronic current leaving the surface under the influence of thermal excitation (*thermionic emission*), or photons (*photoemission*), or strong electric field (*field emission*). The thermionic emission current density is given by the *Richardson–Dushman formula*:

$$j = BT^2 \exp\left(-\frac{W}{k_B T}\right), \quad (17.26)$$

where

$$B = \frac{emk_B^2}{2\pi^2\hbar^3} = 120 \frac{\text{A}}{\text{cm}^2\text{K}^2}. \quad (17.27)$$

The proof of (17.26) is straightforward, since the current density, j , along the z -direction normal to and away from the surface is given by

$$j = -\frac{2e}{V} \sum v_z f = -\frac{e}{4\pi^3} \int_{k_z > 0} d^3k v_z f, \quad (17.28)$$

where $v_z = \hbar k_z/m$ and f is given by

$$f = \frac{1}{e^{\beta(\varepsilon_k - \mu)} + 1} \simeq e^{-\beta(\varepsilon_k - \mu)}. \quad (17.29)$$

However, $\varepsilon_k - \mu = (\hbar^2 k^2/2m) + W$. Performing the integration in (17.28) by setting $d^3k = dk_x dk_y dk_z$, we end up with (17.26) and (17.27). In reality, the

quantity B is not a universal constant as (17.27) implies; its value for various materials is in the range between 60 and 160 A/cm²K². This discrepancy is due to surface scattering effects, which were ignored in our derivation.

The case of photoemission differs from the thermionic emission in two respects: first, the $\varepsilon_k - \mu$ is now equal to $\hbar^2 k^2 / 2m + (W - \hbar\omega)$, where ω is the frequency of the absorbed photon; second, because of the reduction of the energy barrier from W to $W - \hbar\omega$, the quantity $\beta(\varepsilon_k - \mu)$ is now not necessarily much larger than one (it can be even negative), and hence, the Fermi distribution cannot be replaced by the Boltzmann distribution as in (17.29). By introducing cylindrical coordinates, the integration over $dk_x dk_y$ can be done analytically and the final result for the photoemission current density is

$$j = -\frac{em(k_B T)^2}{2\pi^2 \hbar^3} \int_0^\infty \frac{dx}{e^{x-\lambda} + 1}, \quad (17.30)$$

where $\lambda = \beta\hbar\omega - \beta W$.

Problem 17.1t. In the two limiting cases, $\lambda \gg 1$ and λ negative with $|\lambda| \gg 1$, find explicit expression for j in (17.30) by showing that the integral is equal to $(\lambda^2/2) + (\pi^2/6)$ when $\lambda \gg 1$, and $\exp(\lambda)$ when λ is negative and $|\lambda| \gg 1$.

Equation (17.30) is known as the *Fowler equation*.

The current density due to the emission by an electric field $\mathcal{E}$ normal to the surface is given by the so-called *Fowler–Nordheim formula*

$$j = -\frac{e^3 \mathcal{E}^2}{16\pi^2 C \hbar W} \exp \left[-\frac{4(2m)^{1/2} W^{3/2}}{3 \hbar e \mathcal{E}} C' \right], \quad (17.31)$$

where C and C' are numerical factors close to one.

Problem 17.2t. Prove (17.31)

Hint: Start with the expression

$$j = -\frac{2e}{V} \sum_{\mathbf{k}} \frac{\hbar k_z}{m} |t|^2, \quad (17.32)$$

where the transmission coefficient $|t|^2$ of an electron of energy E_1 through the field-induced barrier (see Fig. 17.3) is given by

$$|t|^2 = \exp \left(-\frac{2}{\hbar} \int_0^{z_1} |p| dz \right), \quad (17.33)$$

where

$$|p| = \sqrt{2m[V(z) - E_1]}. \quad (17.34)$$

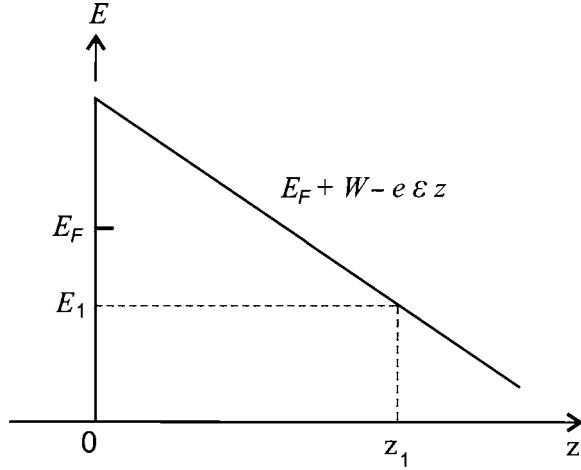


Fig. 17.3. The potential $V(z) = E_F + W - e\mathcal{E}z$ created by an electric field $\mathcal{E}$ normal to the surface (which is located at $z = 0$). The zero of energy has been chosen at the bottom of the conduction band. The thermal excitation is assumed to give a negligible contribution to the emission current. E_1 varies between 0 and E_F .

We shall conclude this section by pointing out that we can reduce the work function of a conductor by depositing alkaline atoms (e.g., Cs). As the surface concentration of the latter increases, the work function is reduced and it reaches a minimum at 30% covering. Further increase of the surface concentration of Cs atoms leads to a gradual increase of W until a monolayer of Cs atoms is reached; then the work function saturates at the Cs value. The overall reduction of the work function by the deposition of alkaline atoms can be attributed to the transfer of their valence electrons to the atoms of the host and the resulting creation of a double layer of opposite sign and of larger size than that of the host metal. It is less obvious why the alkali atoms produce the stronger double layer at about 30% coverage.

17.6 The p-n Homojunction in Equilibrium

The p-n homojunction is one of the simplest man-made interfaces, which plays a crucial role in a host of electronic devices (see Fig. 8.6 in p. 233). To study this interface, we examine first what the concentrations of holes and electrons would be at the two sides of the interface, if the two pieces were disconnected. These quantities are given by (7.77)–(7.79), where $\delta N = -N_a$ for the p-doped part in the left and $\delta N = N_d$ for the n-doped part in the right. Taking into account that $n_i \ll N_a$, N_d , (7.77)–(7.79) become, for the p-side on the left,

$$p_1 = N_a, \quad n_1 = \frac{n_i^2}{N_a}, \quad \mu_{01} = k_B T \ln \frac{N_v}{N_a}, \quad (17.35)$$

while for the n-side on the right

$$p_r = \frac{n_i^2}{N_d}, \quad n_r = N_d, \quad \mu_{0r} = E_g - k_B T \ln \frac{N_c}{N_d}, \quad (17.36)$$

where $N_v = A_v(k_B T)^{3/2}$ and $N_c = A_c(k_B T)^{3/2}$. The quantities A_v and A_c are given in the caption of Fig. 7.6, while $n_i^2 = N_v N_c \exp(-\beta E_g)$. E_c is the bottom of the *CB* and coincides with E_g , if the top of the *VB* is chosen as the zero of energy.

Problem 17.3t. Prove the last relation in (17.35) and in (17.36).

Next we examine how the previous picture is modified in the actual case where the two sides are connected. Obviously, electrons would move from the right side (the n side with the high chemical potential μ_{0r}) to the left side (the p side with the low chemical potential μ_{0l}) until the new chemical potential μ is constant everywhere. This movement of the electrons would set up a charge density $\rho(x)$ which would be negative on the left side and positive on the right side. As a result, an electrostatic potential, $\phi(x)$, would be created according to Poisson's equation

$$\frac{d^2 \phi}{dx^2} = -\frac{4\pi \rho(x)}{\varepsilon}, \quad \text{G-CGS.}^5 \quad (17.37)$$

The equilibrium chemical potential, μ , is given by (5.111)

$$\mu = \mu_0(x) - e\phi(x), \quad (17.38)$$

where $\mu_0(x)$ is a function of the local⁶ electron or hole concentration according to (7.70) or (7.71), respectively

$$\mu_0(x) = E_g + k_B T \ln \frac{n(x)}{N_c}, \quad x > 0, \quad (17.39)$$

$$\mu_0(x) = -k_B T \ln \frac{p(x)}{N_v}, \quad x < 0, \quad (17.40)$$

(we assume that the interface is at $x = 0$). The charge density, $\rho(x)$, is obviously given by the following relation

$$\rho(x) = e [N_d(x) + p(x) - N_a(x) - n(x)], \quad (17.41)$$

where $N_d(x) = N_d$ for $x > 0$ and $N_d(x) = 0$ for $x < 0$, while $N_a(x) = 0$ for $x > 0$ and $N_a(x) = N_a$ for $x < 0$. Far away from the interface, all the quantities would be constant as given below

⁵ In SI, the 4π must be replaced by ε_0^{-1} .

⁶ We assume that $\phi(x)$ and $\mu_0(x)$ vary slowly relative to the interatomic distance.

$$\begin{aligned}
p(-\infty) &= N_a, n(-\infty) = \frac{n_i^2}{N_a}, E_v(-\infty) = -e\phi(-\infty), \\
\varepsilon_\alpha(-\infty) &= \varepsilon_\alpha - e\phi(-\infty), E_c(-\infty) = E_c - e\phi(-\infty), \\
n(+\infty) &= N_d, p(+\infty) = \frac{n_i^2}{N_d}, E_v(+\infty) = -e\phi(+\infty), \\
E_c(+\infty) &= E_c - e\phi(+\infty).
\end{aligned} \tag{17.42}$$

The significant variation will take place in a region around the interface from $x \simeq -d_p$ to $x \simeq d_n$. This is the so-called *depletion region*, because the concentration of carriers there has been drastically reduced.

It is clear from (17.39), (17.40) and (17.41) that both $n(x)$ and $p(x)$, and hence, $\rho(x)$ can be expressed in terms of $\mu_0(x)$. Then the differential equation (17.37) together with the boundaries conditions at $x = \pm\infty$ and the continuity of $\phi(x)$ and $\phi'(x)$ at $x = 0$ determines $\phi(x)$ in terms of $\mu_0(x)$ (apart from a constant that is usually chosen such that $\phi(0) = 0$). Finally (17.38) determines $\mu_0(x)$, and hence, all the other quantities. The accurate implementation of the procedure just outlined requires numerical solution to the differential equation (17.37). However, one can obtain reasonable approximate determination of the quantities of interest by taking

$$\rho(x) \simeq -eN_a, \quad -d_p < x < 0, \tag{17.43}$$

$$\rho(x) \simeq eN_d, \quad 0 < x < d_n, \tag{17.44}$$

and

$$\rho(x) = 0 \quad \text{everywhere else.} \tag{17.45}$$

Problem 17.4t. Based on (17.43)–(17.45), solve the differential equation (17.37), assuming that $\phi(0) = 0$. Using also the continuity of $\phi'(0)$, show that

$$\phi(-\infty) = -\frac{2\pi eN_a}{4\pi\varepsilon_0\varepsilon}d_p^2, \tag{17.46}$$

$$\phi(+\infty) = \frac{2\pi eN_d}{4\pi\varepsilon_0\varepsilon}d_n^2, \tag{17.47}$$

$$N_ad_p = N_nd_n. \tag{17.48}$$

Then taking into account (17.38) and that μ at $-\infty$ is equal to μ at $+\infty$, show that

$$\Delta\phi \equiv \phi(+\infty) - \phi(-\infty) = \frac{E_g}{e} + \frac{k_B T}{e} \ln \frac{N_d N_a}{N_c N_v}. \tag{17.49}$$

Combining (17.46) to (17.48), show that

$$d_n = \left[\frac{N_a}{N_d} \frac{1}{N_a + N_d} \frac{4\pi\varepsilon_0\varepsilon\Delta\phi}{2\pi e} \right]^{1/2}, \tag{17.50}$$

$$d_p = \left[\frac{N_d}{N_a} \frac{1}{N_a + N_d} \frac{4\pi\varepsilon_0\varepsilon\Delta\phi}{2\pi e} \right]^{1/2}, \tag{17.51}$$

$$\mu = \frac{2\pi e^2 N_a}{4\pi\varepsilon_0\varepsilon}d_p^2 - k_B T \ln \frac{N_a}{N_v}. \tag{17.52}$$

In Fig. 17.4, we plot schematically the variation of the various quantities of interest vs. x .

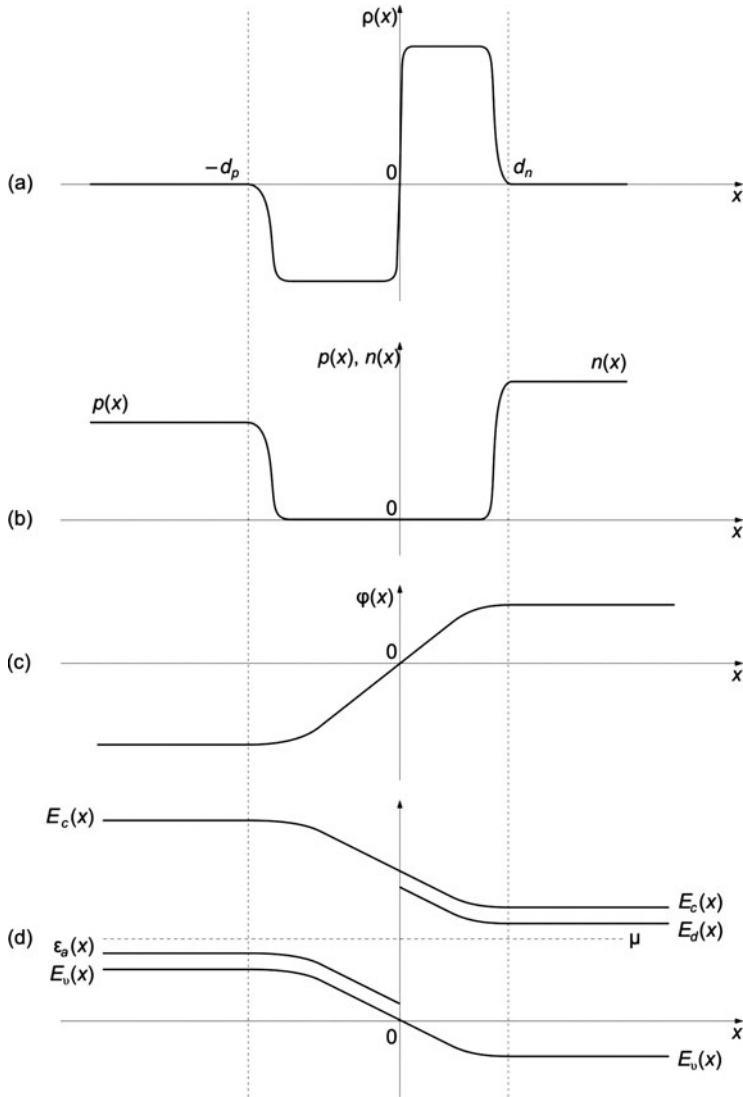


Fig. 17.4. As the distance x from the interface of a p-n homojunction in equilibrium varies so do the following quantities shown schematically here: **(a)** the charge density $\rho(x)$; **(b)** the concentration of holes and electrons $p(x)$ and $n(x)$ respectively; **(c)** the induced electrostatic potential $\phi(x)$; **(d)** the top of the valence band $E_v(x)$, the acceptor level $\epsilon_a(x)$, the chemical potential μ , the donor level $E_d(x) \equiv E_c(x) - \epsilon_d(x)$, and the bottom of the conduction band $E_c(x)$

17.7 The p-n Homojunction Under an External Voltage V

We consider here the case where the p-n homojunction, being part of a closed circuit, is driven by an external voltage, V , which is taken as positive when the positive pole of the external source is connected to the p-side and the negative to the n-side. Positive V is referred to as *forward bias*, while negative V is referred to as *reverse bias* (Fig. 17.5). The external voltage drives the system out of thermodynamic equilibrium to a steady state of current density j , to which both electrons and holes contribute

$$j = j_e + j_h. \quad (17.53)$$

According to (5.114) (in the absence of temperature gradient) and (5.113), $j_e = \sigma_e E + (\sigma_e/e) (\partial\mu_0/\partial n) (dn/dx)$, which can be written as

$$j_e = \sigma_e E + eD_e \frac{dn}{dx}. \quad (17.54)$$

The last relation follows from (8.46) connecting the diffusion coefficient, D_e , to the conductivity, σ_e . Because of the relation (13.67), $\sigma = qn\bar{\mu}$, where q is the charge of the carrier and $\bar{\mu}$ its average mobility. Eqs (8.46) and (8.43) for the coefficient D give

$$D = \frac{\bar{\mu}n}{q} \frac{\partial\mu}{\partial n} = \frac{\bar{\mu}k_B T}{q}. \quad (17.55)$$

Thus, there are two contributions to j_e : one, $\sigma \mathbf{E}$, due to the electric field $\mathbf{E}$, which is called *drift current-density* and the other due to the gradient of the electron concentration, which is called *diffusion current-density*. Similarly, for the hole current density, we have two contributions

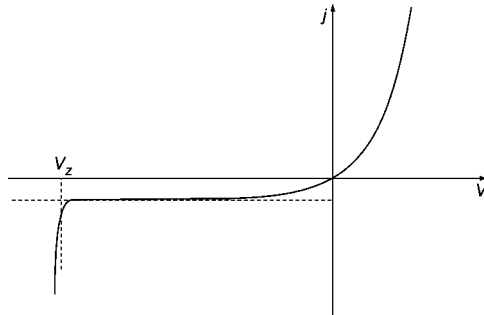


Fig. 17.5. The current-density vs. applied voltage in a p-n homojunction, where positive V means that the positive pole is connected to the p-side (forward bias). In the reverse bias the current tends to *saturate* at the value $|j_{\text{sat}}| = en_i^2(D_n L_n^{-1} N_a^{-1} + D_p L_p^{-1} N_d^{-1})$; for $V \leq -|V_Z|$ the junction undergoes a dielectric breakdown known as the *Zener* breakdown (see [SS82], pp. 422–425)

$$j_h = \sigma_h E - e D_p \frac{dp}{dx}. \quad (17.56)$$

To proceed with the determination of the current densities, we need two more equations connecting the current densities to the concentrations n and p . These are the continuity equations, including creation and annihilation of electrons and holes:

$$\frac{\partial n}{\partial t} = \frac{1}{e} \frac{\partial j_e}{\partial x} + \frac{n^{(0)}}{\tau_n} - \frac{n}{\tau_n}, \quad (17.57)$$

$$\frac{\partial p}{\partial t} = -\frac{1}{e} \frac{\partial j_h}{\partial x} + \frac{p^{(0)}}{\tau_p} - \frac{p}{\tau_p}. \quad (17.58)$$

The terms $n^{(0)}/\tau_n$ and $p^{(0)}/\tau_p$ give the *generation* of carriers per unit time and per unit volume (electrons in the conduction band and holes in the valence band) by thermal excitations. The quantities $n^{(0)}$ and $p^{(0)}$ are the equilibrium concentration of electrons and holes respectively at each point and τ_n and τ_p are the life times of an electron in CB and a hole in the VB respectively. The terms n/τ_n and p/τ_p give the annihilation per unit time and volume of electrons in the CB and holes in the VB by *recombination*. Notice that at equilibrium, i.e., $n = n^{(0)}$ and $p = p^{(0)}$, the generation and the recombination of carriers cancel each other so that the number of electrons and the number of holes at equilibrium are conserved.

Equations (17.54)–(17.58) together with Poisson's equation (17.37) and the boundary and continuity conditions are enough to determine the solution. Here, as we did before, we introduce some reasonable approximation to obtain approximate analytical solutions instead of accurate numerical results. We observe first that the total resistance of the device comes almost exclusively from the depletion region, since there the number of carriers is greatly reduced and – even more significant – the diffusion current is opposite and almost equal to the drift current. Hence, the total voltage $\Delta\phi' = \Delta\phi - V$ appears across the depletion region. From Poisson's equation and the boundary conditions, we find again relations similar to (17.50) and (17.51) with the only difference that $\Delta\phi$ is replaced now by $\Delta\phi' = \Delta\phi - V$. Hence, the extent of the depletion region is now $d'_p + d'_n$ instead of $d_p + d_n$, where

$$d'_p = d_p \left[1 - \frac{V}{\Delta\phi} \right]^{1/2}, \quad (17.59)$$

$$d'_n = d_n \left[1 - \frac{V}{\Delta\phi} \right]^{1/2}. \quad (17.60)$$

It follows that the forward bias reduces the width of the depletion region, and hence, the resistance of the device, leading to greater forward current in comparison with the reverse bias, which increases the width of the depletion region and it increases its resistance. Thus, the p–n junction acts as a rectifier.

Since the total j_e and the total j_h in the depletion region are much smaller than the corresponding drift or diffusion current densities there, we can still use (17.39) and (17.40) in combination with (17.38) to obtain

$$\frac{n(-d'_p)}{n(d'_n)} \approx \frac{e^{\beta e \phi'(-d'_p)}}{e^{\beta e \phi'(d'_n)}} \approx e^{-\beta e \Delta \phi'} = e^{-\beta e \Delta \phi} e^{\beta e V}, \quad (17.61)$$

or

$$n(-d'_p) = (N_d e^{-\beta e \Delta \phi}) e^{\beta e V} = \frac{n_i^2}{N_a} e^{\beta e V}. \quad (17.62)$$

The last relation follows by combining $n(d'_n) = N_d$ with (17.49) and $n_i^2 = N_v N_c \exp(-\beta E_g)$. Similarly, we show that

$$p(d'_n) = \frac{n_i^2}{N_d} e^{\beta e V}. \quad (17.63)$$

Equations (17.62) and (17.63) show that the *minority carriers* (electrons in the p-side and holes in the n-side) do not reach their equilibrium concentrations n_i^2/N_a and n_i^2/N_d respectively at the end points of the depletion region. On the contrary, their concentration varies beyond the depletion region and approaches asymptotically in an exponential way the equilibrium value with characteristic lengths L_n and L_p for the minority electrons (in the p-side) and the minority holes (in the n-side) respectively. There (i.e., for $-(d_p + L_n) \lesssim x \leq -d_p$ and for $d_n \leq x \leq d_n + L_p$) the dominant contribution to the minority current density is due to the diffusion mechanism (the minority drift current density is negligible, because both the electric fields are almost zero and the minority concentration is very low). Thus

$$j_e(x) \simeq e D_n \frac{dn}{dx}, \quad x \leq -d'_p, \quad (17.64)$$

$$j_h(x) \simeq -e D_p \frac{dp}{dx}, \quad d'_n \leq x. \quad (17.65)$$

In the depletion region, we expect that the generation and the recombination probability is negligible, because the differences $n^{(0)} - n$ and $p^{(0)} - p$ are very small and the times τ_n and τ_p are much larger than the time for an electron or a hole to cross the depletion region. This observation together with (17.57) and (17.58) and the fact that $\partial n / \partial t = \partial p / \partial t = 0$ (for a steady state) leads to the conclusion that both j_e and j_h are practically constant in the depletion region, i.e., for $-d'_p \leq x \leq d'_n$. Using this constancy, we can write that the total current density, j , is equal to

$$j = j_e(-d'_p) + j_h(d'_n). \quad (17.66)$$

We have chosen the arguments in $j_e(-d'_p)$ and $j_h(d'_n)$ this way, because we can calculate them using (17.64) and (17.57) as well as (17.65) and (17.58).

Indeed, the first pair of equations leads to the differential equation (taking into account that $\partial n / \partial t = 0$)

$$D_n \frac{d^2 n}{dx^2} = \frac{n - n^{(0)}}{\tau_n}, \quad x \leq -d'_p, \quad (17.67)$$

the solution of which is

$$n(x) = \frac{n_i^2}{N_a} + \left[n(-d'_p) - \frac{n_i^2}{N_a} \right] \exp \left[(x + d'_p) / L_n \right], \quad x \leq -d'_p, \quad (17.68)$$

where

$$L_n = (D_n \tau_n)^{1/2}. \quad (17.69)$$

The second pair of equations for the minority hole concentration gives

$$p(x) = \frac{n_i^2}{N_d} + \left[p(d'_n) - \frac{n_i^2}{N_d} \right] \exp \left[-\frac{x - d'_n}{L_p} \right], \quad d'_n \leq x, \quad (17.70)$$

with

$$L_p = (D_p \tau_p)^{1/2}. \quad (17.71)$$

Substituting (17.68) in (17.64), setting $x = -d'_p$, and taking into account (17.62), we obtain $j_e(-d'_p)$; from (17.70) and (17.65) at $x = d'_n$ and (17.63), we find $j_h(d'_n)$. Substituting in (17.65), we obtain finally

$$j = en_i^2 \left(\frac{D_n}{L_n N_a} + \frac{D_p}{L_p N_d} \right) (e^{\beta e V} - 1). \quad (17.72)$$

It turns out that the saturation current density under reverse bias is the *generation current* density of the *minority* carriers. Indeed, a hole generated in the region $d'_n < x$ in order to contribute to the saturation current density must avoid recombination until it reaches the depletion region. For this to happen, it must reach the depletion region within its lifetime, τ_p , which implies that its travel distance is of the order of $L_p = (D_p \tau_p)^{1/2}$ or less. Hence, the number of holes per unit surface and time to reach the depletion region from $d'_n < x$ is equal to the probability of generation per unit time and volume $p^{(0)} / \tau_p$ multiplied by the effective length, L_p . The current density in the direction from left to right is obtained by multiplying $L_p p^{(0)} / \tau_p$ by the charge e of the hole and by (-1) :

$$j_{h, \text{gen}} = -e p^{(0)} L_p / \tau_p = -e \frac{n_i^2}{N_d} \frac{D_p}{L_p}. \quad (17.73)$$

Similarly, electrons from the p-side (minority carriers) contribute to the density of the generation-current as follows:

$$j_{e, \text{gen}} = -e \frac{n_i^2}{N_a} \frac{D_n}{L_n}. \quad (17.74)$$

Adding (17.73) and (17.74), we find that the total generation-current density of the minority carriers coincides with the saturation-current density according to (17.72).

We can obtain also the final expression (17.72) by considering, besides the generation-current density of the minority carriers in the reverse direction, the current density of the majority carriers (let us start first with holes) in the forward direction. (This is called *recombination-current* density, because when, e.g., the holes cross the depletion region and they find themselves at the opposite side, they will recombine almost immediately due to the high concentration of electrons there.) In order for the holes at the p-side to move in the forward direction, they have to overcome thermally the potential barrier $e\Delta\phi'$. Hence, their contribution to the forward current density is the form

$$j_{h,rec} = A_h e^{-\beta e\Delta\phi'} = A_h e^{-\beta e(\Delta\phi - V)}. \quad (17.75)$$

The electrons would give a similar contribution. Thus, the total recombination-current density is given by

$$j_{rec} = A e^{-\beta e\Delta\phi} e^{\beta eV}. \quad (17.76)$$

The prefactor A in (17.76) can be determined by considering the case, $V = 0$, where $j = 0$ and hence, $j_{rec} + j_{gen} = 0$. It follows that

$$A = -j_{gen} e^{\beta e\Delta\phi}. \quad (17.77)$$

Thus, the total current-density, $j = j_{rec} + j_{gen}$, is equal to the following

$$j = -j_{gen}(e^{\beta eV} - 1), \quad (17.78)$$

which coincides with (17.72) by taking into account (17.73) and (17.74).

Problem 17.5t. Consider a doped Si with $N_a \equiv N_d = 10^{16} \text{ cm}^{-3}$ at $T = 300 \text{ K}$. Taking into account the average electron and hole mobility and the electron and hole effective masses and assuming that $\tau_n = \tau_p = 10^{-7} \text{ s}$, calculate all the relevant quantities for the p-n homojunctions.

Answer: $D_n = 35 \text{ cm}^2/\text{s}$, $D_p = 12.4 \text{ cm}^2/\text{s}$, $N_c = 1.75 \times 10^{19} \text{ cm}^{-3}$, $P_v = 1.14 \times 10^{19} \text{ cm}^{-3}$, $e\Delta\phi = 0.733 \text{ eV}$, $\varepsilon e\Delta\phi = 8.73 \text{ eV}$, $d_n = d_p = 690 \text{ \AA}$, $L_n = 1.86 \times 10^{-3} \text{ cm}$, $L_p = 1.11 \times 10^{-3} \text{ cm}$, $j_{gen} = 2.3 \times 10^{-11} \text{ A/cm}^2$.

17.8 Some Applications of Interfaces

In this section, we mention very briefly some applications of p-n and other junctions.

Light-emitting diodes (LEDs). A forward biased p-n junction acts as a light-emitting device, since the majority carriers producing the forward-current recombine immediately after crossing the depletion region (the holes

from the p-side recombine with the high-concentration electrons at the n-side and the electrons from the n-side recombine with the high-concentration holes at the p-side). This recombination is associated with the emission of photons of energy, $\hbar\omega \simeq E_g$. For a p–n junction to act efficiently as LED, a heterojunction of *direct-gap* semiconductors is needed. In such devices, the efficiency has been raised dramatically recently.

Photovoltaics. Photons reaching the diffusion region in the n-side of a p–n junction can be absorbed by creating electron–hole pairs. As a result, the number of minority-carriers (holes) is increasing, and as a result, an additional photon-generated reverse hole-current density $j_{h,gen,ph}$ will appear. Similarly, photons reaching the diffusion region in the p-side of a p–n junction can be absorbed creating electron–hole pairs and increasing thus the minority-carriers (electrons). Hence, an additional photon-generated reverse electron-current density $j_{e,gen,ph}$ will appear. Let us denote the total photon-generated reverse current by j_L . Then, adding j_L to j given by (17.72), we have the following expression for the total current of a p–n homojunction illuminated by light

$$j = |j_{sat}| (e^{\beta eV} - 1) + j_L; \quad j_L < 0. \quad (17.79)$$

In Fig. 17.6 we plot j vs. V according to (17.79).

To obtain the maximum power out of this photovoltaic device, we have to operate at a voltage V that maximizes the shaded rectangle in Fig. 17.6. The ratio of the maximized rectangle to the product $V_0 j_L$ is called filling factor (FF). Thus, the electrical power, P , per unit area of this device is given by

$$P = (FF)V_0 |j_L|. \quad (17.80)$$

The open-circuit voltage V_0 is no larger than $E_g - \varepsilon_a - \varepsilon_d$. A typical value of V_0 is $2E_g/3e$. The theoretical upper limit for j_L is obtained, if each incoming

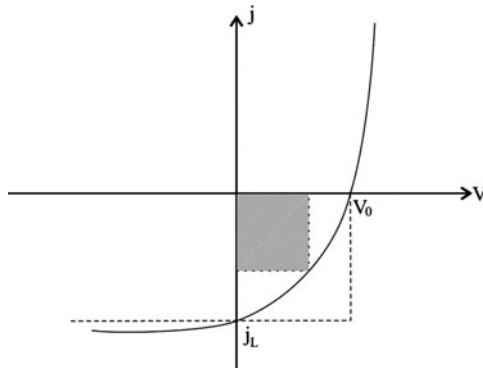


Fig. 17.6. Plot of the current-density j vs. voltage V for a p–n homojunction under illumination; j_L is the short-circuit current density when $V = 0$. V_0 is the open-circuit voltage when $j = 0$

photon is absorbed in the diffusion region generating a minority-carrier, which in turn reaches the depletion region contributing to the reverse current. Under these idealized conditions, $|j_L|$ is equal to

$$|j_L| = |e| \int_{E_g/h}^{\infty} d\omega \frac{I(\omega)}{\hbar\omega}, \quad (17.81)$$

where $I(\omega)$ is the energy per unit-time per unit-area, and per unit-frequency of the photons hitting the p-n junction, and $I(\omega)/\hbar\omega$ is the number of photons per unit-time, per unit-area, and unit-frequency hitting the p-n junction. Of those photons only the ones with $\hbar\omega > E_g$ have the capability of generating electron-hole pairs

Problem 17.6ts. Assuming that $I(\omega)$ is the sunlight distribution (which can be approximated by that of a black body of temperature $T = 5800$ K) and that $FF = 0.75$, calculate under ideal conditions the conversion efficiency η (where $\eta \equiv P/P_t$ and $P_t \equiv \int_0^\infty d\omega I(\omega)$) as a function of E_g . Which value of E_g gives the maximum of η ?

Schottky barriers are formed at the interface between a metal and a type-n-semiconductor under the condition that the work function of metal, W_M , is higher than the work function, W_S , of the semiconductor ($W_M > W_S$). Schottky barriers appear also between a metal and a type-p semiconductor, if $W_M < W_S$. Let us examine the case metal/n-type with $W_M > W_S$. Under these conditions, electrons would depart from the type-n semiconductor to the metal creating a depletion region in the semiconductor (practically there is no depletion region in the metal because of the very high concentration of electrons). Hence, in the semiconductor side, the situation would be similar to that of the side n in Fig. 17.4. Thus, the current density j vs. external voltage⁷ V is similar (but not identical to (17.72)):

$$j = j_0(e^{\beta eV} - 1), \quad (17.82)$$

where j_0 is the *forward*-current when $V = 0$. This current is controlled by the potential barrier W' which is equal to $E_c - E_F \equiv W_M - W_s + \varepsilon_d$, where E_c is the bottom of the conduction band of the semiconductor and E_F is the Fermi level of the metal. The Richardson–Dushman formula (17.26) is applicable to the forward-current j_0 with W replaced by $W' = W_M - W_s + \varepsilon_d$:

$$j_0 = BT^2 \exp \left[-\frac{(W_m - W_s + \varepsilon_d)}{k_B T} \right]. \quad (17.83)$$

In reality the current-density vs. external voltage is more complicated than that of (17.82) and (17.83). The discrepancy is attributed to surface individual electronic states which tend to pin down the Fermi level in the semiconductor side.

⁷ Positive V means forward-bias, i.e., the positive pole connected to the metal side.

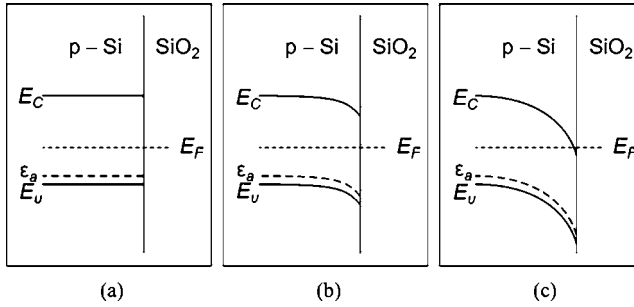


Fig. 17.7. The interface between the SiO₂, and the type p-semiconductor, of the MOSFET (see Fig. 8.6). **(a)** The gate voltage (i.e., the one between the metal above the SiO₂ and the metal below the p-semiconductor) is zero. **(b)** The gate voltage is positive (i.e., the potential ϕ of the metal above the SiO₂ is higher than that of the metal at the bottom); as a result the electron potential energy $\mathcal{V}(x) = -|e|\phi(x)$ is increasing as x increases in the direction from SiO₂ towards the electrode at the bottom and the levels E_C , E_V , ϵ_d are bent as shown. **(c)** If the gate voltage is positive and large enough, E_C at the interface is lower than E_F .

The metal–oxide–semiconductor field effect transistor (MOSFET) is shown in Fig. 8.6. Its principle of operation is outlined in Fig. 17.7. As the gate-voltage increases, the energy-difference between E_C and E_F decreases and the concentration of the minority-carriers is increasing until, at some point, E_F enters the conduction band (i.e., $E_F > E_C(0)$) and a n-channel opens up connecting the source to the drain. This channel is called *inversion layer*. Thus, by changing the gate-voltage, we control the concentration of carriers between source and drain and we achieve thus transistor operation.

The increase of the electron-concentration and the decrease of the hole-concentration with increasing gate-voltage sets up a charge density $\rho(x)$ in the p-side of the interface given by (17.41) with $N_d = 0$. Through Poisson's equation, $d^2\phi/dx = -4\pi\rho(x)/4\pi\epsilon_0\epsilon$, and (17.39) and (17.40), we can obtain a differential equation involving only $\phi(x)$. Taking into account the continuity of $\phi(x)$ and $\phi'(x)$, the relation $d^2\phi/dx^2 = 0$ in SiO₂ (since there are no carriers in SiO₂), and the boundary condition that the applied gate voltage is equal to the difference $\Delta\phi$ between the top and the bottom electrodes, $\phi(x)$ and all other quantities of interest are uniquely determined.

17.9 Key Points

- Preparation of clean surfaces requires ultra-high vacuum of the order of 10^{-13} bar $\simeq 10^{-10}$ torr or less.
- In tetrahedral semiconductors, surfaces of certain orientation such as the (111) and its equivalents are preferred, because their creation in comparison with those of other orientations is energetically favored.

- In metals, the outer surface atomic monolayer (and to a lesser degree the one or two below it) is displaced perpendicularly to the surface by a distance z_1 relative to the ideal bulk lattice position. This process is called *relaxation*. Usually z_1 is negative (meaning displacement towards the interior) and of the order of a few percent (see Table 17.1).
- In tetrahedral semiconductors, besides relaxation, non-uniform displacements parallel to the surface occur. This is called *reconstruction*. The surface atoms are arranged in a two-dimensional lattice $n_1 \mathbf{c}_1 + n_2 \mathbf{c}_2$, where $\mathbf{c}_1, \mathbf{c}_2$ are different from the primitive vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ of a lattice plane in the bulk parallel to the surface. If $\mathbf{c}_1 = p_1 \mathbf{a}_1$ and $\mathbf{c}_2 = p_2 \mathbf{a}_2$, then the reconstruction is denoted as $p_1 \times p_2$. Reconstruction occurs, because of the need to partially passivate energetically unfavorable dangling bonds.
- Surfaces and interfaces, besides reflecting and refracting bulk Bloch waves, can, under certain conditions, sustain surface states, i.e., eigenstates that decay to zero as the distance from the surface(s) or interface(s) increases to infinity. Individual electronic surface states may pin down the Fermi level in semiconductor junctions influencing their performance. Surface phonons are quite common.
- Collective electronic surface states, called *surface plasmons*, occur at the interfaces between a metal and a dielectric. Surface plasmons are solutions to Maxwell equations in the absence of external sources or incident waves such that $\nabla \cdot \mathbf{E} = 0$ in the bulk, while $E_\perp$ is in general different from zero. For a single plane metal–dielectric interface, the eigenfrequency of the surface plasmons in the electrostatic limit ($c \rightarrow \infty$) is given by

$$\varepsilon_m + \varepsilon_d = 0,$$

where ε_m and ε_d are the dielectric functions of the metal and the dielectric respectively.

- The work function, W , of a conductor (or a semiconductor) is equal to the difference $E_0 - E_F$, where E_0 is the minimum energy of an electron outside its surface. A simple approximate formula for W within the JM is as follows

$$W \simeq \frac{7.62 \zeta^{1/3}}{\bar{r}_a} + 0.7 \text{ eV}.$$

- The work function difference between two conductors can be measured by the contact potential method according to which

$$W_1 - W_2 = -e(\phi_1 - \phi_2)$$

where $\phi_1 - \phi_2$ is the potential difference between the two conductors, which remains invariant as their distance varies. The function W enters also in formulas giving the emission-current density from the surface.

- Thus we have

$$j = BT^2 \exp\left(-\frac{W}{k_B T}\right), \text{ thermionic emission,}$$

$$j = -\frac{em(k_B T)^2}{2\pi^2 \hbar^3} \int_0^\infty \frac{dx}{e^{x-\lambda} + 1}, \quad \lambda = \beta \hbar \omega - \beta W, \text{ photoemission,}$$

$$j = -\frac{e^3 \mathcal{E}^2}{16\pi^2 C \hbar W} \exp\left(-\frac{4(2m)^{1/2} W^{3/2}}{3 \hbar e \mathcal{E}} C'\right), \text{ emission by electric field } \mathcal{E}.$$

- The p-n homojunction in the absence of illumination and externally applied voltage is characterized by the concentration of acceptor, N_a , and donor N_d , the gap E_g , the dielectric constant ε , the acceptor-level ε_a , and the donor-level ε_d . Electrons are transferred from the n-side to the p-side creating a region depleted of electrons of extent d_n and a region depleted of holes of extent d_p as well as an additional potential-difference $\Delta\phi$ that equalizes the total chemical potential

$$\begin{aligned} \Delta\phi &\equiv \phi(+\infty) - \phi(-\infty) = \frac{E_g}{e} + \frac{k_B T}{e} \ln \frac{N_d N_a}{N_c N_v}, \\ d_n &= \left[\frac{N_a}{N_d} \frac{1}{N_a + N_d} \frac{4\pi\varepsilon_0 \varepsilon \Delta\phi}{2\pi e} \right]^{1/2}, \\ d_p &= \left(\frac{N_d}{N_a} \right) d_n. \end{aligned}$$

- In the presence of an external voltage V , the extent of the p and n depletion regions is multiplied by a factor

$$\left(1 - \frac{V}{\Delta\phi}\right)^{1/2},$$

where positive V (forward bias) means that the positive pole is connected to the p-side. On both sides of the total depletion region, there are diffusion regions of extent L_n in the p-side and extent L_p in the n-side, where

$$L_n = (D_n \tau_n)^{1/2}, L_p = (D_p \tau_p)^{1/2},$$

D_i , $i = n, p$ is the diffusion coefficient for the minority carriers (electrons in the p-side and holes in the n-side), and τ_n is the lifetime of an electron in the CB in the p-side and τ_p is the lifetime of a hole in the VB in the n-side. The current-density, j , is given by the formula

$$j = j_{\text{sat}} e^{\beta e V} - j_{\text{sat}},$$

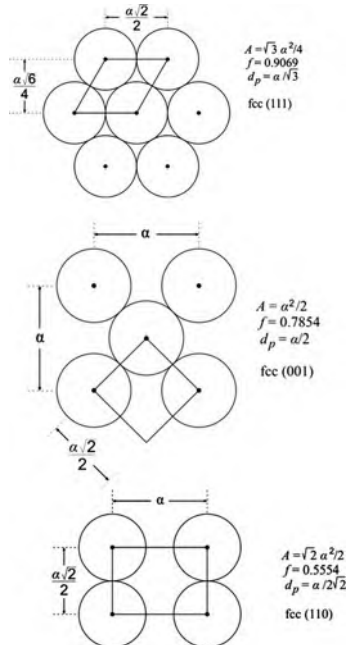
where

$$j_{\text{sat}} = en_i^2 \left(\frac{D_n}{L_n N_a} + \frac{D_p}{L_p N_a} \right),$$

$-j_{\text{sat}}$ is the reversed current-density by the generated minority-carriers, while $j_{\text{sat}} \exp(\beta eV)$ is the so-called recombination-current density by the majority-carriers. In the presence of illumination, a third term must be added, j_L ; $|j_L|$ is the reverse current density by the minority carriers generated by the absorbed photons.

17.10 Problems

- 17.1 Show that the 2D lattice of planes normal to the directions (111), (001), and (110) of an *fcc* lattice of lattice constant a are as shown below (A is the area of the primitive cell, f is the surface fraction by equal touching circles, and d_p is the distance between consecutive lattice planes along their perpendicular direction). Find next the minimum number of bonds per unit area cut by planes normal to the directions (111), (001), and (110) of a diamond lattice.



- 17.2 Consider a regular octahedron of edge length a' and a truncated regular octahedron of edge length a (before the truncation) and edge length b of the truncated square. Show that equality of the volume of the two implies that $a^3 - 3b^3 = a'^3$. The square faces of the truncated octahedron are normal to the direction 100 and its five equivalent ones respectively, while all other faces are normal to 111 and its equivalents. Show that the surface energies of the two shapes are

$$E = 2\sqrt{3}a'^2 E_{111},$$

$$E_t = 2\sqrt{3}(a^2 - 3b^2) E_{111} + 6b^2 E_{100}.$$

- If $E_{100} < \sqrt{3}E_{111}$, prove that the truncated regular octahedron with $b/a = 1 - (E_{100}/\sqrt{3}E_{111})$ has the lower surface energy.
- 17.3 Consider a coated SiO_2 nanoparticle of $R = 100$ nm. The coating layer is by gold of thickness $d = 10$ nm. Find the surface plasmon eigenfrequencies of this nanoparticle. Study the excitation of these surface plasmons by an external laser beam of appropriate frequency.
Hint: See: (a) Scientific American, April 2007, pp. 38–45; (b) E.N. Economou & K.L. Ngai, Adv. Chem. Phys. **27**, 265–354 (c) [E18]; and (d) C.F. Bohren & D.R. Huffman, *Adsorption and Scattering of Light by Small Particles*, Wiley, New York, 1998.
- 17.4 Show that Schrödinger's equation has no surface solution for a potential $V(\mathbf{r}) = -|V_0|$ for $z < 0$ and $V(\mathbf{r}) = 0$ for $z > 0$.
- 17.5 Prove (17.6), (17.7), and (17.8).
- 17.6 Prove (17.30). Show that the integral in (17.30) in the limit $\lambda \gg 1$ is equal to $(\lambda^2/2) + (\pi^2/6)$.
Hint: Change the variables to $t = x - \lambda$; break the resulting integral to one from $-\lambda$ to 0 and one from 0 to ∞ ; in the first one, expand the denominator $\exp(t) + 1$ to a power series in $\exp t$ and then integrate each term in the series.
- 17.7 For a Ge p–n homojunction with $N_a = 2 \times 10^{16} \text{ cm}^{-3}$ and $N_d = 3 \times 10^{16} \text{ cm}^{-3}$ at $T = 300$ K, calculate the various quantities characterizing this junction. Assume that $\tau_p = \tau_n = 5 \times 10^{-6}$ s.

Further Reading

- In the book by Ashcroft and Mermin [SS75]: See pp. 354–364 for the work function and its measurements; pp. 367–371 for electronic surface states; and pp. 590–613 for p–n junctions.
- For semiconductor and other solid state devices, consult the books by R. Dalven, *Introduction to Applied Solid State Physics*, 2nd ed. Plenum Press, New York, 1990 and by S.M. Sze, *Physics of Semiconductor Devices*, 2nd ed., Wiley, New York, 1981 [Se121].

Disordered and Other Nonperiodic Solids

Summary. Various types of disordered materials are mentioned and their main structural and other properties are briefly reviewed. The multiple scattering (in the presence of strong disorder) and the wave interference reduce the diffusion coefficient and tend to localize the electrons. The dimensionality is an important factor, in the sense that for $D < 2$ any amount of disorder is enough to localize all the states, while for $D > 2$ a critical amount of disorder (depending on the energy) is needed for localization. The critical dimensionality, $D = 2$, in the absence of magnetic field it belongs to the $D < 2$ category, while in the presence of magnetic field belongs to the $D > 2$ category, including the possibility of frictionless flow (the Quantum Hall phase). In general, the magnetic field tends to undo the effects of interference. In quasi-one-dimensional systems, the conductance, G , between contacts p and q is related to the transmission coefficient, $\bar{T}_{pq}$, through the relation, $G_{pq} = 2(e^2/h)\bar{T}_{pq}$. The coherent potential approximation is a powerful method for obtaining averages of some quantities by introducing a periodic effective medium determined self-consistently.

18.1 Introductory Remarks

We have seen in Subsect. 8.5.1.4 that there are many solids for which their atoms are not placed in space in an ordered way, in contrast to what happens in crystals. Soft matter such as polymers (see Sect. 3.1.5), organic glasses such as SiO_2 , As_2S_3 , amorphous semiconductor films grown on a substrate, etc are typical examples of positionally disordered solids. There are also solids, the disorder of which is not positional, but compositional, as in most alloys, where, although, the atoms occupy periodic lattice sites, they do so in a random way, in the sense that it is not known which type of atom is at a given site. There are also materials possessing both positional and substitutional disorder. Positionally disordered subsystems, such as impurity subbands, can appear also within a crystalline host, e.g., by randomly placed substitutional impurities of high concentration. There are also artificial micro- or nanostructures where even a minute amount of disorder at very low temperatures, plays

an important role. Finally, we mention the so-called quasi-crystals, which do not exhibit periodic order, although the positions of the atoms are fixed by a fully deterministic algorithm.

As it was stated in Subsect. 8.5.1.4, the novel feature appearing in these disordered or nonperiodic systems is the possibility of localized eigenfunctions due to multiple scattering and interference effects [DS133–DS138, DS152], [DSL156].

18.2 Alloys and the Hume-Rothery Rule

The simplest model of a random alloy is that of a binary system of the form A_xB_{1-x} , which within the framework of LCAO is described by a Hamiltonian of the form (6.11) and (6.12), with each diagonal matrix element ε being a random variable:

$$\begin{aligned}\varepsilon &= \varepsilon_A && \text{with probability } x \\ &= \varepsilon_B && \text{with probability } 1 - x.\end{aligned}\tag{18.1}$$

This model is characterized by two parameters: x and the ratio $(\varepsilon_A - \varepsilon_B)/V_2$. Such a model can describe realistically an alloy, if the latter has been cooled down from the melt suddenly (quenched) so that there is no time for the system to come to a full thermodynamic equilibrium (See Figs. 2 and 3, pp. 622, 623 of [SS74]). Otherwise, the alloy would probably develop some correlations, the simplest form of which can be described by the probability $P_{A/B}$ of a site being A under the condition that a given nearest neighbor is B. All other probabilities for a pair of sites can be expressed in terms of x and $P_{A/B}$.

Problem 18.1t. Show that:

$$\begin{aligned}P_{B/A} &= [(1-x)/x]P_{A/B}, \quad P_{B/B} = 1 - P_{A/B}, \quad P_{A/A} = 1 - P_{B/A}, \text{ and} \\ P_{AB} &= P_{BA} = (1-x)P_{A/B} = xP_{B/A}, \\ P_{AA} &= x - (1-x)P_{A/B}, \quad P_{BB} = (1-x)[1 - P_{A/B}],\end{aligned}\tag{18.2}$$

where P_{AB} is the probability that the first site of the pair is A and the second B, etc. If there is no correlation, $P_{A/B} = x$.

If we assume that the enthalpy $H = U + PV$ depends not only on P, T , and x but also on the pair correlation $P_{A/B}$, we have:

$$\begin{aligned}H &= P_{AA}U_{AA} + P_{BB}U_{BB} + 2P_{AB}U_{AB} \\ &= xU_{AA} + (1-x)U_{BB} + P_{AB}[2U_{AB} - U_{AA} - U_{BB}].\end{aligned}\tag{18.3}$$

For $T = 0$ K and $2U_{AB} < U_{AA} + U_{BB}$, the minimum of H for a given x is obtained for the maximum value of P_{AB} , which is equal to $0.5 - |x - 0.5|$. For a finite temperature, one must calculate the entropy, which is a function of both x and $P_{A/B}$ and then must minimize the Gibbs free energy G

$$G \equiv H(P, T, x, P_{A/B}) - TS(x, P_{A/B})\tag{18.4}$$

The situation is more complicated for alloys consisting of metals of different valence (e.g., Cu–Zn) and – usually – different lattice structure. In this case, going from pure A to pure B, we pass through different phases each one of which may have different chemical composition and different lattice structure. Between two consecutive phases, there is a region where we have the coexistence of these phases.

The change in the lattice structure of a binary alloy A_xB_{1-x} (such that pure A and pure B have different lattice structures) follows reasonably well the so-called *Hume–Rothery rule*: *A lattice change is expected when the average nominal valence $\bar{\zeta} \equiv x\zeta_A + (1-x)\zeta_B$ is such that the unperturbed Fermi sphere just touches the 1st BZ (or in some cases a polyhedron consisting of Bragg planes).*

Problem 18.2t. Show that for a weak pseudopotential and according to the Hume–Rothery rule, the stability of the **fcc** lattice terminates at $\bar{\zeta} = 1.36$ while for the **bcc** the Hume–Rothery value is 1.48. (The corresponding experimental values are in the range 1.27–1.42 and 1.48–1.50).

The physical reasoning behind the Hume–Rothery rule is the following. The point $\mathbf{k}_0$ at which the Fermi sphere just touches the 1st BZ is the centre of the face of the 1st BZ closer to the origin in $\mathbf{k}$ -space. At this point and in the presence of a weak pseudopotential, $\mathbf{v}_{\mathbf{k}} = \partial E(\mathbf{k})/\hbar\partial\mathbf{k}$ is zero; hence, the DOS at $E = E(\mathbf{k}_0)$ develops a van-Hove singularity as shown in Fig. 18.1. As this singularity occurs at a lower energy for **fcc** than **bcc**, the **fcc** DOS is higher than the **bcc** DOS up to E_c , which is larger than E_A . It follows that E_F and the energy

$$U = \int_0^{E_F} d\varepsilon \varepsilon \rho(\varepsilon) \quad (18.5)$$

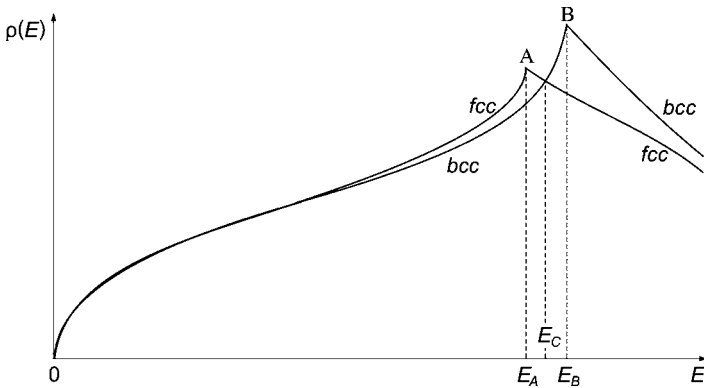


Fig. 18.1. Schematic plot of the DOS for the **fcc** and the **bcc** lattices in the presence of a weak pseudopotential. For the **fcc** lattice $k_{0,\text{fcc}}$ and hence, the corresponding energy E_A of the van Hove singularity are smaller than $k_{0,\text{bcc}}$ and E_B of the **bcc** lattice

are lower for **fcc**, than **bcc** as long as $E_F \leq E_c$. For higher values of E_F , the **bcc** lattice would eventually produce lower energy U than the **fcc** lattice. Thus, according to this reasoning, a lattice change will take place from **fcc** to **bcc** when E_F exceeds E_A by a finite amount, or equivalently, when $\bar{\zeta}$ is such that $k_F = (3\pi^2 n)^{1/3} = (12\pi^2 \bar{\zeta})^{1/3}/a$ exceeds k_0 by a small but finite amount. When the pseudopotential is not so small, this finite amount can be even negative.

18.3 Glasses and other Amorphous Systems

As it was stated in Subsect. 3.1.4, several materials solidify in glassy state as their melt is cooled. Fast cooling (quenching) drives to the glassy state even materials that otherwise would become crystalline solids. Glass formation is favored by structures of low average number of nearest neighbours (coordination number) Z^* ; it has been proposed that materials with $Z^* \lesssim 2.4$ are natural glasses [18.1]¹ ($Z^* = (1 \times 4 + 2 \times 2)/3 = 2.666$ for SiO_2 , $Z^* = (2 \times 3 + 3 \times 2)/5 = 2.4$ for As_2S_3 , etc). The transition from the melt to the glassy state occurs in a very narrow temperature range centered around the so-called *glass transition temperature*, T_G . In Fig. 18.2, we show how the Volume V , the specific heat C_p , and the viscosity η , change around T_G . The viscosity changes by many orders of magnitude in a narrow range (which depends on the rate of cooling) around T_G . This behavior is described by the following expression known as the *Vogel–Fulcher equation*:

$$\eta(T) = \eta_0 \exp \left[\frac{E_0}{k_B(T - T_0)} \right] \quad (18.6)$$

where η_0, E_0, T_0 are assumed to be constants with $T_0 < T_G$. (If $T_0 = 0$ K, then (18.6) becomes an Arrhenius dependence). The microscopic interpretation of the glass transition is a difficult problem that has drawn the interest of many researchers. Among the several models that have been proposed, we mention here the well-accepted *Free Volume theory* (Cohen and Grest [18.2]).

How can the atomic (ionic or molecular) structure of an amorphous solid be characterized? Conceptually, for amorphous metals we employ a model of close-packed hard spheres of random positions. Such a model has been studied both experimentally and by computer simulations. The main results are that the volume fraction, f , covered by the spheres is 64% (as opposed to 74% for the ordered **fcc** or **hcp** lattice) and that each sphere is touched by 8.5 spheres on the average. However, there are metallic glasses with a coordination number close to 12.

For amorphous semiconductors (and other open structures determined by directed bonds), the concept of the *continuous random network* (CRN) is

¹ See J.C. Phillips, Solid State Physics: Advances in Research and Applications, **37**, 93 (1982).

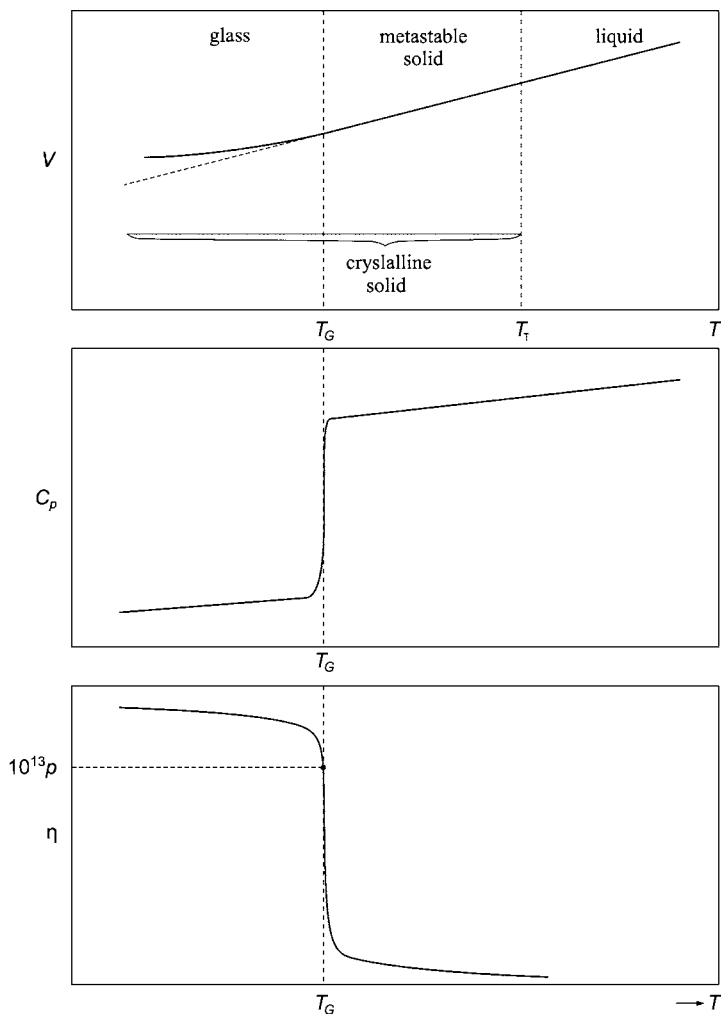


Fig. 18.2. Volume V , specific heat C_p , and viscosity η vs T around the glass transition temperature T_G . The viscosity changes by many orders of magnitude around T_G which is conventionally defined as the temperature at which $\eta = 10^{13}$ poise = 10^{12} kg/m·s. For comparison the volume discontinuity at the freezing point T_f is shown for the transition from melt to crystalline solid

utilized. The CRN consists of a set of points in space each one of which is connected through a fixed and constant number of bonds to its neighboring points. The bond lengths and angles at each point fluctuate around some fixed values. In Fig. 18.3, a CRN of connectivity 3 is shown. If at each point of this CRN, an As atom is placed, and if at the middle of each bond, an S atom is located, we have a first approximation to the structure of amorphous As_2S_3 . By a similar procedure, a first approximation to the structure of amorphous SiO_2 can be obtained, by a CRN of connectivity four. The CRN model is

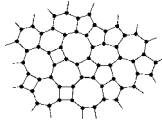


Fig. 18.3. Schematic 2-D representation of a continuous random network (CRN) of connectivity 3

appropriate for glassy semiconductors rather than for thin films of amorphous Si or other tetrahedral semiconductors. The reason is that for high average coordination number, the CRN implies severe deviations from the equilibrium bond lengths and angles. As a result, it is energetically favorable to allow the existence of some dangling bonds in order to relieve the structure from the severe stresses imposed by the requirement of satisfying everywhere the coordination 4 without being crystalline.

Amorphous solids do not seem to be in thermodynamic equilibrium. This conclusion follows from the rather general and unexpected low temperature dependence of specific heat, of the thermal conductivity, of the decay of sound waves, etc in amorphous solids [18.3–18.9]. More specifically, in amorphous semiconductors and insulators, the specific heat at very low temperatures ($0.1 \leq T \leq 1$ K) behaves as follows

$$C = c_1 T^n + c_2 T^3 \quad (18.7)$$

where $n \approx 1$ and c_1, c_2 are constants. The term $c_1 T^n$ cannot be accounted for within an equilibrium model that implies that the only excitations are 3D harmonic vibrations. To account for this almost-linear term in the specific heat a so-called two-level model has been proposed involving two different local atomic configurations [18.3–18.9] corresponding to two different energy levels E_1 and E_2 separated by a small energy barrier (For more references see [DS146], [DS150] and [18.7]). It was further assumed that the difference $\Delta E \equiv |E_1 - E_2|$ possesses a broad, almost-constant probability distribution: $p(\Delta E) = p_0$ for $0 \leq \Delta E < E_0$, and $E_0/k_B T \gg 1$.

Problem 18.3t. Show that the two-level model with $p(\Delta E) = p_0$ produces a specific heat proportional to the absolute temperature, T , for very low T .

Hints: From the partition function $z = 1 + \exp(-\beta \Delta E)$ find the statistically average energy u for a given energy ΔE ; then average u over $p(\Delta E)$ as well.

18.4 Distribution and Correlation Functions

In Chap. 9 we examined the elastic scattering of an external beam of particles by periodically placed scatterers the concentration of which was $n(\mathbf{r})$. Let

$$n(\mathbf{r}) = \sum_{\ell=1}^N n_{\ell}(\mathbf{r} - \mathbf{r}_{\ell}) \quad (18.8)$$

where for an amorphous solid the vectors $\mathbf{r}_\ell$ do not form a periodic lattice. We have seen in Chap. 9 that the scattering amplitude is proportional to $\tilde{n}^*(\mathbf{k})$ where

$$\tilde{n}(\mathbf{k}) \equiv \sum_{\ell=1}^N g_\ell(\mathbf{k}) e^{-i\mathbf{k} \cdot \mathbf{r}_\ell} \quad (18.9)$$

$\mathbf{k} = \mathbf{k}_i - \mathbf{k}_f$ and $g_\ell(\mathbf{k}) = \int d^3r' n_\ell(\mathbf{r}') \exp(-i\mathbf{k} \cdot \mathbf{r}')$ is the atomic form factor defined in the footnote of p. 248. If all atoms N are identical, then $g_\ell(\mathbf{k}) = g(\mathbf{k})$. The differential scattering cross-section is proportional to $|\tilde{n}(\mathbf{k})|^2$. Hence, for $g_\ell(\mathbf{k}) = g(\mathbf{k})$, we have

$$|\tilde{n}(\mathbf{k})|^2 = |g|^2 \sum_{\ell, n} e^{-i\mathbf{k} \cdot (\mathbf{r}_n - \mathbf{r}_\ell)} \quad (18.10)$$

By separating the terms $\mathbf{r}_n = \mathbf{r}_\ell$ from the rest we obtain

$$\frac{|\tilde{n}(\mathbf{k})|^2}{N |g|^2} \equiv S(\mathbf{k}) = 1 + \frac{1}{N} \sum_{n \neq \ell} e^{-i\mathbf{k} \cdot (\mathbf{r}_n - \mathbf{r}_\ell)} \quad (18.11)$$

To proceed further, we need some information about the position vectors $\mathbf{r}_n$ and $\mathbf{r}_\ell$. For an amorphous system, this information is of probabilistic nature. More specifically, we need the combined probability $p^{(2)}(\mathbf{r}_n, \mathbf{r}_\ell) d^3r_n d^3r_\ell$ to find atom n in the elementary volume d^3r_n around $\mathbf{r}_n$ and atom ℓ in the elementary volume d^3r_ℓ around $\mathbf{r}_\ell$. The probability density $p^{(2)}(\mathbf{r}_n, \mathbf{r}_\ell)$ can be expressed in terms of the single probability densities $p^{(1)}(\mathbf{r}_\ell)$ and the so-called *pair distribution function* $h(\mathbf{r}_n, \mathbf{r}_\ell)$:

$$p^{(2)}(\mathbf{r}_n, \mathbf{r}_\ell) \equiv p^{(1)}(\mathbf{r}_n) p^{(1)}(\mathbf{r}_\ell) h(\mathbf{r}_n, \mathbf{r}_\ell) \quad (18.12)$$

Equation (18.12) is the definition of $h(\mathbf{r}_n, \mathbf{r}_\ell)$. Since there is no long-range order in an amorphous system, $\mathbf{r}_n$ and $\mathbf{r}_\ell$ are statistically independent as $|\mathbf{r}_n - \mathbf{r}_\ell| \rightarrow \infty$ and consequently, $p^{(2)} = p^{(1)} p^{(1)}$ and $h(\mathbf{r}_n, \mathbf{r}_\ell) \rightarrow 1$ as $|\mathbf{r}_n - \mathbf{r}_\ell| \rightarrow \infty$. We define also the function

$$c(\mathbf{r}_n, \mathbf{r}_\ell) \equiv h(\mathbf{r}_n, \mathbf{r}_\ell) - 1 \quad (18.13)$$

which is called *pair correlation function* [DS131]. For fully uncorrelated random quantities $\mathbf{r}_n, \mathbf{r}_\ell$, $c(\mathbf{r}_n, \mathbf{r}_\ell)$ is zero. Most amorphous solids are on the average homogenous, which means that $p^{(1)}(\mathbf{r}_n) = p^{(1)}(\mathbf{r}_\ell) = 1/V$ and $h(\mathbf{r}_n, \mathbf{r}_\ell) = h(\mathbf{r}_n - \mathbf{r}_\ell)$. For such solids the average of (18.11) over all positions $\mathbf{r}_n$ and $\mathbf{r}_\ell$ yields

$$\langle S(\mathbf{k}) \rangle = 1 + \frac{1}{V^2 N} \sum_{\ell \neq n} \int d^3r_\ell d^3r h(\mathbf{r}) e^{-i\mathbf{k} \cdot \mathbf{r}} \quad (18.14)$$

or

$$\langle S(\mathbf{k}) \rangle = 1 + \frac{N}{V} \int d^3r h(\mathbf{r}) e^{-i\mathbf{k} \cdot \mathbf{r}} \quad (18.15)$$

By taking into account (18.13) and the relation $\int d^3r \exp(-i\mathbf{k} \cdot \mathbf{r}) = (2\pi)^3 \delta(\mathbf{k})$ (which follows from (B.17) till (B.19)), we can rewrite (18.15) as follows.²

$$\langle S(\mathbf{k}) \rangle = 1 + \frac{N}{V} \int d^3r c(\mathbf{r}) e^{-i\mathbf{k} \cdot \mathbf{r}} + (2\pi)^3 \frac{N}{V} \delta(\mathbf{k}) \quad (18.16)$$

The last term in the rhs of (18.16) is zero, unless $\mathbf{k} = 0$, (i.e., $\mathbf{k}_f = \mathbf{k}_i$), which means that it can be incorporated into the incoming beam and omitted. By taking the Fourier transform of (18.16), we obtain

$$c(\mathbf{r}) = \frac{V}{N} \int \frac{d^3k}{(2\pi)^3} [\langle S(\mathbf{k}) \rangle - 1] e^{i\mathbf{k} \cdot \mathbf{r}} \quad (18.17)$$

or for an isotropic on the average solid,

$$c(r) = \frac{V}{2\pi^2 N r} \int_0^\infty dk k \sin kr [\langle S(k) \rangle - 1] \quad (18.18)$$

Equations (18.17) and (18.18) are very important. They give the pair correlation function, i.e., the main structural information of an amorphous solid, in terms of $\langle S(\mathbf{k}) \rangle$ or $\langle S(k) \rangle$, i.e., in terms of quantities that can be obtained experimentally by the elastic scattering of X-rays or neutrons.

18.5 Quasi-Crystals

An unexpected observation³ was made in the alloy $\text{Al}_{86}\text{Mn}_{14}$, prepared by fast cooling (10^6 K/s) from the melt: X-ray diffraction produced a crystal-like pattern, including peaks associated with five-fold rotational symmetry! However, the latter is incompatible with any periodic symmetry (see Problem 3.12s). Then other materials⁴ were prepared, e.g., the alloy $\text{Al}_{65}\text{Cu}_{15}\text{Co}_{20}$, that exhibited similar unexpected pattern in the X-ray diffraction. Finally, it was found that, these materials do not possess long-range periodic order. In other words, they are non-periodic crystal-like materials, although in some respects they do behave like periodic crystals, in spite of the crystal-like X-ray diffraction pattern. Hence, the name **quasicrystals**.

It is only natural to ask ourselves how a nonperiodic arrangement of scatterers can give a diffraction pattern similar to that of periodically placed

² For an isotropic on the average solid, $c(\mathbf{r})$ and $h(\mathbf{r})$ are functions only of the magnitude r ; thus the quantity $\int d^3r c(r) \exp(-i\mathbf{k} \cdot \mathbf{r})$ can be written as $\int dr [4\pi r^2 c(r)] (\sin kr)/kr$ by integrating over the angles of $\mathbf{r}$. The quantity $4\pi r^2 c(r)$ is called *radial correlation function* and the quantity $4\pi r^2 h(r)$ *radial distribution function*.

³ Shechtman et al. [18.10].

⁴ See the article by A.R. Cortan entitled “Quasicrystals” in Encyclopedia of Applied Physics, ed. by L.G. Trigg, vol. 15, VCH, New York (1996) [18.11].

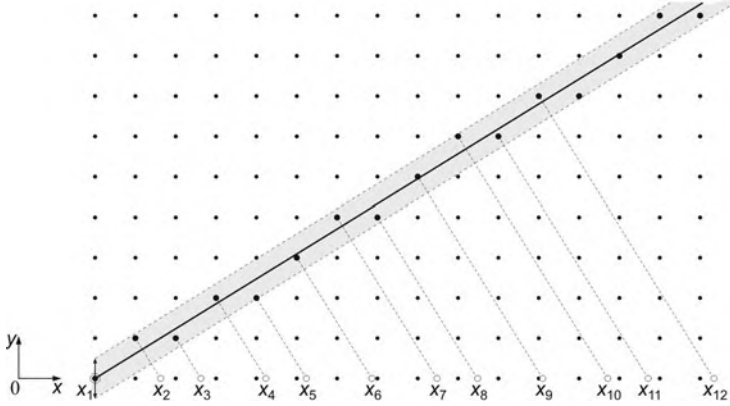


Fig. 18.4. Consider the 2D square lattice of lattice constant 1 and a stripe centered around the straight line passing through the point $(0,0)$ and of slope $\tan \theta = 1/\tau = \tau - 1 = 0.61803 \dots$. The thickness of the stripe is $\tau/\sqrt{1+\tau^2}$ (in the normal direction to the central line). All lattice points lying within the stripe are projected on the x-axis by lines normal to the stripe; their projections $\{x_n\}$, n integer, coincide with those of (18.19)

scatterers. The simplest way to deal with this question is to examine a 1D model of identical scatterers placed at the points x_n where

$$x_n = n + (\tau - 1)[n/\tau], \quad n = \text{integer} \quad (18.19)$$

$\tau = 1 + \tau^{-1} = (\sqrt{5} + 1)/2 \simeq 1.618$ is a “golden ratio” and $[n/\tau]$ is the largest integer that is smaller than n/τ . The difference $x_{n+1} - x_n$ is either 1 or τ , but the sequence of 1s and τ 's is not periodic. However, the points x_n defined by (18.19), although they do not form a periodic sequence themselves, are produced by a proper projection of a two-dimensional periodic structure as shown in Fig. 18.4. Thus, their periodic maternal origin seems to be the culprit for their crystal-like diffraction pattern. The latter is proportional to $|\tilde{n}(k)|^2$, where $\tilde{n}(k)$ is the Fourier transform of the scatterer-concentration $n(x) = \sum_n \delta(x - x_n)$; $\tilde{n}(k)$ is given by:

$$\tilde{n}(k) = \sum_n e^{-ik x_n} \quad (18.20)$$

Problem 18.4t. Show that $\tilde{n}(k)$ is proportional to the following expression

$$\tilde{n}(k) \sim \sum_n \sum_m \frac{1 - \exp[-i(k/\tau - 2\pi m)]}{i(k/\tau - 2\pi m)} \delta\left(\frac{2\pi m}{\tau} - \frac{k}{\tau^2} + 2\pi n - k\right) \quad (18.21)$$

Hint: See the book by Marder [SS82], p. 120.

Equation (18.21) means that the diffraction peaks appear when $k \equiv k_i - k_f$ is equal to

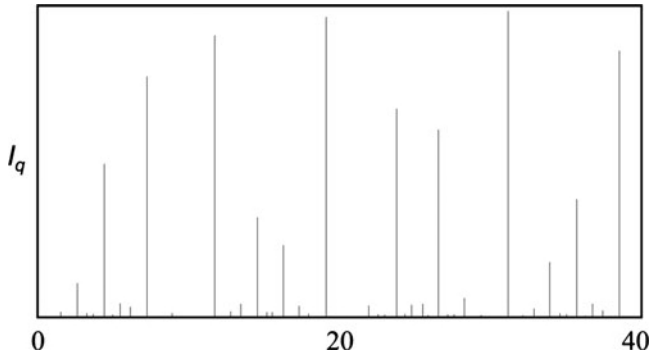


Fig. 18.5. The diffraction strength $I_k \sim |n(k)|^2$ vs. k according to (18.21). Only a few discrete peaks from the dense two parameter infinite sequence of peaks are visible. (After [SS82], p. 121)

$$k = \frac{2\pi n + (2\pi m/\tau)}{1 + \tau^{-2}}, \quad n, m \text{ integers} \quad (18.22)$$

Thus, the peaks on the k axis form a *two-parameter* (m and n) *dense* sequence (dense means that there is a peak arbitrarily close to any chosen value of k). In contrast, for any periodic 1D structure the peaks on the k axis form a one-parameter discrete sequence. This basic qualitative difference between quasicrystals and crystals is practically eliminated at the quantitative level because in the quasicrystal case, the strength of the overwhelming majority of peaks is so small that these peaks are not detectable experimentally. This point is illustrated in Fig. 18.5, where $|\tilde{n}(k)|^2$ according to (18.21) is plotted vs. k . Only a discrete sequence of peaks is visible, although there are peaks “everywhere” but so weak that they are not visible (this is due to very large values of m in the denominator of the prefactor multiplying the δ -function).

A second theoretical question raised by the existence of quasicrystals is the following: Can we fully fill up space without overlaps and without periodicity by the repeated use of a few basic units?

The answer to this question is yes. Penrose (see [18.12]) invented such a 2D structure possessing five-fold symmetry by joining together two rhombic tiles, a “fat” one with the small angle equal to $2\pi/5 = 72^\circ$ and a “thin” one with the small angle $\pi/5 = 36^\circ$. The angles have been selected so that the five-fold symmetry is built in. Notice that the ratio of the long diagonal to the side of the “fat” tile is the “golden ratio” τ , while the ratio of the small diagonal of the “thin” tile to the side is $1/\tau$. In Fig. 18.6, the rules of joining the two tiles are stated. More about the properties of this space filling nonperiodic structure and its connection to the 1D model of (18.19) can be found in the book by Marder [SS82] (p. 122, 123).

A final question concerns the compatibility of the non-periodic structure of a quasicrystal with the principle of minimization of the free energy. Since the overwhelming majority of the ordered solids are periodic, it is only natural

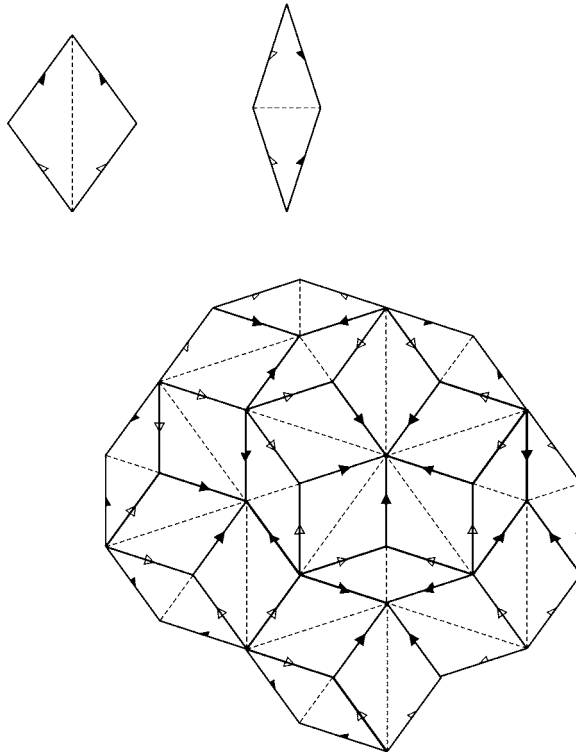


Fig. 18.6. The two rhombic tiles of Penrose, which must be joined in such a way that the semiarrows at each side form a unified arrow (either black or white). Any finite part of the structure is repeated infinite times, although the structure is not periodic

to conclude that the quasicrystals do not achieve the minimum of the free energy, although they seem to be not far away from this minimum. Actually, most of the known quasicrystals have the symmetry of a regular icosahedron. The latter is one of the five regular convex polyhedra (the perfect platonic solids) with 20 equilateral triangles as faces. Each line connecting the center of the icosahedron with each vertex is an axis of five-fold symmetry. The regular icosahedron provides the most symmetric way to surround a given sphere by 12 equal spheres (see Fig. 18.7b); it achieves this way a close-packed arrangement for a small number of spheres. Since the close-packed structure is energetically favorable for most metals, the icosahedral unit, if it can fill the space without empty regions or overlaps, could be competitive from the energetic point of view with close-packed crystalline structures.

We shall conclude this section by mentioning that we can construct 2D and 3D quasicrystals by a proper projection of periodic 3D and 4D lattice structures respectively.

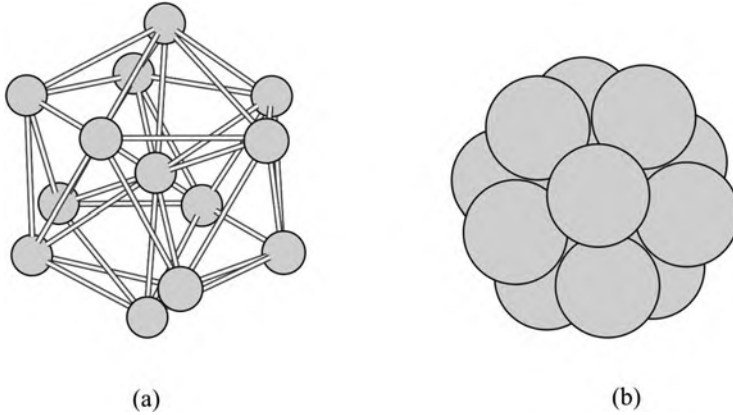


Fig. 18.7. (a) A regular icosahedron. (b) Surrounding a sphere of radius R by 12 spheres of radius R along the 12 axes of five-fold symmetry of the regular icosahedron

18.6 Electron Transport and Quantum Interference

In Chaps. 5 and 8 (Subsect. 8.5.1.1), we have seen that a nonzero DC resistivity appears as a result of the scattering of Bloch waves by point defects and other departures from periodicity. The scattering cross-section, σ_s , by each point defect was connected to the mean free path, ℓ , by (5.36), namely by $\ell^{-1} = n_s \sigma_s$, where n_s is the concentration of scatterers. The phonons, because of their extended nature, do not create local scattering potentials as the point defects do, but a global overall scattering potential the Fourier transform $\tilde{V}(\mathbf{k})$ of which is given by (5.43); in this case, the global cross-section and the mean free path were obtained through (5.40), i.e., by employing the Born approximation. The validity of (5.36) and (5.40) requires weak scattering, i.e., long mean free paths in comparison with the wavelength, λ , $\ell > \lambda$. However, this inequality is not always obeyed. We have seen in Sect. 16.4 and Fig. 16.16 that sound propagation in bubbly water cannot be described even qualitatively by assuming the simple additive formula, $\ell^{-1} = n_s \sigma_s$; since the cross-section, σ_s , in this case was so large, the scattered wave by a single bubble was comparable to, or even larger than, the incoming wave; hence, the result of being scattered again and again by other bubbles is appreciable and it cannot be omitted. This *multiple scattering* process and the resulting coherent interference of individually scattered waves had a dramatic effect in the case of bubbly water as it was shown in Fig. 16.16. Similarly, for periodically placed identical scatterers, systematic interference (due to the periodic position of the scatterers), and quite often, multiple scattering, transform a plane wave to a Bloch wave and permit free propagation in the bands (where the interference is systematically constructive) and no propagation in the gaps (where the interference is destructive and the scattering strong enough).

One may think that for randomly placed scatterers the constructively interfered waves cancel the destructively interfered ones, since at each point the multiple-scattered waves arrived with random phases. If this were true, one could conclude that the formula $\ell^{-1} = n_s \sigma_s$ would be adequate even for very strong scattering. However, we have seen in the example of bubbly water that this is not the case. In strongly disordered systems, multiple scattering processes tend to reduce diffusion and may even lead to *localization*, i.e., to the confinement of the carrier (electron or hole, or classical wave) to a finite region of space.

Bergmann, to examine this problem of strong multiple scattering and interference, considered an electron initially ($t = 0$) located in a small finite region $\delta V(\mathbf{r})$ centred at the point $\mathbf{r}$. Let $A(t)$ be the probability amplitude for the electron to return after time t to the initial region. The probability, $\delta P(t)$, of the electron to be in $\delta V(\mathbf{r})$ after time t is given by $\delta P(t) = |A(t)|^2 \delta V(\mathbf{r})$. Following the path formulation of quantum mechanics, we can write

$$A(t) = \sum_{\nu} A_{\nu}(t) \quad (18.23)$$

where the sum is over *directed* paths⁵, which start from $\delta V(\mathbf{r})$ and end there. Hence, we have for $\delta P(t)/\delta V(\mathbf{r})$

$$\frac{\delta P(t)}{\delta V(\mathbf{r})} = \left| \sum_{\nu} A_{\nu}(t) \right|^2 = \sum_{\nu} |A_{\nu}(t)|^2 + \sum_{\nu \neq \mu} A_{\nu}(t) A_{\mu}^*(t) \quad (18.24)$$

If the $\nu \neq \mu$ double sum in the rhs of (18.24) were zero (as a result of the expected random phases of the product $A_{\nu}(t) A_{\mu}^*(t)$, $\nu \neq \mu$), then, there would be no interference and the additive formula $\ell^{-1} = n_s \sigma_s$ would seem justified. However, the $\nu \neq \mu$ double sum is not zero; actually it is positive. To see the reason, define in each closed contour a forward direction and a backward direction. Thus, each closed contour corresponds to two paths: one in the forward direction and denoted by Greek letters, $\alpha, \beta, \gamma, \dots$, while the other is in the backward direction and denoted by $\bar{\alpha}, \bar{\beta}, \bar{\gamma}, \dots$. With this notation, (18.23) becomes $A(t) = \sum_{\alpha} [A_{\alpha}(t) + A_{\bar{\alpha}}(t)]$, where α runs over all closed contours. It follows that the first term in rhs of (18.24) becomes

$$\sum_{\alpha} |A_{\alpha}(t)|^2 + \sum_{\bar{\alpha}} |A_{\bar{\alpha}}(t)|^2 \quad (18.25)$$

while the second term in the rhs of (18.24) becomes

$$\begin{aligned} & \sum_{\alpha} A_{\alpha}(t) A_{\bar{\alpha}}^*(t) + \sum_{\bar{\alpha}} A_{\bar{\alpha}}(t) A_{\alpha}^*(t) + \sum_{\alpha \neq \beta} A_{\alpha} A_{\beta}^* \\ & + \sum_{\alpha \neq \beta} A_{\bar{\alpha}} A_{\bar{\beta}}^* + \sum_{\alpha \neq \beta} A_{\alpha} A_{\beta}^* + \sum_{\alpha \neq \beta} A_{\bar{\alpha}} A_{\bar{\beta}}^*; \end{aligned} \quad (18.26)$$

⁵ Any loop gives rise to two directed closed paths.

β runs also over all closed contours. The second line in (18.26) involves only pairs of different closed contours; for them, the argument of random phases seems valid and as a result, the last line is expected to be zero.⁶ This conclusion does not apply to the first line in (18.26): Because of the time reversal symmetry (valid in the absence of magnetic forces and inelastic scattering), we have that $A_\alpha = A_{\bar{\alpha}}$; thus, the first line in (18.26) is equal to that of (18.25) (if magnetic forces are absent or negligible). Hence, interference effects (associated with the wave nature of propagation) double the probability of finding the particle in the initial position after time t . We conclude that interference effects reduce the diffusion coefficient, the conductivity, the mobility, and the mean free path. The more severe this reduction is, the stronger the scattering will be or the smaller the “no interference,” “classical” mean free path $\ell = (n_s \sigma_s)^{-1}$ will become. Some remarks and/or questions raised by the previous analysis are in order:

- (a) We must distinguish between elastic and inelastic scattering and the corresponding relaxation times, τ_e and τ_{in} . The second one, in contrast to the first, tends to randomize the phase of $A_a(t)$ relative to $A_{\bar{a}}(t)$ and consequently tends to destroy the equality $A_a(t) = A_{\bar{a}}(t)$. It is clear that the longer the time t is, the larger the difference $|A_a(t) - A_{\bar{a}}(t)|$ would be. Having this in mind, we introduce a characteristic time τ_φ , called *phase coherence time* (which is of the same order of magnitude as τ_{in}), such that for $t \leq \tau_\varphi$, $A_a(t) \simeq A_{\bar{a}}(t)$. Having τ_e and τ_φ , we define the corresponding diffusion lengths. $L_e = (D_f \tau_e)^{1/2}$ and $L_\varphi = (D_f \tau_\varphi)^{1/2}$. (The subscript f was set to distinguish the diffusion coefficient D_f from the dimensionality symbol, D).

Problem 18.5t. Show that $L_e = \ell/\sqrt{D}$, where D is the dimensionality and ℓ is the elastic mean free path ($\ell = v\tau_e$). *Hint:* Use (8.46).

- (b) For the first line of (18.26) to be equal to (18.25) in the absence of magnetic force, we must have the double inequality

$$\tau_e \ll t \lesssim \tau_\varphi \quad (18.27)$$

This is so, since for $t \lesssim \tau_e$ (or $L \lesssim \ell$) the motion is almost ballistic, the probability of returning to the initial region $\delta V(\mathbf{r})$, for $t \leq \tau_e$, is practically zero; also for $\tau_\varphi \lesssim t$ the phase of $A_a(t)$ and $A_{\bar{a}}(t)$ are randomized. Thus, a necessary condition in order to observe the quantum interference effects is the validity of the inequality

$$\tau_e \ll \tau_\varphi \text{ or } \ell \ll L_\varphi. \quad (18.28)$$

This inequality occurs only for very low temperatures for which $L_\varphi \sim T^{-v}$, $v > 0$. For high temperatures, $\tau_\varphi \approx \tau_e$ and the distinction between

⁶ In connection with the argument of (18.26) one speaks sometimes of ‘the Cooperon effect’.

elastic and inelastic scattering tends to be lost; thus, at high temperatures, the quantum interference effects are eliminated.

- (c) The introduction of a magnetic field breaks the time reversal symmetry and, hence, the equality $A_\alpha(t) = A_{\bar{\alpha}}(t)$. Thus, a magnetic field reduces the role of the quantum interference effects and tends to restore the classical result. We shall return to this point later on.
- (d) Is it possible for the quantum interference effects to be so strong as to make the microscopic mobility $\mu(E; T)$, or the conductivity $\sigma(E; T)$, zero as $T \rightarrow 0$ and $L_\varphi \rightarrow \infty$? P.W. Anderson in his classic paper [18.13] “Absence of diffusion in certain random lattices,” Phys. Rev. **109**, 1492 (1958) gave an affirmative answer to this question and thereby created the field of disorder-induced localization, known as *Anderson localization*. In the next section, we present the main results of the localization theory.

18.7 Band Structure, Static Disorder, and Localization

18.7.1 3D Case

We shall consider the simplest 3D model of a disordered system. It is a **sc** lattice with one s-orbital per site; the diagonal elements of its Hamiltonian, $\{\varepsilon_n\}$, are uncorrelated random variables with a common probability distribution $p(\varepsilon_n)$. The latter is usually either rectangular of total width, W , or Gaussian of standard deviation, w , or binary alloy as in (18.1). The nonrandom off-diagonal matrix element of the Hamiltonian is only between nearest neighbors, and it is denoted by V_2 . The model does not include at all the possibility of inelastic scattering; thus, $\ell_{\text{in}} = L_\varphi = \infty$. In Fig. 18.8 we plot the DOS vs. E (averaged over $\{\varepsilon_n\}$) for different values of Gaussian standard deviation.

Notice the following:

- (a) Nonzero disorder, i.e., $w \neq 0$, eliminates the van Hove singularities, both inside the band and at the band edges $\pm E_{\text{B}}^{(0)}$.
- (b) The bandwidth is increasing as the new approximate band edges $\pm E_{\text{B}}$ satisfy the relation, $E_{\text{B}} - E_{\text{B}}^{(0)} \sim w^2 + \mathcal{O}(w^4)$. ($\mathcal{O}$ means of the order of).
- (c) Beyond the new approximate band edges $\pm E_{\text{B}}$, tails in the DOS develop giving rise to the so-called Urbach tails in the optical absorption in semiconductors and insulators;

$$\rho(|E|) \sim \exp(-|E'|/E_0), \quad E' = E - E_{\text{B}} \quad (18.29)$$

where

$$E_0 \sim w^2/|V_2| + \mathcal{O}(w^4) \quad (18.30)$$

For terminating $p(\varepsilon)$, e.g., the rectangular distribution, the tails are quite negligible and terminate.

- (d) In multiband systems, the disorder due widening of consecutive bands reduces the size of the gaps without usually eliminating them. Thus, periodicity, although helpful in opening gaps, is not necessary for their existence.

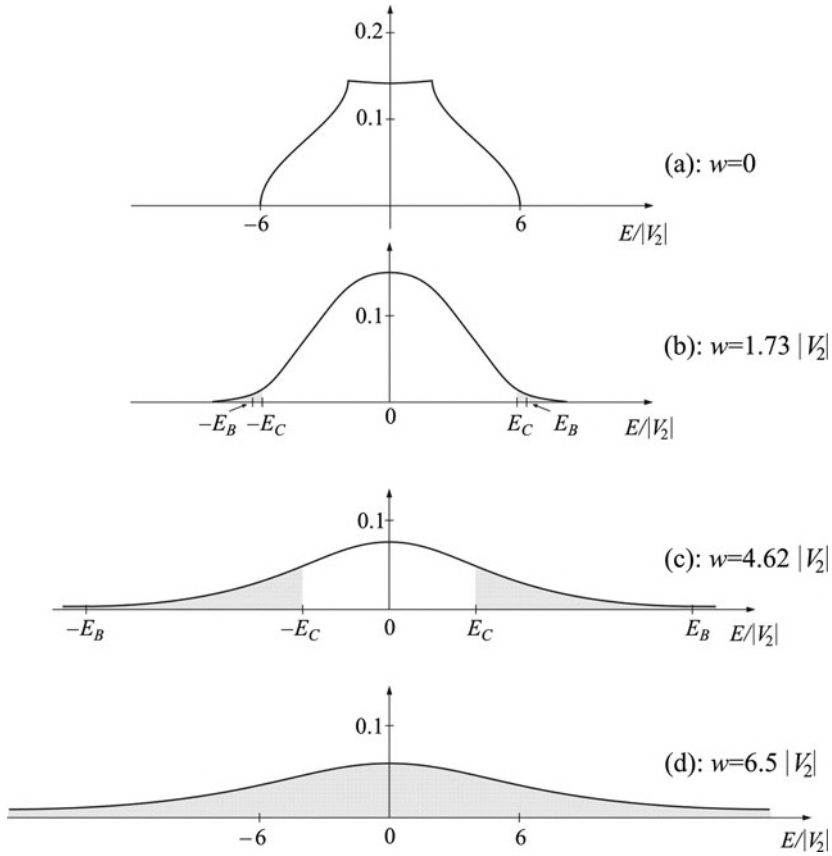


Fig. 18.8. DOS vs. E of a sc TB model with Gaussian diagonal disorder of standard deviation w and average value zero; four values of $w/|V_2|$ are shown. The shaded areas denote a dense spectrum of localized eigenstates (See Sect. 8.5.1.4). This spectrum becomes continuous and smooth (as in the Fig.18.8) only after being averaged over the set $\{\varepsilon_l\}$; before that, only the number of states $R(E)$ is a continuous function of E (in the limit $N \rightarrow \infty$) but nowhere differentiable

- (e) Two critical energies, $\pm E_c$, called *mobility edges*, appear at which the character of the eigenstates changes from extended (for $|E| < E_c$) to localized (for $|E| > E_c$). The microscopic mobility, $\mu(E)$, is zero for $|E| > E_c$ and nonzero for $|E| < E_c$. For not so large disorder, $\pm E_c$ are close to $\pm E_B$ respectively

$$E_B - E_c \sim w^4 / |V_2|^3, \quad w \lesssim 2.5 |V_2| \quad (18.31)$$

- (f) The extended eigenstates of energy E far from the mobility edges are quasi-Bloch states which extend almost uniformly over the whole solid and are characterized by the wave vector $\mathbf{k}$ and the (elastic) mean free path, ℓ . The last one is defined by the relation

$$\langle e^{i\varphi_n} \rangle = \exp\left(-\frac{R_n}{2\ell}\right) \quad (18.32)$$

where the phase φ_n is related to the eigenfunction $\psi_E = \sum_n c_n |n\rangle$, by $c_n = |c_n| \exp(i\varphi_n)$ and the symbol $\langle \rangle$ denotes the average over all random variables $\{\varepsilon_\ell\}$. Thus, by assigning an imaginary part k_I to the wave number, k , such that,

$$k_I = \frac{1}{2\ell} \quad (18.33)$$

we can write approximately the average extended eigenstate of energy E , where E is not so close to E_c , as follows

$$\langle |\psi_E\rangle \rangle \simeq c_0 \sum_n e^{ik \cdot R_n} e^{-k_I R_n} |n\rangle \quad (18.34)$$

In deriving (18.32), it was implicitly assumed that the phases $\varphi_n(\{\varepsilon_\ell\})$ for different set values of the random variables $\{\varepsilon_\ell\}$ tend to become uncorrelated as the distance R_n from the origin tends to very large values ($\varphi_n(\{\varepsilon_\ell\})$ at $n = 0$ was chosen as zero). Thus, by averaging over all sets of $\{\varepsilon_\ell\}$, the quantity $\langle \exp[i\varphi_n(\{\varepsilon_\ell\})] \rangle$ decays exponentially, as $R_n \rightarrow \infty$, since the phases for different sets of $\{\varepsilon_\ell\}$ tend to become uncorrelated. On the other hand, in arriving at (18.32), it was implicitly assumed that the amplitude $|c_n(\{\varepsilon_\ell\})|$ at any given site n had negligible fluctuations around its unperturbed value $c_0 = |c_n|$ for $\{\varepsilon_\ell\} = 0$. In other words, the widely used formula (5.36), $l^{-1} = n_s \sigma_s$, where the scattering cross-section is calculated by employing Born's approximation (see (5.40)), ignores the influence of scattering on the amplitudes, $|c_n|$ as well as the interference. This approximation is only reasonable when the disorder is weak (meaning that $\ell \gg \lambda$). However, as we approach the mobility edge from the extended side, the amplitudes $|c_n|$ are not constant anymore; their standard deviation for a given site n becomes larger and larger and their values, from side to side, fluctuate widely; the largest spatial *extent* of these fluctuations is characterized by a *length*, ξ . For length scale larger than ξ the magnitude of the eigenfunction (before averaging) looks more or less uniform.

Besides the length, ξ , the eigenfunctions are also characterized by the *participation ratio* P , which is a kind of average for the number of sites on which each normalized eigenfunction $\psi = \sum_{n=1}^N c_n |n\rangle$ is appreciable:

$$P \equiv \left(\sum_{n=1}^N |c_n|^4 \right)^{-1} \quad (18.35)$$

For a quasi Bloch state $|c_n| = 1/\sqrt{N}$ and consequently, $P = N$; for a localized state confined to a single site, let us say n_0 , $P = 1$.

Numerical studies for E very close to E_c have demonstrated that

$$\xi \rightarrow \frac{A}{(E_c - |E|)^\gamma}, \quad |E \rightarrow E_c^-| \quad (18.36)$$

where $\gamma \simeq 1.58$ in the absence of magnetic field. Given (18.36), it is possible to have $L \ll \xi$, where L is the linear dimension of a mesoscopic disordered system. Under this condition, numerical studies have shown that P is not proportional to L^D (where D is the dimensionality of space) as one would expect for an extended state. Instead one has

$$P \sim L^d \sim N^{d/D}, \quad |E| \rightarrow E_c^- \quad (18.37)$$

where d is the so-called *fractal dimension*, which is smaller than D . In the present $D = 3$ model, d turns out to be 1.3 ± 0.2 at the mobility edge, so that $d/D \simeq 0.43$. Thus as the size L of the system increases, the percentage of sites $N^{d/D}/N = N^{-(D-d)/D}$ participating in these extended eigenstates is reduced and tends to zero as $N \rightarrow \infty$ (while at the same time, $L/\xi \rightarrow 0$). In the opposite limit, $\xi/L \rightarrow 0$, $P \sim L^D \sim N$. Thus, the amplitude of the eigenfunctions close to a mobility edge is a fractal object (actually a multifractal object) (see Mandelbrot [18.14] or Falconer [18.15]), as long as $L < \xi$; beyond that, i.e., at scales much larger than $L = \xi$, the eigenfunctions look uniform, and $P \sim L^D$. As we approach a mobility edge, $|E| \rightarrow E_c^-$, the expressions (5.36) for $\ell(E)$ and (5.34) or (5.35) for the conductivity $\sigma(E)$ (at $T = 0$ K) cease to be valid. The mean free path, ℓ , becomes smaller than what (5.36) gives, and the conductivity, $\sigma(E)$, (or the mobility, $\mu(E)$), tends to zero as $|E| \rightarrow E_c^-$ and $L \rightarrow \infty$ according to the following formula:

$$\sigma(E) = \frac{e^2}{h} \left[\frac{0.41}{\xi} + \frac{A_3}{L} \right] \quad (18.38)$$

where A_3 has been estimated to be between 0.12 and 0.38, depending on the model, and $h/e^2 = 25812.83 \, \Omega$ is the quantum of resistance R_H (its inverse $R_H^{-1} = e^2/h$) is the well-known “von Klitzing constant”).

- (g) For $|E| > E_c$, the eigenstates are localized. In the most general case, a localized eigenstate is characterized statistically by two lengths: within the first one, L_1 , the eigenfunction may develop strong fluctuations from site to site, but it does not exhibit any systematic tendency to decay; in most cases, L_1 is of the order of the lattice spacing, and consequently, it can be ignored. Beyond L_1 , the eigenfunction still exhibit strong fluctuations from site to site but in addition, it develops a tendency to decay with a characteristic length L_c . This tendency can be quantified by considering the logarithmic average (over the set $\{\varepsilon_l\}$) of $|c_n|$:

$$\langle \ln |c_n| \rangle = -\frac{R_n}{L_c}, \quad R_n \rightarrow \infty \quad (18.39)$$

L_c is called *localization length* and it is the analog of ξ on the other side of the mobility edge. As $|E| \rightarrow E_c^+$, the localization length blows up with the same exponent γ as ξ

$$L_c \rightarrow \frac{A'}{(|E| - E_c)^\gamma}, \quad |E| \rightarrow E_c^+ \quad (18.40)$$

As long as $L \lesssim L_c$, the quantities ℓ , P characterize the localized states as well. The conductivity, $\sigma(E)$, in the limits $T \rightarrow 0$ K and $L \rightarrow \infty$ is zero for E in the localized regimes.

- (h) As the disorder increases, the DOS tends to take the shape of the probability distribution of ε_n and the mobility edges reverse direction and start moving toward the center of the band, making the region of extended states narrower (see Fig. 18.8c), until finally, they merge together (see Fig. 18.8d) making all eigenstates localized. This is called *Anderson's transition*. For the case shown in Fig. 18.8, this transition occurs, when $w = w_c$, where w_c , the critical disorder, is $6.2|V_2|$ (for the rectangular distribution $W_c = 16.5|V_2|$). Thus, for $w \geq w_c$, the conductivity, $\sigma(E)$, and the microscopic mobility, $\mu(E)$, in the limit $T = 0$ K and $L = \infty$ are zero for all energies E .

18.7.2 2D Case

The basic difference between the 3D and the 2D case is that in the latter all the eigenstates become localized for every nonzero disorder and for zero magnetic field. However, for weak disorder the localization length is huge. An approximate formula giving L_c for a square lattice with one s orbital per site and diagonal disorder of Gaussian probability distribution $p(\varepsilon_n)$ is the following [18.30]:

$$L_c(E) \simeq 2.7\ell(E) \exp \left[\frac{S(E)\ell(E)}{4} \right] \quad (18.41)$$

where $\ell(E)$ is the mean free path and $S(E)$ is the length of the renormalized contour in the 2D $\mathbf{k}$ space which corresponds to energy E (see next section (18.79)) regarding what renormalized means). This formula, for $E = 0$ (center of the band) and rectangular probability distribution for each ε_n of total width, $W = 3|V_2|$, gives $S(0) = 4\sqrt{2}\pi/a$ (see Fig. 10.4 for $E = \varepsilon$), $\ell(0) = 2.03a$, and $L_c \simeq 4.5 \times 10^4 a$, where a is the lattice constant.

The presence of the magnetic field induces drastic changes in the behavior of the 2D disordered electronic system, including the appearance of three phases in the disorder/magnetic field plane (besides the insulating with L_c finite and the metallic with $L_c = \infty$, the Quantum Hall phase appears to resemble in some aspects that of superconductivity). In the metallic phase, the 2D electronic system behaves similar to the 3D one, in the sense that the elimination of all extended (current carrying) states requires a finite amount of disorder. In other words, a 2D system in the presence of a magnetic field undergoes an Anderson transition for a nonzero disorder (which depends on the value of the magnetic field).⁷

⁷ Finally, in the special case of spin-orbit interaction one has a particular case of “weak antilocalization” [18.53].

18.7.3 1D and quasi 1D Systems

All eigenstates in a 1D disordered system are localized, no matter how small the disorder is. The localization length, L_c , is proportional to the mean free path, ℓ , with a proportionality constant c_1 , which for weak disorder is 4:

$$L_c = c_1 \ell \quad (18.42)$$

The localization length, L_c , is related to the average DOS per atom and per spin with the following exact relation:

$$L_c^{-1} = \frac{a^{-1}}{N_a} \int_{-\infty}^{\infty} dE' < \rho(E') > \ln \frac{|E - E'|}{|V_2|} \quad (18.43)$$

The transmission amplitude $t_{N1} \equiv t_{N \leftarrow 1}$ of a 1D disordered system of length $L = Na$ connecting point 1 and point N is a strongly fluctuating random variable (being a function of the random variables $\varepsilon_0, \varepsilon_1, \varepsilon_2, \dots, \varepsilon_N$, where $N = L/a$); the logarithm of the corresponding transmission coefficient $T_{N1} \equiv |t_{N1}|^2$, $\ln |t_{N1}|^2$ seems to follow a Gaussian distribution the width of which is negligible in comparison with its average; the latter is equal to

$$\langle \ln |t_{N1}|^2 \rangle = -\frac{2L}{L_c} \quad (18.44)$$

Equation (18.44) is reasonable in view of (18.39); its rigorous proof can be obtained in the framework of the transfer matrix approach.⁸ The DC conductivity in 1D disordered systems of length L is given by the following formula

$$\sigma = \frac{2e^2}{h} \frac{L}{e^{2L/L_c} - 1} \quad (18.45)$$

By introducing the logarithmic average, T , of T_{N1}

$$T \equiv \exp[\langle \ln |T_{N1}| \rangle] \quad (18.46)$$

and taking into account (18.44) and (18.45), we can express the 1D *conductance*, $G \equiv \sigma/L$, as follows

$$G = 2 \frac{e^2}{h} \frac{T}{1 - T} = 2 \frac{e^2}{h} \frac{T}{R} \quad (18.47)$$

where $R \equiv 1 - T$ is the reflection coefficient. Equation (18.47) is the *Landauer formula* for the conductance, which is proportional to T/R times the quantum

⁸ See the books by Landau and Lifshitz, *Quantum Mechanics*, Pergamon Press, Oxford, 3rd edition, 1997, § 25; E. Merzbacher, *Quantum Mechanics*, Wiley, New York, 3rd edition, 1998; E.N. Economou, *Green's Function in Quantum Physics*, Springer, 3rd edition, 2006; and P. Markos and C.M. Soukoulis, *Wave Propagation*, Princeton University Press, Princeton (2008).

of conductance, e^2/h . (The factor 2 is because of the two orientations of the electronic spin).

From the Kubo-Greenwood formula⁹ for the conductivity, $\sigma(\omega)$, one can show,¹⁰ [18.16], that the conductance of a 1D disordered system is given by

$$G = 2 \frac{e^2}{h} T \quad (18.48)$$

This formula can be generalized¹¹ to quasi 1D systems consisting of M coupled 1D channels

$$G = 2 \frac{e^2}{h} \text{Tr}\{tt^+\} = 2 \frac{e^2}{h} MT \quad (18.49)$$

where t is an $M \times M$ matrix with matrix element t_{ij} ; each t_{ij} gives the transmission current amplitude from the left end of the j channel to the right end of the i channel. T is the average transmission per channel: $T \equiv \text{Tr}(tt^+)/M$. In Fig. 18.9, we show an experimental verification of (18.49).

Both the disagreement of (18.47) with (18.48) and the apparently paradoxical result of finite resistance $h/2e^2$ per channel for the perfect conductor require a physical explanation (see, e.g. Imry's book [DS137]). This explanation is related to the fact that a quasi 1D system (with M channels) is connected (through leads or directly) to two macroscopic contacts, each one in internal thermal equilibrium with electrochemical potential, $\mu_i = \mu_0 - |e|V_i$, $i = 1, 2$. The macroscopic nature of the contacts means that they consist of a huge number of channels, M_{ci} ($M_{ci} \rightarrow \infty$). When a current enters a contact of M_{ci} channels from our quasi 1D conductor with M channels ($M \ll M_{ci}$), it encounters a contact resistance. If there is no reflection as the current enters the contacts, one can show (see Datta [DS135], pp. 50–54) that this total contact resistance is given by

⁹ This formula gives the AC conductivity in terms of the electron concentration n and mass m , the exact eigenstates of individual electrons $|\alpha\rangle$, $|\beta\rangle$, the Fermi distributions $f_\alpha = [\exp[\beta(\varepsilon_\alpha - \mu)] + 1]^{-1}$, and a similar expression for f_β , the matrix element of the momentum operator p_x (isotropy is assumed) and $\omega_{\beta\alpha} \equiv (\varepsilon_\beta - \varepsilon_\alpha)/\hbar$. The only approximation is the omission of electron–electron correlations.

$$\sigma(\omega) = \lim_{s \rightarrow 0^+} \frac{i}{\omega + is} \left\{ \frac{e^2 n}{m} - \frac{e^2}{Vm^2} \sum_{\alpha\beta} |\langle \alpha | p_x | \beta \rangle|^2 \frac{f_\alpha - f_\beta}{\hbar\omega_{\beta\alpha}} \right\} - \lim_{s \rightarrow 0^+} i \frac{e^2}{Vm^2} \sum_{\alpha\beta} |\langle \alpha | p_x | \beta \rangle|^2 \frac{f_\alpha - f_\beta}{\hbar\omega_{\beta\alpha}} \frac{1}{\omega_{\beta\alpha} - \omega - is} = \sigma_d(\omega) + \sigma_p(\omega),$$

where the diamagnetic, $\sigma_d(\omega)$, and the paramagnetic $\sigma_p(\omega)$, contributions are

$$\sigma_d(\omega) = \lim_{s \rightarrow 0^+} \frac{ie^2 n}{m(\omega + is)}; \quad \sigma_p(\omega) = - \lim_{s \rightarrow 0^+} \frac{ie^2}{m^2 \hbar \omega V} \sum_{\alpha\beta} |\langle \alpha | p_x | \beta \rangle|^2 \frac{f_\alpha - f_\beta}{\omega_{\beta\alpha} - \omega - is}.$$

¹⁰ [18.16], E.N. Economou and C.M. Soukoulis, Phys. Rev. Lett. **46**, 618, (1981).

¹¹ [18.17], D.S. Fisher and P.A. Lee, Phys. Rev. B. **23**, 6851, (1981).

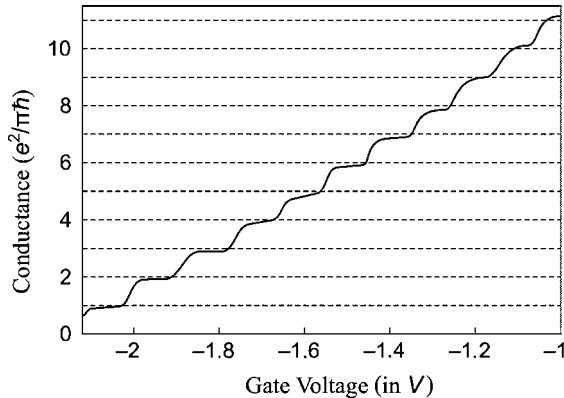


Fig. 18.9. The electrical conductance of a quasi 1D system, measured by a two probe configuration. By changing the gate voltage applied perpendicularly to the quasi 1D system the number of channels is changing (see [18.18], B.J. van Wees et al., Phys. Rev. Lett. **60**, 848 (1988))

$$R_c = G_c^{-1} = \left(\frac{2e^2}{h} M \right)^{-1} \quad (18.50)$$

The total resistance of the system, taking into account the contacts is defined as the ratio $(\mu_1 - \mu_2)/|e|I$, where I is the current through our quasi 1D system; hence, the total resistance is the sum of the contact resistance, R_c , and the resistance of the quasi 1D system per se, given by (18.45)

$$G^{-1} = G_c^{-1} + G_s^{-1} = \frac{h}{2e^2 M} \left(1 + \frac{1-T}{T} \right) = \frac{h}{2e^2 M T} \quad (18.51)$$

Thus, the total conductance, $G = (2e^2/h)MT$, is identical to that given by (18.49). One may conclude that G , as given by (18.49), is equal to $-\frac{|e|I}{\mu_1 - \mu_2} \equiv \frac{I}{\Delta V}$, and it is measured by two probes (c_1 and c_2), while G , as given by $(2e^2/h)MT/(1-T)$ is equal to the ratio $I/\Delta V'$ in Fig. 18.10 and it requires a four probe ($c_1, \dots, c_4$) measurement. Notice that¹² $\Delta V = \Delta V' + \Delta V_c$. Actually, the latter is not always true, because the presence of leads L'_1 and L'_2 in general modifies the corresponding voltages ΔV_0 and $\Delta V'_0$ existing under the same current ($I_0 = I$) but without leads L'_1 and L'_2 . To face this problem,

¹² The total voltage drop, $\Delta V_c = hI/2e^2 M$, at the contacts can be equally divided between contacts c_1 and c_2 . The argument for this is that electrons leaving contact c_1 have a constant electrochemical potential $\mu = \mu_1$ in the perfect quasi 1-D system, until they enter c_2 , where their $\mu = \mu_2$. The ones that leave c_2 have $\mu = \mu_2$, until they enter c_1 , where $\mu = \mu_1$. Thus, the average electrochemical potential in the perfect quasi 1-D conductor is $\bar{\mu} = (\mu_1 + \mu_2)/2$ and the voltage drop is $(\mu_1 - \bar{\mu})/(-|e|) = (V_1 - V_2)/2$ at c_1 and $(\bar{\mu} - \mu_2)/(-|e|) = (V_1 - V_2)/2$ at c_2 .

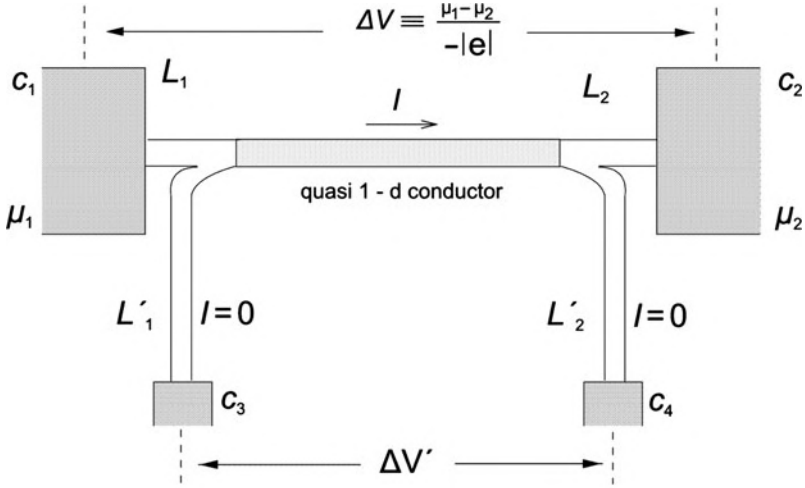


Fig. 18.10. Four-probe arrangement for measuring the conductance of quasi 1D conductor, which through leads L_1 and L_2 is connected to the contacts c_1 and c_2 of electrochemical potentials μ_1 and μ_2 , respectively. Two leads L'_1 and L'_2 (through which no current flows) connect the quasi 1D conductor to voltage probes c_3 and c_4

Büttiker et al. [18.19] and Büttiker [18.20] treated all external contacts (be it current sources or sinks or voltage probes) on equal footing and generalized the equation $I = G(\mu_1 - \mu_2)/(-|e|)$, with $G = (2e^2/h)\text{Tr}\{\hat{t}\hat{t}^\dagger\}$, to

$$I_p = \sum_q G_{pq}[V_p - V_q], \quad (18.52)$$

where

$$G_{pq} = \frac{2e^2}{h} \text{Tr}\{\hat{t}_{pq}\hat{t}_{pq}^\dagger\} \equiv \frac{2e^2}{h} \bar{T}_{pq}, \quad (18.53)$$

$\hat{t}_{pq}$ is a transmission *current* amplitude $M \times M'$ matrix, the matrix elements, t_{pqij} , of which give the transmission *current* amplitude from the j th channel of the q lead to the i th channel of the p lead, and $\bar{T}_{pq}$ is the average transmission probability per pair of channels times the number MM' of channels. Furthermore,

$$V_p = \frac{\mu_p}{-|e|} \quad (18.54)$$

is the voltage at the contact p , and I_p is the total current entering from the contact p . Strictly speaking, (18.52) is valid at zero temperature where only channels at the Fermi level are involved; for finite temperatures, the generalization is straightforward. If the chemical potential difference, $\mu_p - \mu_q$, is small compared with variations of $\bar{T}_{pq}(E)$ vs. E , then

$$G_{pq} = \frac{2e^2}{h} \int \bar{T}_{pq}(E) \left(-\frac{\partial f}{\partial E} \right) dE \quad (18.55)$$

The smoothness of $\bar{T}_{pq}(E)$ as a function of E is increased with increasing temperature and with increasing inelastic scattering energy, δE_{in} . Thus, the validity of linear equation (18.52) with G_{pq} , given by (18.55), is guaranteed, if

$$|\mu_p - \mu_q| \ll \delta E_{\text{in}} + \alpha k_B T, \quad (18.56)$$

where the numerical factor α is larger than 1.

18.8 Calculation Techniques

18.8.1 Coherent Potential Approximation

This important calculation method for obtaining the average DOS (and other average quantities directly related to the DOS) will be presented in the framework of a simple TB model with one s orbital per site and only diagonal disorder. The Hamiltonian is

$$\hat{H} = \sum_n |n\rangle \varepsilon_n \langle n| + V_2 \sum_{\ell n}' |\ell\rangle \langle n|, \quad (18.57)$$

where $\{\varepsilon_n\}$ are uncorrelated random variables with a common probability distribution $p(\varepsilon_n)$; only nonrandom nearest neighbor off-diagonal matrix elements, V_2 , are present. The first step of the coherent potential approximation (CPA) procedure is to replace the random variables $\{\varepsilon_n\}$ by a common value Σ , which is called *self energy* and it is allowed to be energy dependent and complex. This replacement reduces a disordered system to an effective periodic one: $\hat{H} \rightarrow \hat{H}_e = \sum_n |n\rangle \Sigma \langle n| + V_2 \sum_{\ell n} |\ell\rangle \langle n|$. Σ is chosen in such a way as to satisfy as accurately as possible the relation

$$G_e(E) \equiv \frac{1}{E - \hat{H}_e} = \langle \frac{1}{E + is - \hat{H}} \rangle \equiv \hat{G}(E), \quad s \rightarrow 0^+ \quad (18.58)$$

where the symbol $\langle \rangle$ denotes the average with respect to all the random variables $\{\varepsilon_n\}$. The equality of the resolvents, $\hat{G}_e(E) = \langle \hat{G}(E) \rangle$, (see (B.60)), was chosen, because it implies the equality of the DOS, $\rho_e(E) = \langle \rho(E) \rangle$, since the resolvent is directly related to the DOS $\rho(E)$ as shown below (see also Problem 10.2s):

$$\begin{aligned} & -\frac{1}{\pi} \text{Im} \sum_i \left(i \left| \hat{G}(E) \right| i \right) \\ &= -\frac{1}{\pi} \text{Im} \sum_i \frac{1}{E + is - \varepsilon_i} \\ &= \sum_i \delta(E - \varepsilon_i) = \rho(E), \end{aligned} \quad (18.59)$$

where $\{|i\rangle\}$ are the eigenfunctions of $\hat{H}$: $\hat{H}|i\rangle = \varepsilon_i|i\rangle$. In addition, the average resolvent gives the mean free path¹³. The sum of all the diagonal matrix

¹³ At this point the reader must be aware that transport properties, as opposed to the DOS, involve in general the average of the product of two $\hat{G}(E)$ s in the

elements of an operator is the same, no matter what the complete set of orthonormalized functions used for the calculation of the diagonal matrix elements is. This sum is called the *Trace* and is denoted for the various resolvents by $\text{Tr}\hat{G}_e(E)$, $\text{Tr}\hat{G}(E)$, etc. Taking into account (18.58), we have

$$\begin{aligned} \text{Tr}\hat{G}_e(E) &= \sum_{\mathbf{k}} \left\langle \mathbf{k} \left| \hat{G}_e(E) \right| \mathbf{k} \right\rangle = \sum_i \left(i \left| \hat{G}_e(E) \right| i \right) \simeq \left\langle \sum_i \left(i \left| \hat{G}(E) \right| i \right) \right\rangle \\ &= \left\langle \text{Tr}\hat{G}(E) \right\rangle, \end{aligned} \quad (18.60)$$

where $\{|\mathbf{k}\rangle\}$ are the normalized eigenfunctions of $\hat{H}_e$ with eigenenergies

$$E_e(\mathbf{k}) = \Sigma(E) + E_0(\mathbf{k}) \quad (18.61)$$

$E_0(\mathbf{k})$ are the eigenenergies of the Hamiltonian $\hat{H}_0 = V_2 \sum_{\ell,n}' |\ell\rangle \langle n|$. Combining (18.59), (18.60), and (18.61), we obtain

$$\langle \rho(E) \rangle = -\frac{1}{\pi} \text{Im} \left\langle \text{Tr}\hat{G}(E) \right\rangle \simeq -\frac{1}{\pi} \text{Im} \text{Tr}\hat{G}_e(E), \quad (18.62)$$

where

$$\begin{aligned} \text{Tr}\hat{G}_e(E) &= \sum_{\mathbf{k}} \left\langle \mathbf{k} \left| \frac{1}{E - \hat{H}_e} \right| \mathbf{k} \right\rangle = \sum_{\mathbf{k}} \left\langle \mathbf{k} \left| \frac{1}{E - E_e(\mathbf{k})} \right| \mathbf{k} \right\rangle \\ &= \sum_{\mathbf{k}} \frac{1}{E - \Sigma(E) - E_0(\mathbf{k})} = \int dE' \frac{\rho_0(E')}{E - \Sigma(E) - E'}; \end{aligned} \quad (18.63)$$

and $\rho_0(E') = \sum_{\mathbf{k}} \delta(E' - E_0(\mathbf{k}))$ is the DOS for $\hat{H}_0$.

Problem 18.6t. Prove the last equality in (18.63).

Thus, according to (18.63), the average DOS, $\langle \rho(E) \rangle$, can be expressed in terms of the DOS $\rho_0(E')$ associated with the periodic Hamiltonian $\hat{H}_0 = V_2 \sum_{\ell\nu}' |\ell\rangle \langle n|$ and the self energy $\Sigma(E)$

$$\langle \rho(E) \rangle \simeq -\frac{1}{\pi} \text{Im} \int dE' \frac{\rho_0(E')}{E - \Sigma(E) - E'} \quad (18.64)$$

provided that $\Sigma(E)$ is such that (18.58) is satisfied.

Let us consider $\hat{H}_e$ as the unperturbed Hamiltonian and $\hat{H}_1 \equiv \hat{H} - \hat{H}_e$ as the perturbation. Then, by comparing the first and the last line of (B.59) and taking into account that the role of $\hat{G}_0$ is now played by $\hat{G}_e$, we have

form $\langle \hat{G}(E) \hat{B} \hat{G}(E') \rangle$ where $\hat{B}$ is an appropriate non-random operator associated with each particular transport quantity. Moreover, the average of the product of two $\hat{G}(E)$ s is, in general, different than the product of the two averages. Thus, the CPA cannot directly calculate transport-related quantities such as mobility edges, localization lengths, etc., although its results can be used as inputs in other approximate theories concerning such quantities (see Subsect. 18.8.5 below).

$$\hat{G} = \hat{G}_e + \hat{G}_e \hat{H}_1 \hat{G}_e + G_e \hat{H}_1 \hat{G}_e \hat{H}_1 \hat{G}_e + \dots \quad (18.65)$$

By multiplying (B.61) from the left and the right by $\hat{G}_e$ and taking into account (18.65), we obtain

$$\hat{G}_e \hat{T} \hat{G}_e = \hat{G}_e \hat{H}_1 \hat{G}_e + \hat{G}_e \hat{H}_1 \hat{G}_e \hat{H}_1 \hat{G}_e + \hat{G}_e \hat{H}_1 \hat{G}_e \hat{H}_1 \hat{G}_e + \dots = \hat{G} - \hat{G}_e \quad (18.66)$$

Taking the average of (18.66), we have

$$\langle \hat{G} \rangle = \hat{G}_e + \hat{G}_e \langle \hat{T} \rangle \hat{G}_e \quad (18.67)$$

Thus, (18.58) is equivalent to

$$\langle \hat{T} \rangle = 0 \quad (18.68)$$

where the $\hat{T}$ matrix was introduced in App. B, (13.61).

Because of the multiple scattering effects, $\hat{T}$ is a complicated function of all the individual t -matrices, $\hat{t}_n$

$$\hat{T} = f(\{\hat{t}_n\}) \quad (18.69)$$

where $\hat{t}_n$ is associated with a single scattering at the site n by the perturbation $\hat{h}_n = |n\rangle (\varepsilon_n - \Sigma) \langle n|$, while $\hat{T}$ is associated with the multiple scattering by the perturbation $\hat{H}_1 = \sum_n \hat{h}_n$.

Problem 18.7t. Show that

$$\hat{t}_n = |n\rangle t_n \langle n|, \quad t_n = \frac{\varepsilon_n - \Sigma(E)}{1 - (\varepsilon_n - \Sigma(E))g_e(E)} \quad (18.70)$$

where

$$g_e(E) \equiv g_0(E - \Sigma(E)) = \frac{1}{N} \text{Tr} \hat{G}_e(E) = \frac{1}{N} \text{Tr} \hat{G}_0(E - \Sigma(E)) \quad (18.71)$$

Hint: In (18.65) and (B.61), write $\hat{t}_n$ instead of $\hat{T}$ and $\hat{h}_n$ instead of $\hat{H}_1$, then

$$\hat{t}_n = \hat{h}_n + \hat{h}_n \hat{G}_e \hat{h}_n + \hat{h}_n \hat{G}_e \hat{h}_n \hat{G}_e \hat{h}_n + \dots, \quad \text{where } \hat{h}_n = |n\rangle (\varepsilon_n - \Sigma) \langle n|.$$

The approximation in CPA is as follows:

$$\langle \hat{T} \rangle \simeq f(\{\langle \hat{t}_n \rangle\}) \quad (18.72)$$

where f is the same function as in (18.69). Equation (18.72) says that the averaging of $\hat{T}$ can be accomplished approximately by averaging each $\hat{t}_n$ in (18.69).

It follows, from (18.72) and the equality of all $\langle \hat{t}_n \rangle$ (the averaging eliminates the dependence on ε_n in (18.70)), that the $\langle \hat{T} \rangle = 0$ is equivalent to $\langle t_n \rangle = 0$. Hence, the CPA condition for determining $\Sigma(E)$ is as follows:

$$\langle t_n \rangle = \int d\varepsilon_n p(\varepsilon_n) t_n = 0 \quad (18.73)$$

To summarize: *The CPA determines $\Sigma(E)$, i.e., the effective periodic medium, by demanding that the replacement locally of $\Sigma(E)$ by the actual random variable ε_n to produce no change on the average. The applicability of the CPA idea extends to many other disordered systems, besides those of electronic motion.*

Equation (18.73) can be brought to a more convenient form for numerical calculations

$$\Sigma(E) = \int d\varepsilon_n p(\varepsilon_n) \frac{\varepsilon_n}{1 - (\varepsilon_n - \Sigma(E))g_e(E)} \quad (18.74)$$

Problem 18.8t. Starting from (18.70) and (18.73) prove (18.74). *Hint:* In view of (18.73), the identity $\langle [1 - (\varepsilon_n - \Sigma)g_e]/[1 - (\varepsilon_n - \Sigma)g_e] \rangle = 1$ implies that $\langle [1 - (\varepsilon_n - \Sigma)g_e]^{-1} \rangle = 1$; $g_e(E) \equiv g_0(E - \Sigma(E))$.

Problem 18.9ts. Assuming that $\langle \varepsilon_n^\ell \rangle = 0$ for ℓ odd integer, $\langle \varepsilon_n^2 \rangle = w^2$, and $\langle \varepsilon_n^4 \rangle = \mu_4$, show that for weak disorder, $wg_0 \ll 1$, $|E| \lesssim 6|V_2|$ and $|\varepsilon_n| \lesssim w$

$$\Sigma(E) \simeq w^2 g_e - (2w^4 - \mu_4)g_e^3 + \mathcal{O}(w^6) \quad (18.75)$$

In the opposite case, at the far tails, $|E| \gg 6|V_2|$, and $|\varepsilon_n| \gg w$, Σ is very small and $\varepsilon_n - \Sigma \simeq \varepsilon_n$; then the main contribution to the integral (18.74) comes from the pole $\varepsilon_n = \varepsilon_p \simeq g_0^{-1}(E)$ of the integrand. Solve then problem 18.8 to show that

$$\Sigma(E) \simeq -i \frac{\pi}{g_0^2(E)} p(g_0^{-1}(E)), \quad |E| - 6|V_2| \gg w^2 |g_0(E)| \quad (18.76)$$

and

$$\frac{1}{N} \langle \rho(E) \rangle \simeq -\frac{g_0'(E)}{g_0^2(E)} p(g_0^{-1}(E)), \quad |E| - 6|V_2| \gg w^2 g_0(E) \quad (18.77)$$

Assume that the relation between the energy E and the wavenumber k for the Hamiltonian $\hat{H}_0$ is $E = \hbar^2 k^2 / 2m^*$. Then the E vs k relation for H_e is

$$E - \Sigma(E) = \frac{\hbar^2 k^2}{2m^*} \quad (18.78)$$

Since Σ is in general a complex quantity, $\Sigma(E) = \Sigma_R(E) - i\Sigma_I(E)$ ($\Sigma_I > 0$), the quantity k becomes a complex quantity $k = k_R + ik_I$.

$$E - \Sigma_R = \frac{\hbar^2}{2m^*} (k_R^2 - k_I^2) \simeq \frac{\hbar^2 k_R^2}{2m^*} \quad (18.79)$$

$$\Sigma_I = \frac{\hbar^2 k_R k_I}{m^*} \quad (18.80)$$

According to (18.33), $k_I = 1/2\ell$; furthermore, $\ell = v\tau = \hbar k_R \tau / m^*$. Substituting these relations in (18.79), we obtain:

$$\Sigma_I = \frac{\hbar}{2\tau} \quad (18.81)$$

Thus, the real part of Σ renormalizes the energy from E to $E - \Sigma_R(E)$, while the ratio of $\hbar$ over twice the $-\text{Im}\Sigma = \Sigma_I$ gives the relaxation time τ .

18.8.2 Weak Localization due to Quantum Interference

We have seen in Sect. 18.6 that quantum interference effects increase the probability $\delta P(t)$ of an electron returning to the initial neighborhood $\delta V(\mathbf{r})$ after time t . This increase reduces proportionally the conductivity by $\delta\sigma$, i.e., $\delta\sigma/\sigma \sim -\frac{1}{\tau_\phi} \int_{\tau_e}^{\tau_\phi} \delta P(t) dt = -p$. To estimate p , we recall that the dominant contribution to p comes from closed paths adjacent to the classical one, i.e., from those inside a tube of cross-section λ^2 (or λ^{D-1} for a D -dimensional system, where λ is the wavelength) around the classical trajectory. Take also into account that the probability of returning after time t to the original region is proportional to the probability of self-intersection of this orbital tube. Now, within time dt , the wave would move by vdt and would sweep a volume

$$dV \approx \lambda^{D-1} v dt \quad (18.82)$$

The total volume, $V(t)$, swept by the wave during the entire time interval from τ_e to t , $t \gg \tau_e$, is of the order of $L^D = (D_f t)^{D/2}$, where D_f is the diffusion coefficient to be distinguished from the dimensionality D . Hence, the probability of self-intersection during the time dt after the elapsed time t is of the order of the ratio

$$\frac{dV}{V(t)} \approx \frac{\lambda^{D-1} v}{(D_f t)^{D/2}} dt \quad (18.83)$$

It follows that the probability, p , of self-intersection during the time interval from $t = \tau_e$ to $t = \tau_\phi$ is of the order

$$p \simeq \int_{\tau_e}^{\tau_\phi} dt \frac{v \lambda^{D-1}}{(D_f t)^{D/2}} \quad (18.84)$$

Taking into account that

$$L_e = \sqrt{D_f \tau_e} = \frac{\ell}{\sqrt{D}}$$

where $\ell = v\tau$, we have by performing the integration in (18.84)

$$\delta\sigma \sim -p \simeq \begin{cases} 2 \left(1 - \sqrt{\frac{\tau_\phi}{\tau}}\right) = 2 \left(1 - \frac{L_\phi}{L_e}\right), & D = 1 \end{cases} \quad (18.85)$$

$$\delta\sigma \sim -p \simeq \begin{cases} -\frac{\lambda\sqrt{2}}{L_e} \ln\left(\frac{\tau_\phi}{\tau}\right) = -\frac{2\lambda\sqrt{2}}{L_e} \ln\left(\frac{L_\phi}{L_e}\right), & D = 2 \end{cases} \quad (18.86)$$

$$\delta\sigma \sim -p \simeq \begin{cases} -\frac{\lambda^2\sqrt{3}}{L_e^2} \left(1 - \sqrt{\frac{\tau}{\tau_\phi}}\right) = -\frac{\lambda^2\sqrt{3}}{L_e^2} \left(1 - \frac{L_e}{L_\phi}\right), & D = 3 \end{cases} \quad (18.87)$$

Equation (18.85) shows that in 1D, $\delta\sigma/\sigma$ depends linearly on $-L_\phi/L_e$; from (18.45), we see that $\delta\sigma/\sigma$ is proportional to $-L/L_c \sim -L/L_e$ in the limit of $L \ll L_c$, i.e., in the limit of weak disorder. A similar comment can be made by comparing (18.87) with (18.38). These observations suggest that (18.85), (18.86), and (18.87) are valid in the weak disorder limit and they cannot be extrapolated to the localization limit. Nevertheless, they are indicative of a pending phase transition to localization (since $-\delta\sigma/\sigma$ becomes unphysically large, as L_ϕ/L_e increases without limit). For this reason, it is said that (18.85) to (18.87) represent the so-called *weak localization* regime, at which the interference effects produce a $\delta\sigma$ such that $|\delta\sigma| \ll \sigma_0$.

The second comment concerns the appearance of several lengths that have a role similar to that of an upper cut off length: the length of the specimen, L , and the phase incoherence length, L_ϕ , are two of them. The presence of an AC electric field of frequency ω introduces a length $L_\omega = \sqrt{D/\omega}$; a static magnetic field introduces the cyclotron radius,¹⁴ $L_B = \sqrt{\hbar c/eB}$. Obviously the shortest of these lengths plays a more important role as an upper cutoff length. It has been suggested that the effective upper cutoff length, L_u , is given by

$$L_u^{-2} \simeq c_1 L^{-2} + c_2 L_\phi^{-2} + c_3 L_\omega^{-2} + c_4 L_B^{-2} + \dots \quad (18.88)$$

We shall conclude this section by examining the role of the magnetic field in $\delta\sigma$. The presence of a magnetic field, B , adds a term to the Lagrangian of the form $(q/c)\mathbf{A} \cdot \mathbf{v}$, where q is the electric charge of the particle, $\mathbf{v}$ is its velocity, and $\mathbf{A}$ is the vector potential: $\mathbf{B} = \nabla \times \mathbf{A}$ (in SI c in the denominator must be set equal to one). Obviously, the term $(q/c)\mathbf{A} \cdot \mathbf{v}$ breaks the time invariance of the Lagrangian [since $\mathbf{v}(t) = -\mathbf{v}(-t)$], and as a result, the derivations of (18.85) to (18.87) (which were based on time invariance) need to be reconsidered. The basic equation

$$A_\alpha(t) = \exp \left[\frac{i}{\hbar} \int_0^t L(\mathbf{r}_\alpha(t')) dt' \right] \quad (18.89)$$

in the presence of $\mathbf{B}$ becomes

$$A_\alpha(t) = A_{\alpha 0}(t) \exp(i\phi_\alpha) \quad (18.90)$$

where $A_{\alpha 0}(t)$ is the contribution of the path α in the absence of magnetic field.

Problem 18.10t. Taking into account (18.89), $\mathbf{v}dt = d\mathbf{r}_\alpha$, and $\oint \mathbf{A} \cdot d\mathbf{r}_\alpha = \int \mathbf{B} \cdot d\mathbf{S}_a = \Phi_a$, show that

$$\phi_\alpha = -\pi \frac{\Phi_\alpha}{\Phi_0}, \quad \Phi_0 = \hbar c/2e \quad (18.91)$$

¹⁴ In this subsection set $c = 1$ to obtain the formula in SI.

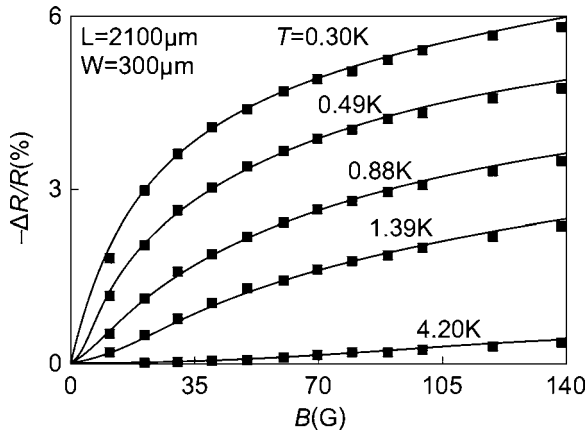


Fig. 18.11. Experimental data and theoretical results for the relative negative magnetoresistance (see [18.21], K.K. Choi et al., Phys. Rev. B **36**, 7751 (1987)) of a two-dimensional system with electronic 2D density $n_s = 1.6 \times 10^{11} \text{ cm}^{-2}$ and mobility $\mu = 27,000 \text{ cm}^2/\text{V} \times \text{s}$

Thus, in the presence of the magnetic field, instead of $4 \sum_a |A_{a0}|^2$ we had before, we now have $2 \sum_\alpha |A_{\alpha 0}|^2 (1 + \cos 2\phi_\alpha) \equiv 2[1 + \cos(2\pi\Phi(t)/\Phi_0)] \sum_\alpha |A_{\alpha 0}|^2$, where $\Phi(t)$ is a properly defined average magnetic flux. As a result, there is an increase $\Delta\sigma(B) = \sigma(B) - \sigma(0)$ in the conductivity of the following form:

$$\Delta\sigma(B)/\sigma \sim \frac{v\lambda^{D-1}}{D_f^{D/2}} \int_{\tau_e}^{\tau_\phi} \frac{dt}{t^{D/2}} \left[1 - \cos\left(\frac{2\pi\Phi(t)}{\Phi_0}\right) \right] \quad (18.92)$$

This increase in σ implies a decrease in the resistance as shown in Fig. 18.11.

For special geometries such that $\phi_\alpha \equiv -\pi\Phi_\alpha/\Phi_0$ is the same for all paths that count, the factor $[1 - \cos(2\pi\Phi/\Phi_0)]$ can be taken out of the integral in (18.92). In such a case, the conductivity will exhibit a sinusoidal periodic variation with the magnetic flux with the period $\Phi_0 = hc/2e$. This is the so-called *hc/2e Aharonov–Bohm effect* and has been observed in cylindrical tubes with very thin walls so that the flux, Φ_α , is an integer multiple of BS , where S is the cross-section of the tube. If S is of the same order of magnitude as πL_ϕ^2 , then the only paths that count are those that go around the circumference of the tube only once; for all such paths $\Phi = BS$.

Another case where the presence of magnetic field produces impressive results is the one shown in Fig. 18.12. In this case, the probability amplitude, A , for a particle to go from point 1 to point 2 is

$$A = \sum_\nu A_\nu + \sum_{\nu'} A_{\nu'} = \sum_\nu A_{\nu_0} \exp(i\phi_\nu) + \sum_{\nu'} A_{\nu'_0} \exp(i\phi_{\nu'})$$

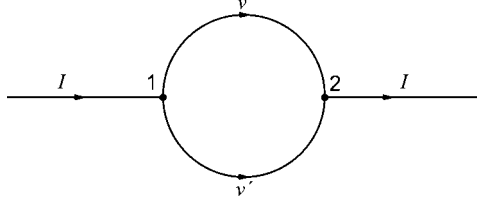


Fig. 18.12. The current I flowing from point 1 to point 2 follows the two paths (ν and ν') of the very thin ring-shaped wire

where

$$\phi_\nu = \frac{e}{\hbar c} \int_1^2 \mathbf{A} \cdot d\mathbf{r}_\nu, \quad (18.93)$$

$$\phi_{\nu'} = \frac{e}{\hbar c} \int_1^2 \mathbf{A} \cdot d\mathbf{r}_{\nu'}, \quad (18.94)$$

Denoting by A' each of the sums $\sum_\nu A_{\nu_0}$ and $\sum_{\nu'} A_{\nu'_0}$ (they are equal by symmetry), we have

$$A = A' [\exp(i\phi_\nu) + \exp(i\phi_{\nu'})] \quad (18.95)$$

The probability $|A|^2$ is then

$$\begin{aligned} |A|^2 &= |A'|^2 [2 + 2 \cos(\phi_\nu - \phi_{\nu'})] = 2 |A'|^2 \left[1 + \cos \left(\frac{e}{\hbar c} \oint \mathbf{A} \cdot d\mathbf{r} \right) \right] \\ &= 2 |A'|^2 \left[1 + \cos \left(\frac{2\pi\Phi}{ch/e} \right) \right], \end{aligned} \quad (18.96)$$

where Φ is the magnetic flux through the ring. In this case, the conductivity would be a periodic sinusoidal function of Φ with period ch/e (not $ch/2e$). This is the so-called¹⁵ *ch/e Aharonov–Bohm effect* [18.22]. (See also [DS135], p. 168).

18.8.3 Scaling Approach

The foundation of this approach is the assumption that there is just one relevant parameter Q (equal to the ratio of transfer strength $|V_2|$ over an average energy mismatch $\delta\varepsilon = \langle \delta\varepsilon_n^2 \rangle^{1/2}$), which completely characterizes the answer to the localization question for each dimensionality D . The existence of just *one* parameter Q is obvious in the simple TBM of (18.57). What is not so obvious is whether a single parameter Q can still characterize more

¹⁵ In SI c must be deleted.

complicated models, where there are many energies per site and more than one off-diagonal matrix elements. Such complicated Hamiltonians may arise even from the simple TBM if, e.g., one enlarges artificially the unit cell of the lattice by a factor x so that the new “unit” cell has linear dimension $L_1 = ax$ and contains $n_1 = x^D$ original sites (a is the lattice spacing). If each new “unit” cell is considered as an effective “site”, there must be (according to our initial assumption) a quantity $Q(L_1)$ that characterizes the localization properties of the reformulated problem. By repeating the procedure of unit cell augmentation, one produces a sequence, $Q(L_2), Q(L_3), \dots, Q(L_m), \dots$, where the “unit” cell after the m th step has linear dimension L_m equal to ax^m and contains $n_m = x^{mD}$ sites. Abrahams et al. [18.23], realized that the derivative of $Q(L)$ with respect to L , or for that matter the logarithmic derivative, β , where

$$\beta = \frac{d \ln[Q(L)]}{d \ln L} \quad (18.97)$$

is an extremely important quantity for localization. Indeed, if β is larger than a positive number, no matter how small, the successive transformation will monotonically increase Q toward infinity as $L \rightarrow \infty$, which means that the initial problem is mapped into one, where the effective energy mismatch is zero, and hence, the eigenstates are extended. If β is less than a negative number, Q monotonically decreases toward zero; this means that the initial problem has been mapped into one where the effective transfer matrix element is zero, and consequently, the eigenstates are localized. Hence, the quantity β completely characterizes the localization problem. The assumption that there is just one parameter Q that determines localization forces the conclusion that β is a function of Q :

$$\beta = f(Q) \quad (18.98)$$

To proceed further with these ideas, one needs to identify what Q in the general case is. Thouless and coworkers [18.24, 18.25] argued that in the general case, where the “unit” cell has linear dimension L , the role of $|V_2|$ is played by ΔE (where ΔE is a measure of how much the eigenenergies of an isolated “unit” cell change upon changing the boundary conditions from periodic to antiperiodic) and the role of $\delta\varepsilon$ is played by the level spacing, which is just the inverse of the total DOS $\rho_V L^D$ per spin; ρ_V is the DOS per unit “volume” and per spin. In other words

$$Q = \rho_V L^D \Delta E \quad (18.99)$$

It was further argued (Licciardello and Thouless [18.25]) that $\Delta E = \hbar/\tau$, where τ is the time it takes a particle to diffuse from the center to the boundary of the “unit” cell: $\tau = (L/2)^2/D_f$, where D_f is the diffusion coefficient. D_f can be written in terms of σ , according to (8.46). Thus, $\Delta E = 4\hbar D_f/L^2 = 2\hbar\sigma/e^2\rho_V L^2$. Substituting in (18.99), we obtain that $Q = 2\hbar\sigma L^{D-2}/e^2$, but σL^{D-2} is the DC conductance, G , of the unit cell,

$$G = \sigma L^{D-2} \quad (18.100)$$

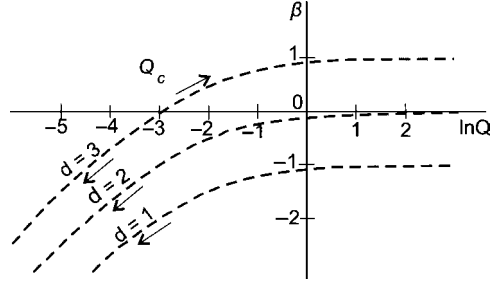


Fig. 18.13. Plot of β vs $\ln Q$ for 1D, 2D, and 3D disordered systems assuming monotonic behavior of Q ; the latter is the dimensionless conductance of a D -dimensional cube of length L ; $\beta = d \ln Q / d \ln L$. As L increases, one moves along the curves in the direction indicated by the arrows

Thus, we reached the very important conclusion that the quantity Q is nothing but the dimensionless DC conductance, i.e.,

$$Q = \frac{\hbar}{e^2} G \quad (18.101)$$

(In (18.101), we redefined Q to eliminate a factor of 2). In view of the fact that higher values of both Q and β favor extended states, it is not unreasonable to assume, as Abrahams et al. [18.23] did, that β is a monotonically increasing function of Q or of $\ln Q$. We are now in a position to find the qualitative features of β vs $\ln Q$. In the weak scattering limit, when the conductance, Q , is very large, one is almost in the metallic regime, where σ is independent of L and $Q \sim L^{D-2}$. In this limit, $\beta = d \ln Q / d \ln L$ approaches $D - 2$. In the other extreme of very strong disorder, the localization length is much less than L , and the conductance decays exponentially with L . Hence, $\beta = \ln Q$ in this limit. This asymptotic behavior, together with the assumption of monotonicity¹⁶ leads to a β vs $\ln Q$ relation, as shown in Fig. 18.13.

Problem 18.11ts. Is a true metallic behavior of a disordered system possible? Base your answer on Fig. 18.13; distinguish three cases according to dimensionality. Under what condition is a quasi-metallic behavior possible for $D = 2$?

Problem 18.12ts. Assume that

$$\beta \approx D - 2 - \frac{A_D}{Q} \text{ as } Q \rightarrow \infty \quad (18.102)$$

Taking into account (18.97), (18.102), and (18.101), show that

¹⁶ This assumption breaks down in the presence of magnetic forces.

$$\sigma \simeq \sigma_{01} - \frac{A_1 e^2}{\hbar} L, \quad D = 1 \quad (18.103)$$

$$\sigma \simeq \sigma_{02} - \frac{A_2 e^2}{\hbar} \ln \frac{L}{L_e}, \quad D = 2 \quad (18.104)$$

$$\sigma \simeq \sigma_{03} - C_3 + \frac{A_3 e^2}{\hbar L}, \quad D = 3 \quad (18.105)$$

Notice that the L dependence in (18.103)–(18.105) is the same as the L_ϕ dependence in (18.85)–(18.87) respectively. Equations (18.103), (18.104), and (18.105) give the weak localization corrections to the “classical” conductivity. The numerical values for the constants are: $A_1 = 1/2\pi$ and $A_2 = A_3 = 1/\pi^2$.

18.8.4 Quasi-One-Dimensional Systems and Scaling

The most reliable numerical method for checking the scaling assumption and for producing results for various quantities of interest (such as critical disorder, mobility edge trajectories in the energy vs. disorder plane, critical exponents, etc.) is the one proposed and applied by Pichard and Sarma, [18.26, 18.27], and Mackinnon and Kramer, [18.28], as reviewed by Kramer and Mackinnon, [18.29]. Several other authors, e.g. [18.30–18.40]; (for more references see a recent book edited by Brandes and Kettermann [DSL159]).

The method determines numerically the longest localization length, L_M , of a quasi 1D tight-binding system consisting of either M coupled channels arranged in a planar strip, or $M \times M$ coupled channels forming a wire of a $Ma \times Ma$ square cross-section (a is the lattice spacing). The probability distribution of the diagonal matrix elements of $\hat{H}$ is usually chosen to be a rectangular of total width W . For the wire case (which becomes 3D as $M \rightarrow \infty$), the behavior depends on whether or not the disorder exceeds a critical value W_c . For $W < W_c$, $L_M(M)$ behaves as $M^2 a^2 / 4.82\xi$ (up to the largest M examined), and hence, it seems to approach infinity parabolically as $M \rightarrow \infty$ (or equivalently, proportionally to the cross-section of the wire); the characteristic length, ξ , is the one introduced in Subsect. 18.7.1 and interpreted as being the largest length beyond which the eigenfunctions look uniform in amplitude. Since a uniform amplitude implies a classical metallic behavior, the quantity ξ can also be interpreted as the length (for a given disorder) at which β is almost 1. For $W > W_c$, $L_M(M)$ increases with M slower than linearly, and it seems to saturate to a value $L(\infty)$, which is the localization length, L_c . For the strip case (which becomes 2D, as $M \rightarrow \infty$), $L_M(M)$ increases with M slower than linearly and it seems to saturate to a finite value at least for disorders down to $W/|V| = 4$ [18.28]. Around $W/|V| \approx 6$ (which early work identified erroneously as a critical point), the localization length seems to change very fast (e.g., $L_c \approx 40$, for $W/|V| = 6$, while $L_c \approx 500$, for $W/|V| = 4$). Such large localization lengths make conclusive numerical work rather difficult. For a recent review, including various references, the readers are referred to [18.36–18.40].

18.8.5 Potential Well Analogy

We have seen that for $D \leq 2$, a D -dimensional disordered system in the absence of inelastic scattering and in the absence of magnetic forces sustains only localized states (although for $D = 2$ and weak disorder the localization length is huge). On the other hand, for $D > 2$, localized eigenstates at a given energy E appear only when the disorder exceeds a critical value $W_c(E)$. This behavior is reminiscent of the elementary problem of a bound state in a D -dimensional potential well (see Problem 2.11s); such a well always sustains a bound state for $D \leq 2$, no matter how shallow it is, while for $D > 2$, the dimensionless quantity $|\varepsilon|a^2m^*/\hbar^2$ must exceed a critical value for a bound state to appear; ε is the depth and a the linear extent of the potential well and m^* the effective mass of the particle [18.31].

Problem 18.13t. Consider the problem of the bound state in a potential well within the framework of a simple tight-binding model where the unperturbed Hamiltonian is $\hat{H}_0 = V_2 \sum_{\ell, m} |\ell \rangle \langle m|$ and the potential well, located at a single site, is $\hat{h}_0 = -\varepsilon |0 \rangle \langle 0|$. Show that:

- The t -matrix is given by $t = |0 \rangle \langle 0| (-\varepsilon) / (1 + \varepsilon g_0(E)) \langle 0|$, where $g_0(E)$ is as in (18.71), i.e., $g_0(E) = [a^D / (2\pi)^D] \int d\mathbf{k} [E - E_0(\mathbf{k})]^{-1}$, and $E_0(k) \approx \hbar^2 k^2 / 2m^*$.
- The pole of the resolvent $\hat{G}(E) = (E + is - \hat{H}_0 - \hat{h}_0)^{-1}$ and hence, the pole of $\hat{t}(E)$, $E = E_p$, gives the bound state energy.
- Taking into account that $E_p = \hbar^2 / 2m^* \lambda_c^2$, where λ_c is the decay length, show that λ_c satisfies the relation

$$\frac{\hbar^2}{2m^* a^D \varepsilon} = a_1 \int_{\text{BZ}} \frac{d\mathbf{k}}{(2\pi)^D} \frac{1}{k^2 + \lambda_c^{-2}} \quad (18.106)$$

where the numerical constant a_1 corrects for the replacement of $E_0(\mathbf{k}) = 2V_2 \sum_{\ell=1}^D \cos k_\ell a$, by $\hbar^2 k^2 / 2m^*$.

A self-consistent approximate theory of localization ends up with the following relation satisfied by the localization length

$$\frac{\pi \hbar}{2 e^2} \sigma_0 = a_2 \int_{\text{BZ}} \frac{d\mathbf{k}}{(2\pi)^D} \frac{1}{k^2 + L_c^{-2}} \quad (18.107)$$

where a_2 is another numerical constant and σ_0 is the classical conductivity given by (5.34). By comparing (18.106) and (18.107), we see that the two problems become mathematically equivalent by making the correspondences $\hbar^2 / 2m^* a^D \varepsilon a_1 \leftrightarrow \pi \hbar \sigma_0 / 2e^2 a_2$ and $\lambda_c \leftrightarrow L_c$. We also need the length corresponding to a . We choose $a \leftrightarrow c_0 \ell$, where c_0 is a numerical constant. The reasoning behind this choice is that as the lattice spacing a is the shortest relevant length in the potential well of the TBM so is ℓ for the disordered system (see (18.27) or (18.84)). Then by comparing (18.106) with (18.107) and taking into account (5.34), we have the correspondence

$$\begin{aligned}
\frac{\varepsilon}{\hbar^2/2m^*a^2} &\leftrightarrow \frac{24\pi^2c_3}{c_0} \frac{1}{S_F\ell^2}, & 3D, \\
&\leftrightarrow \frac{4c_2}{k_F\ell}, & 2D, \\
&\leftrightarrow c_0c_1, & 1D,
\end{aligned} \tag{18.108}$$

together with the correspondence

$$a \leftrightarrow c_0\ell \tag{18.109}$$

The numerical constant a_2/a_1 have been replaced by c_i ($i = 1, 2, 3$) for $D = 1, 2, 3$ respectively; c_1, c_2, c_3 are determined by comparing the results of the potential well analogy (PWA) with the numerical results of the quasi 1D scaling approach.

Employing the CPA, we can calculate the average DOS, the mean free path, ℓ , the conductivity σ_0 , and the renormalized Fermi surface, $S_F(E - \Sigma_R(E))$. Then, using the PWA, we can obtain: (a) The length, ξ , from the relation $E_r(E) = \hbar^2/2m^*\xi^2$ (where E_r is the resonance energy appearing just before the creation of the bound state); (b) the mobility edge in 3D from the relation.

$$S_F\ell^2 \simeq \text{constant}, \quad D = 3 \tag{18.110}$$

(where numerical data show that the constant is around 9); (c) the localization length, L_c , from (18.107); and (d), the conductivity, σ . (See [18.41, 18.42] and [18.31].) Notice, however, that the exponent γ in (18.36) is equal to 1 within the PWA, instead of the numerically determined value of $\gamma \simeq 1.58$.

18.9 Quantum Hall Effect

In 2D systems created at interfaces (e.g., GaAs/Al_xGa_{1-x}As or metal/oxide/semiconductor), at very low temperatures (a few Kelvins or subKelvins) and very high magnetic fields (at least a few Teslas), the Hall effect exhibits a spectacular quantum behavior as shown in Fig. 18.14. There are regions of values of B , where the resistance R_{xx} is practically zero (for these regions of values of B , the 2D electron gas is in the Quantum Hall phase mentioned in Subsect. 18.7.2). For these same regions, the Hall resistance, $R_{yx} = V_{CD}/I_x$, exhibits plateaus at which

$$-R_{yx} = \frac{h}{e^2} \frac{p}{q} = 25812.8 \frac{p}{q} \Omega \tag{18.111}$$

where q is integer and p a small odd integer ($p = 1, 3, 5, 7, \dots$). For $p = 1$, we have the so-called *Integral Quantum Hall Effect* (IQHE) [18.43], while for $p = 3, 5, 7, \dots$ we have the so-called *Fractional Quantum Hall Effect* (FQHE) [18.44]. Both the almost-zero R_{xx} resistance (indicating a frictionless flow)

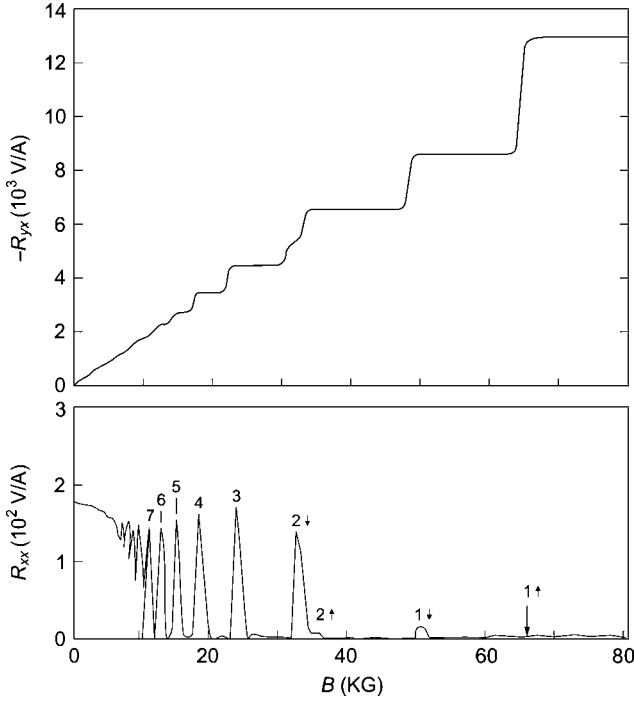


Fig. 18.14. Plot of the Hall resistance, $-R_{yx}$, and the magnetoresistance, R_{xx} , vs the applied magnetic field B in a 2D electronic system at very low temperature. The plateaus in $-R_{yx}$ correspond to the regions of practically zero R_{xx} [18.46]

and the accuracy of the plateau values of $-R_{yx}$ (in parts per million) are unexpected and impressive for a system possessing a nonzero disorder.

There are several different but essentially equivalent ways to explain the IQHE. Here, we follow Datta's approach, [DS135], which is physically more transparent. Consider an electron of mass m and charge $q = -e$ moving in a 2D strip as in Fig. 5.4 or 18.15 in the presence of a perpendicular magnetic field B and possibly under the electrochemical differences $\mu_A - \mu_B = V_{AB}$ and $\mu_C - \mu_D = V_{CD}$ (the x -axis is along the direction AB and the y -axis along CD). The Hamiltonian, according to (B.68) and (B.69), is

$$\hat{H} = \frac{1}{2m} \left(\mathbf{p} - \frac{q}{c} \mathbf{A} \right)^2 + q\phi(\mathbf{r}) - \mathbf{m} \cdot \mathbf{B}, \quad \text{G-CGS} \quad (18.112)$$

where $\mathbf{A} = A_x \mathbf{i}$, $A_x = -By$, $q\phi(\mathbf{r})$ is the potential due to disorder plus the one which confines the electrons within the 2-D strip, and $\mathbf{m} = -2\mu_B \mathbf{s}$ is the magnetic moment of the spin $\mathbf{s}$. To start with, we shall set $\phi(\mathbf{r}) = 0$; then the eigenenergies and the eigenfunctions of $\hat{H}_0 \equiv (\mathbf{p} - q\mathbf{A}/c)^2/2m - \mathbf{m} \cdot \mathbf{B}$ are

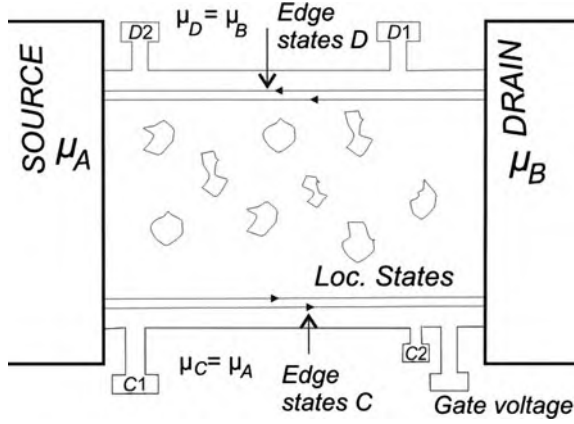


Fig. 18.15. Schematic representation of the experimental set up, for the measurements of quantities pertaining to the QHE. The probes C_1, C_2, D_1, D_2 are voltage probes for measuring V_{C_1, C_2} and V_{CD} . The current I from source to drain is also measured; by changing the gate voltage or the magnetic field the position of the Fermi energy is changed

$$\varepsilon_n = \hbar\omega_c \left(n + \frac{1}{2} + s_z \right), \quad n = 0, 1, 2, \dots \quad (18.113)$$

$$\Psi_{n, k_x}(x, y) = \frac{1}{\sqrt{L}} \exp(ik_x x) \exp \left[-\frac{1}{2} \left(\frac{y - y_k}{R_B} \right)^2 \right] H_n \left(\frac{y - y_k}{R_B} \right) \quad (18.114)$$

where

$$\omega_c \equiv |q| B / mc, \quad R_B \equiv \sqrt{\hbar c / |q| B}, \quad y_k \equiv -\frac{ch k_x}{qB} \quad (18.115)$$

For $B = 10$ tesla, $m = m_e$, $q = -e$, and $T = 1$ K, we have the following typical values $\hbar\omega_c = 1.16$ meV, $k_B T = 0.086$ meV, $R_B = 81$ Å. The degeneracy η of the Landau levels ε_n is given by (5.69). Notice that there is an additional degeneracy between the state $n, s_z = 1/2$ and the state $n + 1, s_z = -1/2$. The potential $q\phi(\mathbf{r})$ will lift, in general, this degeneracy and will broaden the Landau levels to overlapping bands. The absolute square of each Ψ_{n, k_x} is independent of x and it is centered along a straight line $y = y_k$. The distance δy between two consecutive lines $y = y_k$ for a given n satisfies the relation $b/\delta y = \eta$ (where b is the width and L is the length of the 2D strip) or $\delta y = ch / |q| BL = b(2\Phi_0/\Phi)$; similarly, because of (18.115), $\delta k_x = \delta y / R_B^2$. For electrons for which $q = -e$, we have the relation

$$y_k = R_B^2 k_x = \frac{\hbar c}{|e| B} k_x \quad (18.116)$$

which means that for positive k_x the centered line y_k is positive, i.e., parallel to the line AB in Fig. 5.4 and to its left (closer to the point D than the point C); eigenstates with negative k_x are centered along lines parallel to AB but closer to C rather than D. This spatial separation of positive k_x from the negative

k_x states is of central importance in explaining the frictionless flow. Indeed, the spatial separation $2R_B^2 |k_x|$ between a pair of states k_x and $-k_x$, if it is much larger than $2R_B$, makes their overlap practically zero. This zero overlap implies zero backscattering, and hence, no degrading of the flow in spite of the presence of scattering centers giving rise to the random potential, $q\phi(\mathbf{r})$. This is particularly true for the edge states on opposite sides (C and D in Fig. 5.4) of the 2D strip, since their distance is typically several tens of micrometer apart (i.e., about 500,000 Å) as against 100 Å for the typical value of R_B . Furthermore, the edge states are under the influence of the strong confining potential preventing the electrons from escaping the 2D system. Hence, their eigenenergy acquires an extra term depending on y_κ and n

$$\varepsilon_n(y_\kappa) = \hbar\omega_c \left(n + \frac{1}{2}\right) + f(y_\kappa) \quad (18.117)$$

On the other hand, states with k'_x s of opposite sign located far from the edges have a nonzero overlap. As a result, they can be backscattered under the action of the random potential, $q\phi(\mathbf{r})$, and become localized; their eigenenergies have various values, and hence, as it was mentioned before, they broaden the unperturbed degenerate Landau levels of Fig. 5.6(a) to bands. These bands have tails in the DOS that fill up the gap. The eigenenergies of the edge states are also located somewhere in each broadened band corresponding to every Landau level, because of the presence of $f_n(y_\kappa)$ in (18.117).

In Fig. 18.15, we show schematically the experimental setup for the QHE. When the Fermi energy is the region of the energies (18.117) corresponding to the edge states, electrons leaving the source A are transferred to the drain B through the edge states C having a *constant* electrochemical potential $\mu_C = \mu_A$ (since there is free flow, and hence, no voltage drop, $V_{C1,C2} = 0$). Electrons leaving the drain B are transferred to the source A through the edge states D keeping a constant electrochemical potential $\mu_D = \mu_B$ (no voltage drop, $V_{D1,D2} = 0$). Hence, the net current flow is¹⁷

$$\begin{aligned} I &= e \sum_n \int_{\mu_D}^{\mu_C} \frac{dk}{2\pi} v_n(k) = e \sum_n \int_{\mu_D}^{\mu_C} \frac{dk}{2\pi} \frac{1}{\hbar} \frac{\partial \varepsilon_n(y_\kappa)}{\partial k} \\ &= \frac{e}{h} M (\mu_A - \mu_B), \end{aligned} \quad (18.118)$$

where M is the number of channels between μ_A and μ_B , which is equal to the number of edge states corresponding to the occupied Landau levels. Hence,

$$R_{xx} = \frac{V_{C1,C2}}{I} = \frac{V_{D1,D2}}{I} = 0 \quad (18.119)$$

and

$$-R_{yx} \equiv \frac{\mu_C - \mu_D}{eI} = \frac{\mu_A - \mu_B}{eI} = \frac{h}{e^2 M} \quad (18.120)$$

If the Fermi energy is not in the range of energies given by (18.117), then the transmission coefficient, T , is less than one and a function of E_F ; there is also

¹⁷ We enter e and not $2e$, because the strong magnetic field separated the spin-up and spin-down electrons.

a voltage drop from C_1 to C_2 or from D_1 to D_2 ; thus, $-R_{yx} = h/e^2 MT$ until the Fermi energy enters again in a region given by (18.117) but for different value of n . M is equal to the number of Landau levels below the Fermi energy.

Equation (18.20) explains the IQHE. The interpretation [18.47] of the FQHE [18.44] requires the explicit inclusion of the modifications of the single electronic wavefunctions by many-body effects (i.e. by specific electron-electron correlations). This goes beyond the scope of this book. See [18.48, 18.49, 18.54] and the books by Shankar [Q34], pp. 587-592 and by J.K. Jain, [18.55] in the latter the concept of a bound electron-vortex quasiparticle is introduced as the basis for interpreting the FQHE.

18.10 Key Points

- Binary alloys consisting of metals of different lattice structure undergo usually structural phase transitions when the Fermi energy is in the vicinity of a van Hove singularity in the unperturbed DOS (Hume–Rothery rule).
- Around the glass transition temperature, T_G , the viscosity, η , changes by many orders of magnitude following usually a Vogel–Fulcher equation

$$\eta(T) = \eta_0 \exp \left[\frac{E_0}{k_B(T - T_0)} \right],$$

where the Vogel–Fulcher parameter T_0 is smaller than T_G .

- Amorphous metals are approximated by a random collection of touching spherical atoms, while amorphous semiconductors by a CRN of fixed connectivity.
- The X-rays or neutron average, dimensionless, elastic, scattering cross-section $\langle S(\mathbf{k}) \rangle$ is related to the two-atom correlation function $c(\mathbf{r})$ as follows:

$$c(\mathbf{r}) = \frac{V}{N} \int \frac{d^3k}{(2\pi)^3} [\langle S(\mathbf{k}) \rangle - 1] e^{i\mathbf{k} \cdot \mathbf{r}}$$

- Quasi-crystals possess nonperiodic but fully deterministic structure based on canonical icosahedral units of fivefold symmetry. Their X-ray pattern resembles that of crystals.
- Multiple-scattering (by random strong and/or dense scatterers) and wave interference tend to reduce the diffusion coefficient and the conductivity [18.51], [18.56]. A magnetic field tends to undo the effects of interference. Under special geometric conditions, the magnetic field induces a periodic dependence of the conductivity with a period $\Phi_0 = hc/2e$ (the $hc/2e$ Aharonov–Bohm effect) or hc/e (the hc/e Aharonov–Bohm effect). The observation of these multiple-scattering/interference effects requires very low temperatures and hence the elastic mean free path must be much smaller than the inelastic mean free path.

- Disorder of magnitude w in 3D systems creates regions of localized eigenstates usually at the DOS. The transition from extended to localized states occurs at critical energies $E_c(w)$; E_c is called mobility edge. For very strong disorder, it is possible for all states in a band to become localized (Anderson transition).
- Systems of dimensionality D in the presence of disorder, no matter how weak, sustain only localized states, if $D < 2$.
- For the critical dimensionality, $D = 2$, in the absence of magnetic forces, all states are localized. In the presence of a magnetic field, a QHE phase exists that allows frictionless flow. This phase, under $\hbar\omega_c \gg k_B T$, leads to a Hall resistance R_{yx} vs B exhibiting plateaus of quantized values

$$-R_{yx} = \frac{\hbar}{e^2} \frac{p}{q} = 25812.8 \frac{p}{q} \Omega$$

where q is an integer and $p = 1$ (IQHE) or $p = 3, 5, 7$ (FQHE). The longitudinal resistance, R_{xx} , is practically zero for the range of values of B corresponding to the plateaus.

- In 1D systems, the conductance, G , is related to the logarithmically averaged transmission coefficient, T , as follows

$$G = 2 \frac{e^2}{h} \frac{T}{R}$$

or

$$G = 2 \frac{e^2}{h} T$$

The first formula (Landauer formula) does not include the contact resistance, while the second does include it. These relations can be generalized to quasi 1D systems with several channels M and possibly with many contacts

$$G = 2 \frac{e^2}{h} MT, \text{ two contacts, } M \text{ channels}$$

$$I_p = \sum_q G_{pq}(V_p - V_q), \text{ many contacts}$$

$$G_{pq} = 2 \frac{e^2}{h} \bar{T}_{pq}$$

- The CPA calculates the average DOS, the mean free path, ℓ , etc by replacing each random element ε_n by a common complex, energy-dependent quantity $\Sigma(E)$ called self-energy. $\Sigma(E)$ is determined by the requirement of the replacement of $\Sigma(E)$ *locally* at the site n by ε_n produces no change on the average. This condition implies that

$$\langle \hat{t}_n \rangle = 0$$

or equivalently

$$\Sigma(E) = \int d\varepsilon_n p(\varepsilon_n) \frac{\varepsilon_n}{1 - (\varepsilon_n - \Sigma(E))g_0(E - \Sigma(E))}$$

The $\Sigma_R(E) \equiv \text{Re}\Sigma$ renormalizes the energy $E \rightarrow E - \Sigma(E)$ and the $\Sigma_I(E) \equiv -\text{Im}\Sigma$ gives the relaxation time τ

$$\tau = \frac{\hbar}{2\Sigma_I(E)}$$

- The scaling approach summarizes nicely the main, and relevant, features of the localization theory, and in addition, accounts for the interference phenomena due to (what one calls) weak localization

$$\begin{aligned}\delta\sigma &= -\frac{A_1 e^2}{\hbar} L, & D &= 1, \\ \delta\sigma &= -\frac{A_2 e^2}{\hbar} \ln \frac{L}{L_c}, & D &= 2, \\ \delta\sigma &= -C_3 + \frac{A_3 e^2}{\hbar L}. & D &= 3.\end{aligned}$$

- The quasi-one-dimensional scaling approach (based on transfer-matrices) provides reliable numerical results for various quantities related to the localization question.
- The localization problem exhibits similarities to the problem of bound state in a shallow potential well.

18.11 Problems

- 18.1s Show that the entropy $s(x, p_{A/B})$ per bond in (18.4) is equal to $s = -k_B [p \ln p + (1-p) \ln(1-p)]$, for 1D systems and $x = 0.5$.
- 18.2 Starting from (18.17) prove (18.18).
- 18.3 Calculate the standard deviation, σ , for the rectangular distribution of total width W and the binary distribution given by (18.1).
- 18.4s Assume that the unperturbed DOS per site is $\rho_0(E)/N = 2(B^2 - E^2)^{1/2}/\pi B^2$. Calculate the unperturbed $g_0(E)$. To order $w^2 = \sigma^2$ obtain the difference $E_B - E_B^{(0)}$ (see Subsect. 18.8.1) by employing (18.75) and (18.64).
- 18.5 Assuming a Gaussian $p(\varepsilon_n)$ and a $\rho_0(E)$ as in Pr.18.4s, calculate the DOS in the tails according to (18.77). Check whether (18.29) and (18.30) are obeyed approximately in a finite energy region.
- 18.6 With a proper choice of the numerical constants c_2, c_0 in (18.108) and (18.109), prove (18.41) by employing the PWA and the solution to problem 2.11s.
- 18.7 Show that the Kubo–Greenwood formula, [18.45, 18.50, 18.52], for the AC conductivity (as given in the footnote of p. 519) can be written in terms of the diamagnetic $\sigma_d(\omega)$ and the paramagnetic $\sigma_p(\omega)$ contributions where $\sigma_d(\omega)$ is given in the footnote of p. 519
- 18.8 Prove (18.75), (18.76), and (18.77). *Hint:* Use (18.64) with $\Sigma = 0$.

- 18.9 Using the PWA, in particular (18.108, 18.109) and the solution to problem 2.11, show that $L_c \sim \ell$ in 1D.
- 18.10 Show that ψ_{n,k_x} as given by (18.114) satisfies the equation $\hat{H}_0 \psi_{n,k_x} = \varepsilon_n \psi_{n,k_x}$, where ε_n is given by (18.113).

Further Reading

- A general presentation of the subject of disordered materials is given in the book by Mott and Davis [DS133], although the elder editions do not contain more recent developments.
- The theory of disordered media, and in particular, their transport properties are presented in many books. Among them I mention the books by Datta [DS135], Imry [DS137], Lifshitz et al. [DS134], and by Economou [DSL153], Chaps. 6–9.

Finite Systems

Summary. Finite systems may consist of a few tens of atoms, but they may include millions of atoms as well. Almost spherical, close-packed, metallic clusters exhibiting increased stability at certain “magic” numbers are one group of finite systems. Carbon clusters, such as the so-called fullerenes, form hollow “cage” stable structures starting from the almost-spherical (actually truncated icosahedron) C_{60} to larger elongated “molecules”; fullerenes may combine with themselves and with other atoms as well to create solids with interesting properties. Another class of carbon clusters are the carbon nanotubes exhibiting a wealth of impressive features; they can be viewed as rolled-up graphene strips. Finally quantum dots are semiconductor nanostructures that show size- and shape-dependent optical and transport properties.

19.1 Introduction

Finite systems are usually intermediate between small or medium-size molecules and solids. Usually, they differ from the molecules in the sense that the addition of an extra atom does not change their properties in a *qualitatively* way, in contrast to what happens to the molecules. They differ from ordinary solids in the sense that the addition of an extra atom affects quantitatively their bulk properties in contrast to solids.

Finite systems include *metallic clusters* (consisting of a few tens to a few thousand of atoms), carbon clusters (such as *fullerenes* and *nanotubes*, which can be viewed as folded finite pieces of graphene), *other clusters* (involving either covalent bonds or both metallic and covalently bonded atoms). In finite systems we shall include also the so-called *quantum dots*, which are Si or compound semiconductor nanoparticles of size, depending on their type, ranging from 2 to 10 nm, or from 10 to 50 nm, or over 100 nm. Finally, big biomolecules such as DNA or proteins can also be classified as finite systems. In this chapter, we, give a brief presentation of the various types of finite systems (with the exception of big biomolecules). The interested readers are referred to Chap. 13 of the book by Kaxiras, where in 53 pages an excellent introduction to this important subject is given.

19.2 Metallic Clusters

These clusters consist usually of valence-one metal atoms such as sodium (*Na*), caesium (*Cs*), silver (*Ag*), gold (*Au*), etc. The most common way of their preparation is by supersonic expansion of the gas phase. This way, clusters of a wide range of sizes are produced. However, the size distribution is not smooth. Clusters consisting of $n = 8, 20, 40, 58, 92$ atoms are much more common than others corresponding to values of n between these “magic” numbers. Of course, there is nothing magical about these “magic” numbers; energy stability associated with fully occupied shells explains the preference to those numbers; in this sense “magic” number clusters resemble noble gas atoms. Indeed there is a correspondence of the “magic” numbers with the following fully occupied shells:

$$\begin{aligned} n = 8 &\leftrightarrow [1s^2, 1p^6]; \quad n = 20 \leftrightarrow [[8] 1d^{10} 2s^2]; \\ n = 40 &\leftrightarrow [[20] 1f^{14} 2p^6]; \quad n = 58 \leftrightarrow [[40] 1g^{18}]; \\ n = 92 &\leftrightarrow [[58] 2d^{10} 3s^2 1h^{22}], \end{aligned} \quad (19.1)$$

where the notation $n_r + 1, \ell$ has been used to characterize each one of the $(2\ell + 1)$ degenerate levels in a spherical potential (e.g., the 2p corresponds to $n_r = 1$ and $\ell = 1$). The nonnegative integer n_r ($n_r = 0, 1, 2, \dots$) is the radial quantum number related to the principal quantum number n by $n_r = n - \ell - 1$; for a given ℓ , the inequality $n_r > n'_r$ is by definition equivalent to $\varepsilon_{n_r} > \varepsilon_{n'_r}$; it is also evident that for the same n_r , the level with higher ℓ has higher energy (because of the term $\hbar^2 \ell(\ell + 1)/r^2$ in the Hamiltonian). The letters s, p, d, f, g, h, etc. correspond to $\ell = 0, 1, 2, 3, 4, 5$, etc. respectively. Although some of the following inequalities (on which the “magic” numbers of (19.1) are based) $\varepsilon_{1s} < \varepsilon_{1p} < \varepsilon_{1d} < \varepsilon_{2s} < \varepsilon_{1f} < \varepsilon_{2p} < \varepsilon_{1g} < \varepsilon_{2d} < \varepsilon_{3s} < \varepsilon_{1h}$ are obvious, others (the shaded ones), although reasonable (see problem 19.1s), need justification in order to be used for the explanation of the “magic” numbers according to (19.1). This justification was obtained by detailed self-consistent calculations based on DFT and LDA within the framework of the jellium model(JM); both the JM and LDA are reasonable approximations for alkalis, Ag and Au, where the detached electron density is almost uniform. Besides the filling up of successive energy levels by the available electrons, the total energy of a cluster is expected to be determined also by the way that the atoms arrange themselves in space. Each particular arrangement will break the spherical symmetry (which is a first rough approximation for the electronic levels), will lift to some extent the degeneracy and modify the energy levels in a specific way. It turns out that every one of these modifications is small enough, so that the gross ordering of the levels in the spherical potential is not disturbed (This means that the spreading of each degenerate level is much smaller than the energy separation of two successive levels (at least up to the 1h level)). Anyway, we expect, based on our experience up to now, that the atoms will arrange themselves in a close-packed or dense-packed way such

as fcc, or bcc, or icosahedral, or even variations of these with some degree of disorder for the surface atoms.

19.3 Fullerenes

The prototypical fullerene is the molecule C_{60} discovered by Kroto, Heath, O'Brien, Curl, and Smalley [19.1]. In this molecule the nuclei of the 60 carbon atoms are located in a very symmetrical way on the surface of a sphere of diameter¹ 6.825 Å; each atom is connected to three neighboring atoms; thus the number of bonds n_b is $3 \times 60/2 = 90$. These bonds define the edges of a polyhedron, while the nuclei of the carbon atoms are at its vertices. According to Euler's theory the number n_f of the faces is equal to, $n_e - n_v + 2$, where $n_e = n_b$ are the number of edges and n_v is the number of vertices. Thus in the present case, there are 32 faces, 12 of which are regular pentagons and 20 almost² regular hexagons as shown in Fig. 19.1. Each pentagon is surrounded only by hexagons as shown in Fig. 19.1.

The fact that the bond lengths around each pentagon are 1.455 Å, i.e., larger than that of graphite and toward the value in diamond, suggest that

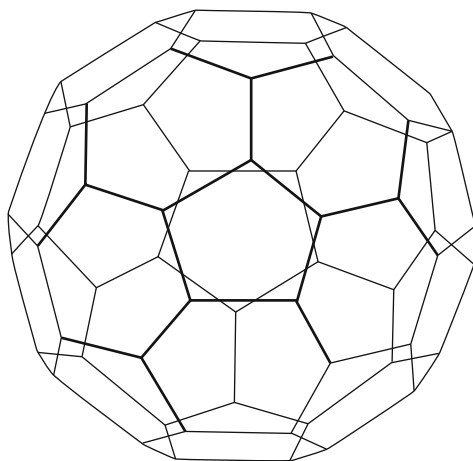


Fig. 19.1. The hollow almost spherical molecule C_{60} consists of 60 carbon atoms at the vertices of a truncated regular icosahedron; it has 90 edges, 60 vertices and 32 faces (12 regular pentagons and 20 almost regular hexagons). The length of the bonds shared by two hexagons is 1.395 Å, while the length of the bonds shared by a pentagon and a hexagon is 1.455 Å. (In graphite the bond length is 1.421 Å, and in benzene it is 1.395 Å, while in diamond it is 1.545 Å)

¹ The value 10.34 Å often quoted in the literature for C_{60} 's diameter refers to the outer diameter which includes the finite size of each carbon atom.

² The bond lengths in each hexagon alternate between 1.395 and 1.455 Å.

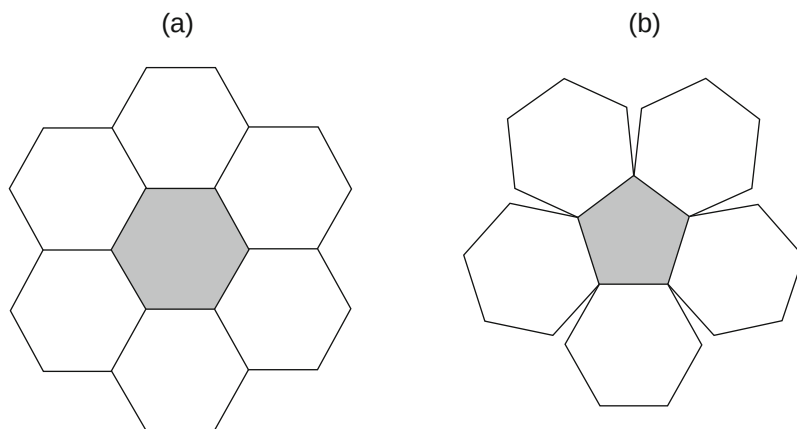


Fig. 19.2. (a) A plane structure as that of graphene consisting only of regular hexagons cannot be folded without serious distortions. (b) On the other hand, the presence of a regular pentagon surrounded by hexagons allows some space for the hexagons to undergo a small rotation around each pentagon side, as to be connected smoothly and to form a convex structure without distortions. This small rotation makes the solid angle at each pentagon side less than 180° ; as a result the pentagon bonds acquire a small sp^3 component

the pentagon bonds are not purely sp^2 but they involve a small admixture of sp^3 ; anyway, both the presence of pentagons and the sp^3 admixture in their bonds are necessary for allowing a flat structure such as graphene to fold into a polyhedron without serious distortions as shown in Fig. 19.2. The procedure described in the caption of Fig. 19.2 implies that three sides of each hexagon (the ones shared by pentagons) are rotation axes (hence, they acquire an sp^3 component), while the other three (between the rotation axes) remain almost intact, and consequently, have an sp^2 - sp^2 bond and a $p_\perp$ - $p_\perp$ bond³ as in benzene. This is shown in Fig. 19.3, where the edges with the sp^3 admixture that acted as rotation axes are single line, while the almost-intact hexagon edges are shown as double lines indicating the double bond. This picture is strongly supported by the fact that the double bond length is $1.395 \text{ \AA}$ the same as in benzene.

How stable is the elegant structure of C_{60} ? The answer of course depends on the size of the energy difference between the lowest unoccupied level (LUMO) and the highest occupied level (HOMO). To obtain the value of this gap, we must allow the delocalization of the thirty $p_\perp$ - $p_\perp$ bonding and the thirty $p_\perp$ - $p_\perp$ antibonding orbitals among the 30 double bonds of the C_{60} . The first crude approximation to this problem is to assume that the sixty electrons occupying the 60 $p_\perp$ atomic orbitals are free to move on the surface of sphere.

³ By $p_\perp$ we denote a p atomic orbital normal to the short bond, along the radial direction; this is the analogue of the p_z orbital in benzene or in graphene.

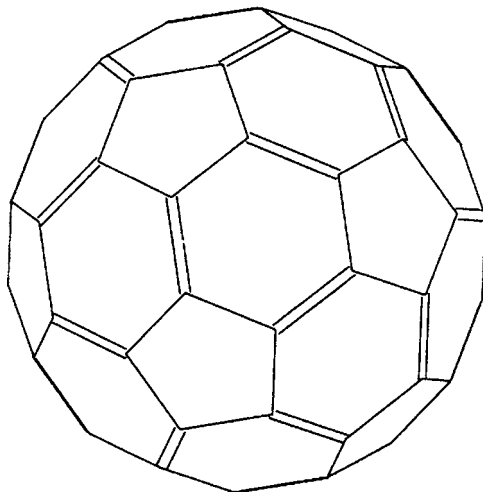


Fig. 19.3. C_{60} 's geometry and bond nature. The double bonds (30 in total) are the same as those in benzene and have the same length of $1.395 \text{ \AA}$. The single lines, (60) in total, indicate a bond intermediate between sp^2 and sp^3 and have a length of $1.455 \text{ \AA}$.

Then the energy levels are given by $\hbar^2 \ell(\ell + 1) / 2mR^2$, where $R = 3.42 \text{ \AA}$ is the radius of the sphere; the result for each degenerate level ℓ is $0.32\ell(\ell + 1) \text{ eV}$. Up to the g level ($\ell = 4$) the number of electrons which can be accommodated is 50, while the level h ($\ell = 5$) can accommodate another 22 electrons. Thus according to this crude approximation our 60 electrons would fully occupy the levels s, p, d, f, g and they will occupy also another 10 of the 22 degenerate h ($\ell = 5$) levels. Hence, the gap would be zero and the molecule would be unstable according to this spherical cell approximation. Actually, the reduced symmetry of the C_{60} structure partially lifts the degeneracies of the spherical symmetry as shown in Fig. 19.4 taken from the book of Kaxiras. Notice that the partially occupied spherical level h ($\ell = 5$) splits, in the presence of C_{60} icosahedral symmetry, to a lower five times degenerate level, which accommodates the 10 electrons residing on the h level and two other degenerate level (the t_{1u} 3 degenerate level, and the t_{2u} 3 degenerate level). Thus, a gap opens up between the highest occupied level (the h_u) and the lowest empty level t_{1u} . The size of the gap is about 1.6 eV . This is quite a substantial gap for such a big molecule. Thus, the elegant symmetric structure of C_{60} accounts for the gap and hence, it leads to its stability.

It must be pointed out that there are many more fullerenes such as C_{70} , C_{80} , C_{140} , C_{180} , C_{240} , etc. All of them are closed hollow polyhedral consisting of pentagon and hexagon faces. It is easy to show that the number n_p of pentagons is always equal to 12. Indeed, if n_h is the number of hexagons, the total number n_f of faces is $n_f = n_p + n_h$; the number n_e of edges is $n_e = (5n_p + 6n_h) / 2$ and the number n_v of vertices is $n_v = 2n_e / 3$. Substituting

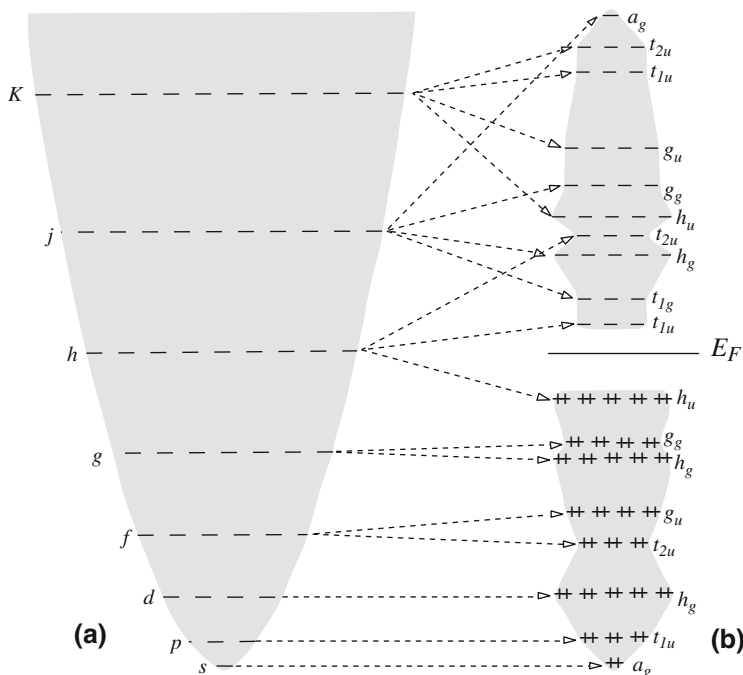


Fig. 19.4. (a) The eigenenergies of free particles moving on a spherical surface; the letters s, p, d, f, g, h, j, k , correspond to $\ell = 0, 1, 2, 3, 4, 5, 6, 7$; these eigenenergies are given by $\epsilon \ell(\ell + 1)$, where ϵ is a constant, and the degeneracy of each of them is $(2\ell + 1)$ (omitting the two spin orientations); the total number of electrons accommodated up to the level ℓ is $2(\ell + 1)^2$. (b) Schematic (not in scale) eigenenergies of π states in C_{60} labeled according to the irreducible representations of the icosahedral group. Two short vertical lines indicate occupancy of the corresponding eigenstates by two electrons. Within the LCAO, the π eigenstates are linear combinations of the 60 $p_{\perp}$ states. The splitting of the degenerate spherical levels by the icosahedral symmetry is also indicated. (After Kaxiras [SS83])

in Euler's relation, $n_f = n_e - n_v + 2$, we have $n_p + n_h = (n_e/3) + 2 = (5n_p/6) + n_h + 2$ or $n_p = 12$. Most of these structures possess icosahedral symmetry, although there are fullerenes with no such symmetry. The smallest possible closed hollow molecule would be the one with $n_p = 12$ and $n_h = 0$, i.e., the dodecahedron. However, in such a molecule all bond angles are 108° , i.e., very close to the 109.47° which is the angle between the sp^3 hybrids. Hence, in the dodecahedron, three of the four almost sp^3 hybrids of each carbon, are involved in the bonding with the hybrids of the three nearest neighbor carbons, while the fourth hybrid is unsaturated forming a dangling bond. As a result, the molecule is unstable, unless the 12 dangling bonds are passivated by forming bonds with additional atoms or radicals of valence one. For example, the dodecahedron molecule $C_{12}H_{12}$ would be a stable one.

The conclusion is that a *stable* polyhedron carbon-only cluster consisting of pentagons and hexagons obeys the “isolated pentagon rule,” i.e., each of the twelve pentagons must be surrounded by hexagons only. The smallest such cluster obeying this rule is the one, where each hexagon is surrounded by the maximum number of pentagons under the isolated pentagon rule, i.e., three; then the number n_h of hexagons is $n_h = 5n_p/3 = 20$ and the number of vertices is 60. We conclude that the C₆₀ is the smallest carbon-only cluster consisting of pentagons and hexagons, which obey the stability implying isolated pentagon rule.

19.4 C₆₀-Based Solids

The molecule C₆₀, being almost spherical with a completed energy shell, resembles the atoms of noble gases. Hence, the molecular solid made exclusively of C₆₀s is expected to crystallize in an **fcc** lattice structure and to behave similarly to the van der Waals elemental solids. Indeed, this is the case with some noticeable differences. One difference is that the size of the energy gap in *fulleride*, as the C₆₀ solid is called, is about 1.5 eV, which makes the fulleride a semiconductor, in contrast to noble gas solids, which are large-gap insulators.

Problem 19.1ts. Take $R_a = 3.4125 \text{ \AA}$ and in the place of IP set $1.8E_g \simeq 3.0 \text{ eV}$; then use (14.12) and (14.13) to estimate σ and ε for the C₆₀ solid. For the polarizability $\tilde{\alpha}$ use the approximate formula

$$\tilde{\alpha} \simeq 4e^2 \frac{R_a^2}{IP}. \quad (19.2)$$

Compute next the nearest neighbor distance d , the de Boer parameter Λ (see (14.9) and the cohesive energy per molecule. Compare with the experimental values for d , $d = 10.013 \text{ \AA}$ and for $U_c/N = 0.4 \text{ eV}$ per molecule. Notice that d is 3% smaller than the external diameter, $D = 10.34 \text{ \AA}$ of C₆₀, which shows that in fulleride the neighboring C₆₀s have a small overlap.

Another difference between C₆₀ and say, Ar, is that the C₆₀ does not possess spherical symmetry (as the Ar does) but icosahedral symmetry. Thus, the question arises as to what the orientation of each C₆₀ molecule relative to the cubic **fcc** axes is. The preferable orientation would be the one that minimizes the electron repulsion between each pair of C₆₀ molecules. This can be achieved by minimizing the electronic overlap, e.g., by placing the electron-rich double bond of one C₆₀ opposite to the electron deficient centre of the hexagon face of the other. The gain in energy by such an orientation is expected to be a small fraction of the cohesive energy per molecule, probably less than 10%. When the temperature (times k_B) becomes comparable to this gain in energy, we expect that the C₆₀ will rotate freely as to effectively become a spherical entity. Indeed, for $T_0 > 261^\circ \text{ K}$, this is what happens.

A third difference of C_{60} from noble gas atoms is, of course, the large size of the former and the corresponding drop in the effective IP . The most important consequence of this size difference is that, in fulleride, the space left empty among C_{60} s is quite large as to accommodate foreign atoms.⁴ Of special interest is the case of alkali atoms, which occupy the tetrahedral sites (located at the body diagonals of the unit cell and at a distance $\sqrt{3}a/4$ from its center) and the octahedral sites (located at the middle of every edge of the cubic unit cell and at its centre). There are eight tetrahedral sites and four octahedral sites $((12/4) + 1)$ per unit cubic cell of the **fcc**. Thus, if all tetrahedral and octahedral sites are occupied, there are 12 alkali atoms and four C_{60} s per cubic unit cell, so that the chemical formula is M_3C_{60} , where M stands for any alkali atom.⁴ The compound M_3C_{60} is an ionic solid where one electron from each of the three alkali atoms are transferred to the C_{60} molecule, which is strongly electronegative (its electron affinity is 2.6 eV).

Problem 19.2ts. Estimate the size of the cohesive energy per unit M_3C_{60} for Rb_3C_{60} . Assume that the Madelung constant is equal to $(2\alpha_{ZnS} + \alpha_{NaCl})/3 = 1.6746$ and that a , the lattice constant, remains the same.

The compounds of the type $M_2M'C_{60}$ or M_3C_{60} , although ionic, are not insulating or semiconducting but metallic. The reason is simple: While the alkali cations, M or M' , have fully occupied electronic shells and consequently do not contribute to the conductivity, the anion C_{60}^{-3} places the three extra electrons to the next available level, the t_{1u} in Fig. 19.4, which, however, is threefold degenerate and needs six electrons to be fully occupied. This t_{1u} level in the fulleride would be broadened to a narrow band which will be exactly half filled. Hence, the metallic character of this type of compounds⁵ follows. Actually, these compounds become superconducting at relatively high critical temperatures: E.g., Li_2CsC_{60} (with eight Li^+ at the tetrahedral sites of the cubic unit cell and four Cs^+ at the octahedral sites) has a $T_c \simeq 12$ K while, K_2CsC_{60} has a $T_c \simeq 24$ K and Rb_2CsC_{60} has a $T_c \simeq 31.3$ K. The larger the cation is, the higher the critical temperature is. This feature is explained as follows: The larger size of the cation implies smaller matrix element V_2 for transferring an electron from a C_{60} cluster to a neighboring one. Smaller V_2 leads to a narrower band and a higher DOS at the Fermi energy. But a higher DOS at E_F increases T_c , according to (8.51) and (8.52). This interpretation implies that external pressure, which squeezes the structure and tends to bring

⁴ The size of the tetrahedral hole, 1.12 Å, is smaller than that of the octahedral hole, 2.06 Å; thus, it is possible that one alkali ion may fit in the large hole but not in the small hole. This is why it is very common to have two different alkali atoms M, M' in a 2 to 1 ratio e.g. Na_2CsC_{60} .

⁵ Compounds of the type $M_6^{+1}C_{60}^{-6}$ are expected to be insulating and, indeed, they are.

the C_{60} s closer to each other, would increase V_2 , decrease ρ_F , and, hence, lower T_c . Indeed, this is what happens.⁶

We conclude this section by pointing out that many other structures involving fullerenes and atoms of various kinds exist. The latter may react strongly with the fullerenes breaking some of C–C bonds; or they may attach themselves around the fullerenes molecule without disrupting the cage structure (*exohedral* fullerenes). Finally, a metallic atom (or even atoms) may enter in the interior of a fullerene, leaving the cage essentially intact (*endohedral* fullerenes denoted as $M @ C_{60}$). Examples of endohedral fullerenes are $La @ C_{60}$, $La @ C_{44}$, $M @ C_{84}$, and $M_3 @ C_{82}$ with $M = La, Y, Sc$. Examples of exohedral fullerenes are the following: $M_{32}C_{60}$ (where 12 alkali atoms are attached above the pentagon centres and 20 above the hexagon centres), $M_{62}C_{60}$ (where $M = Ti, V, Zr$ with 32 above the pentagon and hexagon centres and 30 above the double hexagon bonds), $M_{80}C_{60}$ (where $M = V$ and 20 V atoms above the hexagon centres and 60 above the carbon atoms).

19.5 Carbon Nanotubes

In 1991 Iijima demonstrated that graphene sheets can be rolled up (in one direction only) to create tubes [19.4]. There are single-wall nanotubes (SWNT) and multiple wall nanotubes (MWNT) in which SWNT are nested one within another. There are also random networks of carbon nanotubes. Typical size of a SWNT is about 10–20 Å in diameter, while the length can be as short as several nanometers and as long as many micrometers.

Carbon nanotubes have attracted a lot of interest because of their intriguing properties. Besides their unusual mechanical strength, they exhibit impressive electrical and optoelectronic features. As we shall see, depending on the way they are rolled up, SWNTs can be very good conductors of electricity (with conductivity comparable to that of copper) or they can be semiconductors. Random network of metallic MWNT are excellent conductors, while, due to their minute thickness, they are very transparent; thus, they can be ideal metallic contacts in photovoltaic systems. Semiconducting nanotubes can serve as the basis for field effect transistors; furthermore, these nanotubes are direct gap semiconductors; as such they offer intriguing possibilities for optoelectronic applications.

In Fig. 19.5 we show the three ways in which a strip of graphene can be rolled up to create a tube. In the first two, the direction of rolling up⁷ is either parallel (case (a)) or perpendicular (case (b)) to sides of hexagons. In the third more complicated case (c), it is neither perpendicular nor parallel to sides of hexagons. Both the direction of rolling up as well as the perimeter of

⁶ In a recent paper, [19.3] it was shown that the fulleride Cs_3C_{60} of A15 lattice structure, while not superconducting at ambient pressure, becomes superconducting at $T_c = 38$ K under pressure of about 8 kbar.

⁷ This direction is normal to the axis of the resulting tube.

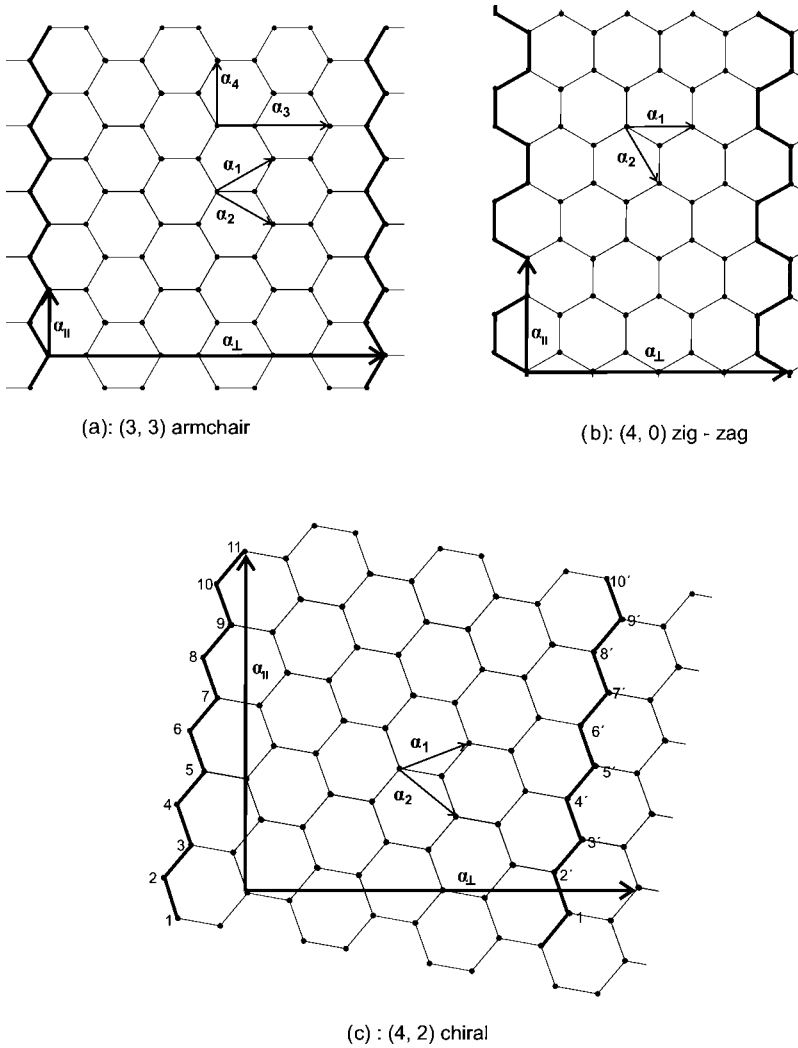


Fig. 19.5. Strips of graphene (of primitive vectors $\mathbf{a}_1, \mathbf{a}_2$) which, when rolled up, form single wall nanotubes (SWNT). The vector $\mathbf{a}_\perp = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 \equiv (n_1, n_2)$ (and the parallel to it), characterizing the rolling up, connect points on the two boundaries which will coincide upon rolling up; the vector $\mathbf{a}_\parallel = m_1 \mathbf{a}_1 + m_2 \mathbf{a}_2$ (m_1, m_2 integers) is the smallest vector parallel to the axis of the tube and normal to $\mathbf{a}_\perp$; $\mathbf{a}_\parallel$ determines the periodicity in the direction of the axis of the tube. There are three types of SWNT: (a) the $\mathbf{a}_\perp = (n, n)$ which is called *armchair*, (b) the $\mathbf{a}_\perp = (n, 0)$ which is called *zigzag*, and (c) the $\mathbf{a}_\perp = (n_1, n_2)$ with $n_1 > n_2 > 0$ which produces a *chiral* tube

the resulting tube is determined by the vector $\mathbf{a}_\perp = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 \equiv (n_1, n_2)$ where n_1, n_2 are integers and $\mathbf{a}_1, \mathbf{a}_2$ are the primitive vectors of the graphene structure shown in Fig. 13.14. (In the present case $\mathbf{a}_2$ has been chosen as $-\mathbf{a}_2$ of Fig. 13.14).

Another characteristic vector of the SWNT is the $\mathbf{a}_\parallel$ (defined in Fig. 19.5) which determines the periodicity in the direction parallel to the axis of the nanotube. The magnitude of the vectors $\mathbf{a}_\perp$ and $\mathbf{a}_\parallel$ are

$$|\mathbf{a}_\perp| = \sqrt{3}d (n_1^2 + n_2^2 + n_1 n_2)^{1/2}, \quad (19.3)$$

$$|\mathbf{a}_\parallel| = \sqrt{3}d (m_1^2 + m_2^2 + m_1 m_2)^{1/2}, \quad (19.4)$$

where $d = 1.42 \text{ \AA}$ is the bond length in graphene. According to (19.3), the diameter of $10 \text{ \AA}$ in the zigzag case implies that $n \simeq 13$. From the orthogonality of $\mathbf{a}_\parallel$ and $\mathbf{a}_\perp$ follows that $\mathbf{a}_\parallel \cdot \mathbf{a}_\perp = 0$ or $n_1 m_1 + n_2 m_2 + \frac{1}{2}(n_1 m_2 + n_2 m_1) = 0$ or

$$1 + qq' + \frac{1}{2}(q' + q) = 0 \quad (19.5)$$

where $q \equiv n_2/n_1$ and $q' \equiv m_2/m_1$. Knowing q , we determine from (19.5) $q' = -(1 + \frac{1}{2}q)/(q + \frac{1}{2})$ and then $\mathbf{a}_\parallel = (m_1, q'm_1)$ with $|m_1|, |q'm_1|$ the smallest integers.

Problem 19.3ts. Show that the vector $\mathbf{a}_\parallel$ for the three cases shown in Fig. 19.5 are the following: (a) $\mathbf{a}_\parallel = \mathbf{a}_1 - \mathbf{a}_2$; (b) $\mathbf{a}_\parallel = \mathbf{a}_1 - 2\mathbf{a}_2$; (c) $\mathbf{a}_\parallel = 4\mathbf{a}_1 - 5\mathbf{a}_2$.

In the armchair case, the period in the direction normal to the tube axis is defined by $\mathbf{a}_3 \equiv \mathbf{a}_1 + \mathbf{a}_2 = (1, 1)$, while the period in the parallel direction is $\mathbf{a}_4 \equiv \mathbf{a}_1 - \mathbf{a}_2 = (1, \bar{1})$. It is very easy to show that the dot product of $\mathbf{a}_3$ and $\mathbf{a}_4$ is zero, as expected, while the cross product of $\mathbf{a}_3$ and $\mathbf{a}_4$ is twice as large in magnitude as the quantity $|\mathbf{a}_1 \times \mathbf{a}_2|$. These relations mean that the vectors $\mathbf{a}_3$ and $\mathbf{a}_4$ define a rectangular primitive cell of twice the area of the primitive cell of the graphene lattice. Hence, the first Brillouin zone corresponding to $\mathbf{a}_3$ and $\mathbf{a}_4$ is a rectangular of half the area of the 1st BZ of graphene as shown in Fig. 19.6. However, not all points in this 1st BZ are allowed. Because of the rolling up in the $\mathbf{a}_3$ direction, we have periodic boundary conditions which restrict the values of k_x (see Fig. 19.6) to those satisfying the relation

$$k_x a_\perp = 2\pi\ell \Leftrightarrow k_x = \frac{2\pi}{|\mathbf{a}_3|} \frac{\ell}{n} = \frac{2\pi\ell}{9d}; \quad a_\perp = n |\mathbf{a}_3|, \quad (19.6)$$

where $\ell = 0, \pm 1, \dots, \pm(n-1)/2$ if n is odd, and $\ell = 0, \pm 1, \pm 2, \dots, n/2$ if n is even. (In the case of Fig. 19.5a where $n = 3$, the allowed values of k_x are the following three: $k_x = 0$ and $k_x = \pm 2\pi/3 |\mathbf{a}_3| = \pm 2\pi/9d$). For long carbon

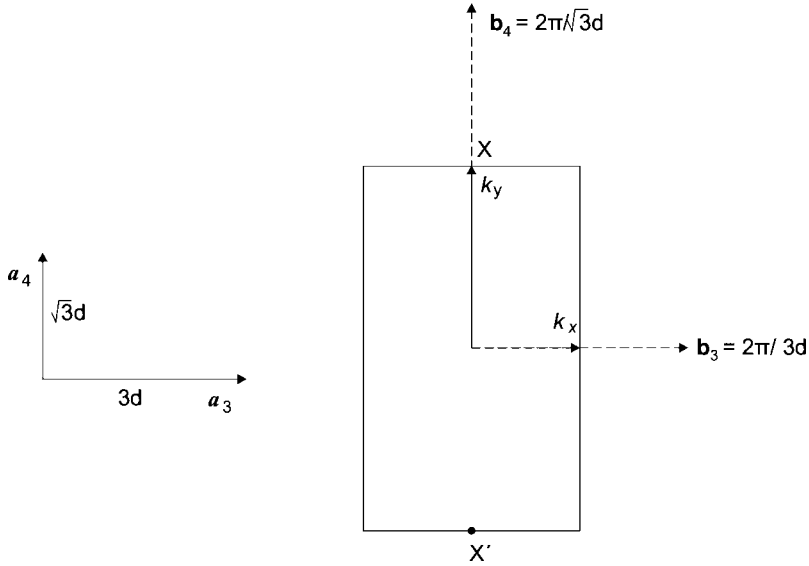


Fig. 19.6. The primitive vectors $\mathbf{a}_3, \mathbf{a}_4$ for the armchair case, the corresponding reciprocal vectors $\mathbf{b}_3$ and $\mathbf{b}_4$, and the 1st BZ (for the armchair case); d is the bond length of the graphene

nanotubes (CNT) k_y is quasi-continuous.⁸ Hence, the allowed values of $\mathbf{k}$ for the armchair case are along n equally spaced straight segments parallel to the k_y axis (including this axis) within the 1st BZ shown in Fig. 19.6.

To examine the question of whether a SWNT is conducting or semiconducting, we assume (for the sake of simplicity) that the rolling up does not change appreciably the dispersion relation $\varepsilon_n(\mathbf{k})$ of graphene. In the latter (as we have seen in Sect. 13.8), the Fermi level corresponds to the point P in its first BZ (see Fig. 13.14). The point P (and the other two equivalent to it) translated by appropriate vectors $\mathbf{G} = \ell_3 \mathbf{b}_3 + \ell_4 \mathbf{b}_4$ of the reciprocal lattice can be mapped to points P' within the 1st BZ of the armchair case shown in Fig. 19.6. If any of the points P' coincide with allowed value of $\mathbf{k}$ (say, $\mathbf{k}_{P'}$), then the dispersion $\varepsilon_n(k_y)$ around the point $\mathbf{k}_{P'}$ would be as in graphene and the SWNT would be as conducting as graphene. On the other hand, if P' does not coincide with allowed value of $\mathbf{k}$ in the 1st BZ of Fig. 19.6, the graphene dispersion in the immediate neighborhoods of the points P is not transferred to the SWNT. Since, the only neighborhoods where the energy

⁸ Actually, if the length of the tube is L , the number of periods N along the direction of the axis in the armchair case is $N = L/|\mathbf{a}_4|$ and the allowed values of k_y are the following: $k_y = (2\pi/|\mathbf{a}_4|)(\ell'/N)$, where ℓ' is integer such that $|\ell'| \leq N/2$. Two consecutive values of k_y are separated by $\delta k_y = 2\pi/N|\mathbf{a}_4|$; if the energy separation $\delta\varepsilon \equiv |\partial\varepsilon_{\mathbf{k}}/\partial k_y| \delta k_y$ is sufficiently smaller than the thermal broadening $k_B T$, then the discreteness in k_y can be ignored.

gap closes are those around the point, P , we can conclude that their absence implies the appearance of a gap in the SWNT around the Fermi energy and a semiconducting behavior (unless the perturbation produced by the rolling up accidentally closes the gap).

According to this analysis, the SWNT is expected to be conducting, if any point P' (where $\Gamma P' = \Gamma P + \mathbf{G}$) coincides with allowed point $\mathbf{k}$ in the 1st BZ of the SWNT; if no such point P' coincides with allowed point $\mathbf{k}$, the SWNT is expected to be semiconducting.

Problem 19.4t. Given that the coordinates of the points P are $(2\pi/3d)(1, \pm 1/\sqrt{3})$ or $(4\pi/3\sqrt{3}d)(0, 1)$, show that they are mapped to two symmetric points on the k_y axis at a distance from the centre equal to $2/3$ of the ΓX : $P' = (0, \pm (2\pi/3\sqrt{3}d))$.

Thus, according to the above result the points P' coincide with allowed points in the armchair 1st BZ, no matter what the value of n is. Therefore, the armchair SWNTs are expected to show metallic conductivity similar to that of graphene.

The preceding analysis of the armchair case can be used for the zigzag case as well, because the 1st BZ of Fig. 19.6 constructed for the armchair case is also the 1st BZ of the zigzag case as well. Indeed, by rotating the armchair case (Fig. 19.5a) by 90° it becomes the zigzag with the vector $\mathbf{a}_1 - \mathbf{a}_2 \equiv \mathbf{a}_4$ (in 19.5(a)) playing the role of $\mathbf{a}_1$ in 19.5(b) and the vector $\mathbf{a}_1 + \mathbf{a}_2 \equiv \mathbf{a}_3$ (in 19.5(a)) playing the role of $-\mathbf{a}_\parallel$ in 19.5(b). Hence, in the 90° rotated Fig. 19.5a, the general zigzag case is characterized by the rolling-up vector $\mathbf{a}_\perp = n\mathbf{a}_4$ and the periodicity vector parallel to the axis of the tube, $\mathbf{a}_\parallel = \mathbf{a}_3$, where n is positive integer. It follows that the 1st BZ of the zigzag case is the same as in Fig. 19.6, but with the k_x being now parallel to the axis of the tube and k_y in the direction of the rolling up. Hence, in the zigzag case, the k_x is quasi-continuous, while the k_y satisfies the periodic boundary conditions

$$k_y a_\perp = 2\pi\ell \Leftrightarrow k_y = \frac{2\pi}{|\mathbf{a}_4|} \frac{\ell'}{n} = \frac{2\pi\ell'}{\sqrt{3}dn}, \quad (19.7)$$

where ℓ' is integer such that $|\ell'| \leq (n/2)$. It follows that the allowed values of $\mathbf{k}$ for the zigzag case are n equally spaced straight segments parallel to the k_x axis in Fig. 19.6 (including the k_x axis).

Problem 19.5t. By combining the results of problem 19.4t with (19.7) show that the points P are mapped to allowed values of $\mathbf{k}$ for the zigzag case only when $n = 3p$, where p is integer. If $n = 3p + 1$ or $n = 3p + 2$, then the points P are mapped to nonallowed values of $\mathbf{k}$ in the zigzag 1st BZ.

This result leads to the conclusion that the zigzag SWNT are exhibiting metallic conductivity as that of graphene, if $n = 3p$, while, if $n = 3p + 1$ or $n = 3p + 2$, a semiconducting behavior is expected (unless the perturbation due to rolling-up closes accidentally the gap). Assuming that the value of

the integer n is selected randomly and with a probability independent of n , we can conclude that $1/3$ of the zigzag SWNT are conducting, while $2/3$ are semiconducting. A similar analysis leads to the conclusion that small, $D \lesssim 20$ Å, chiral carbon nanotubes (n_1, n_2) with $n_1 > n_2 > 0$ are metallic when $2n_1 + n_2 = 3\ell$ with ℓ integer,⁹ while $2n_1 + n_2 = 3\ell + 1$ or $2n_1 + n_2 = 3\ell + 2$ are expected to give rise to semiconducting behavior.

The actual situation is more complicated than the preceding analysis suggests, because the rolling up changes the bond lengths and mixes the graphene hybrid atomic orbitals (see the book by Kaxiras [SS83], p. 480, where the eigenenergies $\varepsilon_n(k_{\parallel})$ are plotted vs. $k_{\parallel}$ for several cases, where $k_{\parallel}$ is in the direction of the nanotube axis; these results are based on the LCAO method by Mehl and Papaconstantopoulos [19.5]).

19.6 Other Clusters

There are many other types of clusters, such as Si clusters, clusters of noble-gas atoms, organometallic clusters involving metal and carbon atoms, etc.

The Si clusters exhibit “magic” number behavior at $N = 33, 39, 45$, as N varies in the range $20 \leq N \leq 50$ [19.6, 19.7]. At these magic numbers, the reactivity of the cluster shows sharp and deep minima indicating that clusters consisting of 33 or 39 or 45 Si atoms are very stable. One interpretation of this impressive stability is based on the idea that the central core of the cluster consists of a Si atom with four nearest neighbors at the tetrahedral directions as in the bulk. Attached to this inner core are configurations of Si atoms similar to the ones appearing in the 7×7 and 2×1 reconstructions of the bulk silicon 111 and 001 surfaces [19.8–19.10]. Thus, according to this picture, which is known as surface-reconstruction induced geometries (SRIG), there are no dangling bonds and, hence, very low reactivity. Detailed quantum mechanical calculations show that the SRIG have lower energy than some other structural configurations [19.9]. However, these calculations do not provide conclusive evidence in support of the SRIG, neither lead directly to the magic numbers, since they tend to produce more compact overcoordinated structures [19.12].

Noble-gases clusters, because of the absence of directionality in their bonding and the strong binding of their electrons to the atoms, are the simpler ones to study. On general grounds, one expects that the more compact structures to be the more stable. Thus, the icosahedron structure with 12 atoms surrounding the central one is expected to be of low energy. Indeed, calculations employing the Lennard–Jones potential show that a 13-atom cluster in the icosahedron configuration has the lowest energy; also the 19-atom cluster in the double icosahedron¹⁰ configuration was found to have the lowest

⁹ The condition $2n_1 + n_2 = 3\ell$ is equivalent to $n_1 - n_2 = 3\ell'$, where ℓ, ℓ' are integers.

¹⁰ In the double icosahedron configuration a pair of two atoms is surrounded by three (normal to the pair axis) rings of five atoms each; the structure is capped by two atoms, one below and the other above.

energy. Diffraction experiments have shown the predominance of the fivefold symmetry axes at low temperatures supporting thus the theoretical results. Furthermore, the abundance of clusters with the “magic” number 13 or 19 provides another evidence in support of the stability of the icosahedral (single or double) configuration. It was found by computer simulations that this minimum energy configuration undergoes a rather sharp melting transition (see, e.g., [19.13]). We shall conclude this section by mentioning briefly the case of metal-carbon clusters discovered by Castleman and coworkers [19.14]. These clusters consist of 20 atoms, eight atoms of transition metals (Ti, Zr, Hf, V) and 12 atoms of carbon. The metal atoms occupy the vertices of a cube, while the 12 carbon atoms, arranged in six pairs, are located above the six faces of the cube resembling somehow a rounded version of the unit cell of the $A15$ structure (see Fig. 15.19) (more correctly it looks like a distorted dodecahedron). Each carbon atom has three nearest neighbors, namely two metal atoms and a carbon atom (its partner in the pair); each metal atom has three carbon atoms as nearest neighbors. If we keep bonds only between nearest neighbors, there are twelve pentagonal faces, (with three carbons and two metal corners). Two different M_8C_{12} clusters can be joined at their faces forming larger structures.

19.7 Quantum Dots

19.7.1 An Overview

A quantum dot (QD) is usually a semiconductor nanoparticle deposited, or grown, or etched in a substrate; the diameter D of a QD is in the range from 2 nm to about 100 nm, or larger, depending on the method of fabrication.

The main characteristic of a quantum dot is the confinement of the electrons and the holes in all of its three dimensions.^{11,12} [19.15]. The term confinement means that the available length for movement is comparable to, or smaller than, the length $2r_{ex}$, $d \leq 2r_{ex}$, where $2r_{ex} = (2\epsilon(\infty)/m^*)a_B$ with $m^* = m_{\ell h}m_c/(m_{\ell h} + m_c)$. For GaAs with $\epsilon(\infty) = 10.88$, $m_{\ell h} = 0.082m_e$, $m_c = 0.067m_e$ we obtain $2r_{ex} \simeq 31$ nm. Thus, an almost-spherical GaAs quantum dot of diameter, let us say, of 50 nm, provides a weak confinement, one of 25 nm an intermediate confinement, and one, e.g., of 10 nm a strong

¹¹ If the confinement in the vertical direction is much stronger than in the planar directions, the QDs can be treated as 2-D disks of finite radius. Such 2-D QDs appear in a 2-D electron gas in graphene, etc; they are important for controlling transport properties and, hence, they are considered as elements in various devices (see 19.7.3).

¹² In a **quantum well** the motion of electrons (or holes) in one direction is restricted, leaving them free to move in the other two dimensions. In the **quantum wires** there is confinement in two directions and unrestricted possibility of motion in the third direction.

confinement. The confinement of a particle (electron or hole) of effective mass m^* within an ellipsoidal quantum dot of dimensions d_x, d_y, d_z , increases the minimum kinetic energy by an amount of the order of

$$\delta\varepsilon \simeq \frac{\hbar^2}{2m_x^*d_x^2} + \frac{\hbar^2}{2m_y^*d_y^2} + \frac{\hbar^2}{2m_z^*d_z^2}. \quad (19.8)$$

As a result, the energy levels in a quantum dot made of a direct-gap semiconductor (e.g., CdSe with $E_g = 1.83$ eV) are different from those of the same material in the bulk. By making the quantum dot smaller and smaller one blue-shifts the absorption and emission spectrum so that the fluorescence emission can change from red, yellow, green, blue, to violet and beyond. The possibility of tailoring the emission and absorption spectrum and controlling the quantum yield by changing the size and the shape of quantum dots is one reason for the increased interest in these nanoparticles. The superior optical properties of quantum dots open up many technological possibilities such as increasing the yield of silicon photovoltaic cells, of developing white light emitting diodes and making displays, of creating artificial fluorophores for molecular imaging, etc. Quantum dots are studied also as a possible vehicle for quantum computers, since they offer the all-important advantage of solid state [19.16, 19.17], namely the integrability with existing semiconductor technology. Finally, quantum dots (QDs) can be connected by tunnel barriers to external conducting leads [19.2, 19.18] acting this way like single-electron transistors and exhibiting *Coulomb blockade* effects; these electronic aspects can be used for improved flash memory devices.

The simplest way for the fabrication of QDs is by colloidal synthesis according to which the QD material is supplied in a liquid suspension or dispersed in plastic host and then processed onto the substrate; QDs of this type can be as small as 2–10 nm. Self-assembled QDs nucleate spontaneously under certain conditions during molecular beam epitaxy or during metallorganic vapor phase epitaxy when there is a lattice mismatch between the material of the QD and that of the substrate; this way of growing QDs, which produces sizes in the range 10–50 nm, is common in studies aiming at quantum cryptography and quantum computing. Quantum dots, defined by lithographic patterning or by etching the heterojunction at which 2D electron (or hole) gas is trapped, can exceed in lateral size the 100 nm and their main use is in transport properties. QDs appear sometimes accidentally in quantum wells due to fluctuations in the thickness of the well.

19.7.2 Optical Transitions

For most applications, the important optical transitions involve the excitation of an electron–hole pair. The hole resides in one of the four (including spin) branches at the top of the VB with total angular momentum, $J = 3/2$. These branches have to be re-diagonalized in the presence of the QD confining potential. On the other hand, the eigenenergies of an electron in the CB

are obtained immediately by adding the extra kinetic energy due to the QD. Thus, to study optical transitions in a QD, we must find the eigenstates and eigenfunctions of the holes in the VB. For a bulk semiconductor the holes at the top of the VB are characterized by the crystal wavevector $\mathbf{k}$ and the four projections, $(J_z = \pm\frac{1}{2}, \pm\frac{3}{2})$, of the total angular momentum¹³ ($J = \frac{3}{2}$). The corresponding Hamiltonian is a 4×4 matrix, which has been diagonalized in Chap. 11 (see (11.68) and (11.69)) by the $\mathbf{k} \cdot \mathbf{p}$ method in terms of the Luttinger parameters $\gamma_1, \gamma_2, \gamma_3$ (see also the book by Yu and Cardona [Se119], pp. 72–82). In studying a QD we have to add to the Luttinger Hamiltonian the confining potential associated with this QD and then, as usually, to employ the effective Hamiltonian approximation of Sect. 10.3. The diagonalized expressions (11.68) and (11.69) appropriate for the bulk are inappropriate for handling the additional QD potential (because of their complicated square root dependence on $k_i \rightarrow -i\partial/\partial x_i$ ($i = x, y, z$)). Thus, we are forced to employ the undiagonalized 4×4 Luttinger Hamiltonian the matrix elements of which are simple quadratic expressions of the Cartesian components k_i as shown below.¹⁴

$$J_z \equiv \begin{vmatrix} \frac{3}{2} & -\frac{1}{2} & \frac{1}{2} & -\frac{3}{2} \\ \frac{3}{2}P+Q & R & -S & 0 \\ -\frac{1}{2} & R^\dagger & P-Q & 0 & S \\ \frac{1}{2} & -S^\dagger & 0 & P-Q & R \\ -\frac{3}{2} & 0 & S^\dagger & R^\dagger & P+Q \end{vmatrix} = H_L, \quad (19.9)$$

$$P = \frac{\hbar^2}{2m}\gamma_1 k^2, \quad Q = \frac{\hbar^2}{2m}\gamma_2 (k_x^2 + k_y^2 - 2k_z^2), \quad (19.10)$$

$$S = \frac{\sqrt{3}\hbar^2}{m}\gamma_3 k_z (k_x - ik_y), \quad (19.11)$$

$$R = -\frac{\sqrt{3}\hbar^2}{2m}\gamma_2 (k_x^2 - k_y^2) + i\frac{\sqrt{3}\hbar^2}{m}\gamma_3 k_x k_y. \quad (19.12)$$

The Hamiltonian of a quantum dot, as it was mentioned before, has the general form $\hat{H} = \hat{H}_B + \mathcal{V}(\mathbf{r})$, where $\hat{H}_B = \hat{H}_L$ is the Hamiltonian for the bulk material and $\mathcal{V}(\mathbf{r})$ is the confining potential associated with the QD. To simplify the analytical calculations, we shall choose for $\mathcal{V}(\mathbf{r})$ a separable harmonic potential:

$$\mathcal{V}(\mathbf{r}) = \sum_{i=1}^3 \mathcal{V}_i(x_i); \quad x_1 = x, \quad x_2 = y, \quad x_3 = z \quad (19.13)$$

with

$$\mathcal{V}_i(x_i) = \frac{1}{2}\kappa_i x_i^2. \quad (19.14)$$

¹³ The split-off hole with $J = 1/2$ is usually well below the top of the VB and it is ignored.

¹⁴ The rows and the columns of this matrix have been written in this sequence because in QDs under certain approximation S turns out to be zero and thus the decoupling is more obvious.

We shall also employ the effective Hamiltonian approximation (see Sect. 10.3), according to which in the Luttinger Hamiltonian $\hat{H}_L$ of (19.9)–(19.12) we shall replace k_i by $-i\partial/\partial x_i$:

$$k_i \rightarrow -i\frac{\partial}{\partial x_i}, \quad i = 1, 2, 3 \quad (19.15)$$

To proceed further we shall omit initially the off-diagonal matrix elements in the Hamiltonian (19.9) in order to define a basic set of states (not yet the QD hole eigenstates) in terms of which we shall express the Hamiltonian $\hat{H}_L(\mathbf{k}) + \mathcal{V}(\mathbf{r})$ where $\mathbf{k} = -i\nabla$. By setting $\hat{R} = \hat{S} = 0$, all the J_z components are decoupled in (19.9) and we have for the $J_z = \pm 3/2$ the following Schrödinger equation:

$$\left[\hat{P} + \hat{Q} + \mathcal{V}(\mathbf{r}) \right] \Psi_{3/2}(\mathbf{r}) = E_{3/2} \Psi_{3/2}, \quad (19.16)$$

where the operator $\hat{P} + \hat{Q}$ is given by

$$\begin{aligned} \hat{P} + \hat{Q} &= -\frac{\hbar^2}{2m} \left[(\gamma_1 + \gamma_2) \frac{\partial^2}{\partial x^2} + (\gamma_1 + \gamma_2) \frac{\partial^2}{\partial y^2} + (\gamma_1 - 2\gamma_2) \frac{\partial^2}{\partial z^2} \right] \\ &= -\frac{\hbar^2}{2} \left[\frac{1}{m_{p,3/2}} \frac{\partial^2}{\partial x^2} + \frac{1}{m_{p,3/2}} \frac{\partial^2}{\partial y^2} + \frac{1}{m_{z,3/2}} \frac{\partial^2}{\partial z^2} \right] \end{aligned} \quad (19.17)$$

with

$$m_{p,3/2} \equiv m/(\gamma_1 + \gamma_2); \quad m_{z,3/2} \equiv m_{hh}^{(100)} = m/(\gamma_1 - 2\gamma_2). \quad (19.18)$$

In view of (19.13) and (19.17), we can write for the $J_z = \pm 3/2$ Hamiltonian

$$\hat{H}_{3/2} = \hat{H}_{x,3/2} + \hat{H}_{y,3/2} + \hat{H}_{z,3/2}. \quad (19.19)$$

The additivity of the Hamiltonian $H_{3/2}$ implies that its eigenenergies are additive and its eigenfunctions are multiplicative.

$$\Psi_{3/2}(\mathbf{r}) = \Psi_{x,3/2}(x) \Psi_{y,3/2}(y) \Psi_{z,3/2}(z). \quad (19.20)$$

Each of the $\Psi_{i,3/2}$ ($i = x, y, z$) have the form of a 1D harmonic oscillator eigenfunction

Problem 19.6t. Write down explicitly the three functions, $\Psi_{i,3/2}$, ($i = x, y, z$).

Problem 19.7t. Show that the Hamiltonian for the $J_z = \pm 1/2$, $H_{1/2}$, has the same form as the $H_{3/2}$ with the replacements $m_{p,3/2} \rightarrow m_{p,1/2} = m/(\gamma_1 - \gamma_2)$ and $m_{z,3/2} \rightarrow m_{z,1/2} = m/(\gamma_1 + 2\gamma_2)$.

Problem 19.8ts. Show that the only non zero matrix element of $\hat{S}$ and $\hat{R}$ between $\Psi_\ell(\mathbf{r})$ and $\Psi_m(\mathbf{r})$ is $\hat{R} \equiv \langle \Psi_{1/2}(\mathbf{r}) | \hat{R} | \Psi_{3/2}(\mathbf{r}) \rangle = -\frac{\sqrt{3}\hbar^2}{2m}\gamma_2 \langle \Psi_{1/2}(\mathbf{r}) | \left(\hat{k}_x^2 - \hat{k}_y^2 \right) | \Psi_{3/2}(\mathbf{r}) \rangle$.

Problem 19.9t. Show that $\tilde{R}$ is equal to

$$\tilde{R} = +\frac{\sqrt{3}\hbar^2}{2m}\gamma_2 I_z (I_y R_x - I_x R_y), \quad (19.21)$$

where

$$I_{x_i} \equiv \langle \Psi_{x_i,1/2}(x_i) | \Psi_{x_i,3/2}(x_i) \rangle, \quad x_i = x, y, z, \quad (19.22)$$

$$R_x \equiv \left\langle \Psi_{x,1/2}(x) \left| \frac{\partial^2}{\partial x^2} \right| \Psi_{x,3/2}(x) \right\rangle, \quad (19.23)$$

$$R_y \equiv \left\langle \Psi_{y,1/2}(y) \left| \frac{\partial^2}{\partial y^2} \right| \Psi_{y,3/2}(y) \right\rangle. \quad (19.24)$$

Thus, the ground state eigenenergies¹⁵ of the heavy and light holes in a QD is given by

$$E_{\pm} = \frac{1}{2}(\delta E_{1/2} + \delta E_{3/2}) \pm \left[\frac{1}{4}(\delta E_{1/2} - \delta E_{3/2})^2 + \tilde{R}^2 \right]^{1/2}, \quad (19.25)$$

where

$$\delta E_{1/2} = \frac{1}{2}\hbar [\omega_{x,1/2} + \omega_{y,1/2} + \omega_{z,1/2}], \quad (19.26)$$

$$\delta E_{3/2} = \frac{1}{2}\hbar [\omega_{x,3/2} + \omega_{y,3/2} + \omega_{z,3/2}]. \quad (19.27)$$

The gap $E_{g, \text{QD}}$ in the QD is given by

$$E_{g, \text{QD}} = E_g + E_- + \frac{1}{2}\hbar(\omega_x + \omega_y + \omega_z), \quad (19.28)$$

where E_g is the gap in the bulk and ω_i , $i = x, y, z$ is equal to $\sqrt{\kappa_i/m_{\text{CB}}}$.

Problem 19.10t. Use the $\gamma_1, \gamma_2, \gamma_3$ values for GaAs to obtain the 2×2 matrix of the Hamiltonian $H_L + \mathcal{V}(\mathbf{r})$ in the basis $\Psi_{1/2}(\mathbf{r}), \Psi_{3/2}(\mathbf{r})$. Diagonalize this matrix to obtain the heavy hole and light hole ground state eigenenergies in a QD with $\kappa_x = 10^{-7}$ a.u., $\kappa_y = 10^{-7}$ a.u., and $\kappa_z = 10^{-4}$ a.u.

It is worthwhile to mention that in cryptography and quantum information application, an external electron is injected to the CB of the QD and at the same time an electron-hole pair in an exciton form is created by optical excitation. Thus, the excited state, called *trion*, consists of three particles, one hole and two electrons.

19.7.3 QDs and Coulomb Blockade

In Fig. 19.7 we show schematically the experimental setup that can inject electron(s) to the QD, while its state can be influenced by the voltage V_p of the electrode P. To start with, we shall ignore the kinetic energy of the injected electron(s) (and the external current) because the main contribution

¹⁵ Positive hole energy is in the direction toward the interior of the VB.

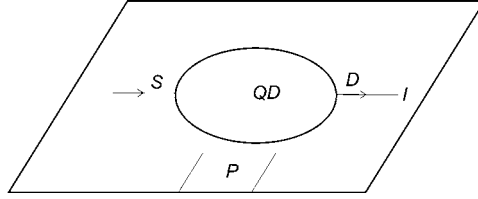


Fig. 19.7. Schematic view of the experimental setup for the Coulomb blockade measurements. The current I through the QD from source (S) to drain (D) is measured, as well as the voltage V_{SD} between the contact points S, D. There is also a metallic contact, P, called plunger, connected to an external reservoir which controls the voltage V_P of the plunger

to the energy of the electrons is the electrostatic energy. The charge on the QD is $q_d = -Ne$, where N is the number of the injected electrons; there is also induced charge q_p on the plunger.

The electrostatic energy U_e is

$$U_e = \frac{1}{2} [q_d V_d + q_p V_p] + [Q_r - q_p] V_p \quad (19.29)$$

where Q_r is the charge on the (huge) reservoir (when $q_p = 0$) which controls the voltage of the plunger. Now the charges on the QD, q_d , and the plunger, q_p , can be expressed in terms of the corresponding voltages V_d and V_p through the diagonal and off-diagonal matrix elements of the capacitance matrix

$$q_d = C_d V_d + C_{dp} V_p, \quad (19.30)$$

$$q_p = C_{pd} V_d + C_p V_p, \quad (19.31)$$

where the off-diagonal matrix elements are symmetric and negative¹⁶ ($C_{dp} = C_{pd}$). If no current flows through the dot and $V_S = V_D = V_d$, then the charge on the dot would depend on the difference $V_d - V_p$, since there is no other quantity on which q_d may depend. Hence

$$C_d = -C_{pd} = -C_{dp} \quad (19.32)$$

From (19.30) and (19.32) we have

$$V_d = \frac{q_d}{C_d} + V_p \quad (19.33)$$

and from (19.31), (19.32) and (19.33)

$$q_p = -C_d V_d + C_p V_p = -C_d \frac{q_d}{C_d} - C_d V_p + C_p V_p. \quad (19.34)$$

¹⁶ See Landau and Lifshitz' book on '*Electrodynamics of Continuous Media*'. Eqs. (2.8) and (2.11).

We substitute (19.33) and (19.34) in (19.29) and obtain

$$\begin{aligned}
 U_e &= \frac{1}{2} \frac{q_d^2}{C_d} + \frac{1}{2} q_d V_p - \frac{1}{2} q_p V_p + Q_r V_p \\
 &= \frac{1}{2} \frac{q_d^2}{C_d} + \frac{1}{2} q_d V_p + \frac{1}{2} q_d V_p + \text{terms independent of } q_d \text{ and } V_d \\
 &= \frac{1}{2} \frac{q_d^2}{C_d} + q_d V_p + \text{terms independent of } q_d \text{ and } V_d.
 \end{aligned} \tag{19.35}$$

The value of $q_d = -N_0 e$ which minimizes the electrostatic energy U_e is given by¹⁷

$$q_{d_0} = -N_0 e = -C_d V_{p_0} \Rightarrow V_{p_0} = \frac{N_0 e}{C_d}. \tag{19.36}$$

Notice that, at the symmetrical (with respect to the minimizing charge $q_{d_0} = -eN_0$) values of $q_d^{(+)} = -e(N_0 + 1/2)$ and $q_d^{(-)} = -e(N_0 - 1/2)$, the value of U_e is the same. Hence, the injection of an extra electron (such that their number changes¹⁸ from $N_0 - \frac{1}{2}$ to $N_0 + \frac{1}{2}$) does not cost any energy. This zero energy cost for an electron injection implies easy transfer of electron from the source S to the drain D, and consequently, large current, I , even with a minute voltage difference V_{SD} . Hence, if we plot the current I vs. the plunger voltage V_p or the conductance $G \equiv I/V_{SD}$ vs. V_p , we expect equally spaced sharp peaks when $V_p = (e/C_d)(N_0 \pm 1/2)$; two consecutive such peaks are at a distance $\delta V_p = e/C_d$ apart. The experimental data confirm this impressive theoretical prediction associated with the disappearance of the Coulomb blockade effect at the values of $V_p = (e/C_d)(N_0 \pm \frac{1}{2})$. If we assume a voltage $V_{SD} = 0.5 \text{ mV}$ and ballistic propagation of the electron within the QD we obtain a conductance of about $0.5e^2/h$ which clearly is an ideal upper limit.

If the plunger voltage does not satisfy the condition $V_p = (e/C_d)(N_0 \pm \frac{1}{2})$, then in order to have a current from the source to the drain, there must be another provider of energy to overcome the energy cost of injecting an extra electron; this energy cost is at least of the order $e^2/2C_d$. Hence, we expect to have a nonzero current (independently of the value V_p) if the source/ drain voltage difference is such that $eV_{SD} \simeq e^2/2C_d$ or $V_{SD} \simeq e/2C_d$. Another provider of energy for overcoming the energy cost of injecting an electron (assuming that the values of V_p are not favorable) is thermal fluctuation. If $k_B T \gtrsim e^2/2C_d$ we expect current at any value of V_p ; hence, at temperatures higher than about $e^2/2k_B C_b$ we expect the sharp G vs. V_p peaks to be washed out.

QDs used in transport properties are usually of the 2-D type; their planar restriction can be obtained either by a fixed hard wall potential or by

¹⁷ Notice that N_0 is not necessarily integer.

¹⁸ This change can be achieved by increasing the plunger voltage V_p by e/C_d from $(e/C_d)(N_0 - \frac{1}{2})$ to $(e/C_d)(N_0 + \frac{1}{2})$.

an experimentally controllable confining potential quite frequently parabolic. The energy levels of such a potential in the presence of a vertically oriented magnetic field have been determined by V. Fock [19.19] and by C.G. Darwin [19.20] the corresponding states are shown in the tutorial “2d Fock-Darwin states” accessible through the Google. See also [19.15], and [19.2, 19.16, 19.17]. A recent reference, [19.18], shows how the coupling of 2-D QDs with the surrounding 2-D electron gas can be tuned in order to study under controllable conditions basic physics problems such as the Kondo effect.

19.8 Key Points

- Metallic clusters, consisting of a few tens to several hundreds close-packed alkali or noble atoms, have an almost-spherical shape and exhibit “magic” number features corresponding to closed-shell electronic structure.
- Fullerenes are carbon molecules forming a hollow cage consisting of pentagon and hexagon faces and obeying the isolated pentagon rule; they can be thought of as folded graphene pieces, where the inclusion of pentagons facilitates the folding. The prototypical fullerene is the C_{60} which has the shape of a truncated icosahedron. Most of the fullerenes possess icosahedral symmetry.
- C_{60} s form a molecular **fcc** solid called fulleride. C_{60} s combined with alkali atoms occupying empty spaces between the C_{60} molecules form conducting ionic solids, some of which exhibit superconductivity with a rather high T_c .
- Carbon atoms form nanotubes of typical diameter 10–20 Å and length that reaches several micrometers; they can be viewed as rolled up graphene strips. There are three types of nanotubes depending on the direction of rolling up relative to the sides of the hexagons (parallel to sides, perpendicular to sides and neither parallel nor perpendicular to any sides). Carbon nanotubes can be conducting or semiconducting. There are single-wall or multiwall nanotubes; in the latter, nanotubes are nested within larger diameter nanotubes (For a recent review see [19.21]).
- There are several other types of cluster involving noble gas atoms, or silicon atoms, or mixed organometallic cluster consisting of transition metal and carbon atoms.
- Quantum dots are semiconductor nanoparticles (usually Si or *III – Vs*) grown or deposited on a substrate; their sizes can be as small as 2 nm and as large as several hundred nm. Their main feature is that their optical and transport properties depend on their size and shape. The tailoring of these properties opens up many technological possibilities. The confinement of holes and electrons in all three directions discretizes the energy levels and pushes both the electron levels and the hole levels to higher energies, increasing thus the effective gap and blue shifting the emission and absorption spectrum.

- Quantum dots with a proper setup can act somehow as a single electron field effect transistor; at certain values of the gate voltage, $V_p = (e/C_d)(N_0 \pm 1/2)$, the energy cost of injecting an extra electron in the QD can disappear; at these values of V_p the conductance exhibits sharp peaks. The energy cost of injecting an extra electron in the QD is due to the electrostatic repulsion of other extra electrons already residing in the QD; this is the Coulomb blockade effect.

19.9 Problems

- 19.1 Consider a spherical potential well with infinite walls. Find the single particle energy levels and plot them in order of increasing energy. Do these levels follow the inequalities shown in Sect. 19.2?
- 19.2 For the zig-zag nanotube shown in Fig. 19.5b, estimate the size of the semiconducting gap. The same for the zig-zag (7, 0). Compare the last case with Fig. 13.11 in Kaxiras book [SS83].
- 19.3 Verify that (11.68) and (11.69) are indeed eigenvalues of (19.9).

Further Reading

- See Chap. 13 in Kaxiras' book [SS83].
- See pp. 553–556 in Marder's book [SS82].
- For some applications of carbon nanotubes see [19.2, 19.16, 19.17] and [19.18].

Correlated Systems

Magnetic Materials, I: Phenomenology

Summary. As we shall see in Chap. 21, magnetism is an intrinsically quantum phenomenon dominated usually by electronic spin. However, in this chapter we restrict ourselves to a phenomenological description of the basic features and the various categories of magnetic materials. Concepts such as magnetic domains, saturation magnetization, Bloch walls, hysteresis, soft and hard magnetic materials, remanance, and coercivity are also introduced. The temperature dependence of the saturation magnetization and the magnetic susceptibility for simple ferromagnets, ferrimagnets, and antiferromagnets and the corresponding universal critical exponents are presented. Representative materials of each category of magnetic solids are mentioned and their properties are summarized. Thermodynamics provide an explanation for the temperature dependence of the saturation magnetization and the susceptibility, for the thickness of the Bloch walls, etc. Finally, the topic of spintronics is summarized, by briefly reviewing the efforts to exploit the electronic spin degrees of freedom up to the time of this writing.

20.1 Which Property Characterizes These Materials?

Magnetic materials are characterized by a nonzero value of the *time average microscopic current density* $\mathbf{j}_\mu(\mathbf{r})$, or equivalently, by a nonzero *time averaged microscopic magnetization*¹ $M_\mu(\mathbf{r})$ ² at least in some region(s) within the primitive cell (*pc*). The role of spin in particular, and quantum mechanics in general, in establishing a non-zero $M_\mu(\mathbf{r})$ will be examined in the next

¹ These quantities are related as follows: $\nabla \times \mathbf{M}_\mu(\mathbf{r}) = \mathbf{j}_\mu(\mathbf{r})/c$ (in SI replace c by 1).

² The subscript μ is for distinguishing these quantities from their macroscopic counterparts; the latter are defined as the spatial average value of $\mathbf{j}_\mu$ and $\mathbf{M}_\mu$ over a volume ΔV much larger than the volume per atom but much smaller than any “macroscopic” volume.

chapter. For the time being, keep in mind that the majority of materials are nonmagnetic.³

Magnetic materials are classified as *antiferromagnetic*, (if $\mathbf{m}_{\text{pc}} = 0$), or *ferromagnetic* (if $\mathbf{m}_{\text{pc}} \neq 0$), according to the value of the magnetic moment $\mathbf{m}_{\text{pc}}$, of the magnetic primitive cell, where

$$\mathbf{m}_{\text{pc}} \equiv \int_{V_{\text{pc}}} \mathbf{M}_{\mu}(\mathbf{r}) d^3r \quad (20.1)$$

Ferromagnetic materials can be further divided into *simple ferromagnetic*, where $\mathbf{M}_{\mu}(\mathbf{r})$ does not change sign or direction within the primitive magnetic cell, and *ferrimagnetic*, where $\mathbf{M}_{\mu}(\mathbf{r})$ does change direction (or even sign) within the primitive magnetic cell so that $|\mathbf{m}_{\text{pc}}|$ turns out to be smaller than what it would be if $\mathbf{M}_{\mu}(\mathbf{r})$ did not change direction. Quite often it is more convenient to introduce the magnetic moment of each atom $\mathbf{a}$, $\mathbf{m}_{\mathbf{a}}$, where

$$\mathbf{m}_{\mathbf{a}} \equiv \int_{V_{\mathbf{a}}} \mathbf{M}_{\mu}(\mathbf{r}) d^3r \quad (20.2)$$

and the integration is over the volume $V_{\mathbf{a}}$ corresponding to atom $\mathbf{a}$. Obviously, $\mathbf{m}_{\text{pc}} = \sum_{\mathbf{a}} \mathbf{m}_{\mathbf{a}}$ where the summation is over all atoms belonging to the primitive magnetic cell⁴. In Fig. 20.1 we present schematically in a simplified 1-D way several configurations of the atomic magnetic moments $\mathbf{m}_{\mathbf{a}}$ in magnetic materials.

One would expect in simple ferromagnetic and ferrimagnetic materials, where $\mathbf{m}_{\text{pc}}$ is nonzero, the total magnetization of the whole solid, $\mathbf{M} \equiv \mathbf{m}_{\text{t}}/V$, to be always nonzero. ($\mathbf{m}_{\text{t}} \equiv \sum_{\text{pc}} \mathbf{m}_{\text{pc}}$ is the sum over all primitive magnetic cells, i.e., the total magnetic moment of the material). However, this is not the case. As we shall see, the ferromagnetic material, in order for its total magnetic energy to be reduced, is spontaneously divided into magnetic regions of proper size (much larger than the atomic size) and shape. Within each such region, called *magnetic domain*, all magnetic moments of the primitive cells, $\mathbf{m}_{\text{pc}}$, have the same direction and magnitude; thus, the magnetic moment $\mathbf{m}_{\text{d}}$ and the magnetization $\mathbf{M}_{\text{d}} \equiv \mathbf{m}_{\text{d}}/V_{\text{d}}$ of each domain has the maximum possible value, which is called saturation magnetic moment and *saturation magnetization* respectively. However, the orientation of the magnetic moments, $\mathbf{m}_{\text{d}}$, of each domain is *not* necessarily the same; thus, the sum of $\mathbf{m}_{\text{d}}$ s over all domains,⁵ which is equal to the total magnetization, could be zero:

³ If the equilibrium state of a system is unique, the system ought to be nonmagnetic.

Indeed, for a unique state, the symmetry transformation $t \rightarrow -t$ will map the state to itself, and hence, $\mathbf{j}_{\mu}(-t) = \mathbf{j}_{\mu}(t)$; on the other hand $\mathbf{j}_{\mu}(-t) = -\mathbf{j}_{\mu}(t)$, by definition. It follows then that $\mathbf{j}_{\mu}(t) = 0$.

⁴ Notice that it is not unusual for some (not all) atoms of the primitive cell to have $\mathbf{m}_{\mathbf{a}} = 0$.

⁵ For very small particles with diameter in the range 10–100 nm, there is only one domain; for such single-domain particles the magnetization is always at its saturation value.

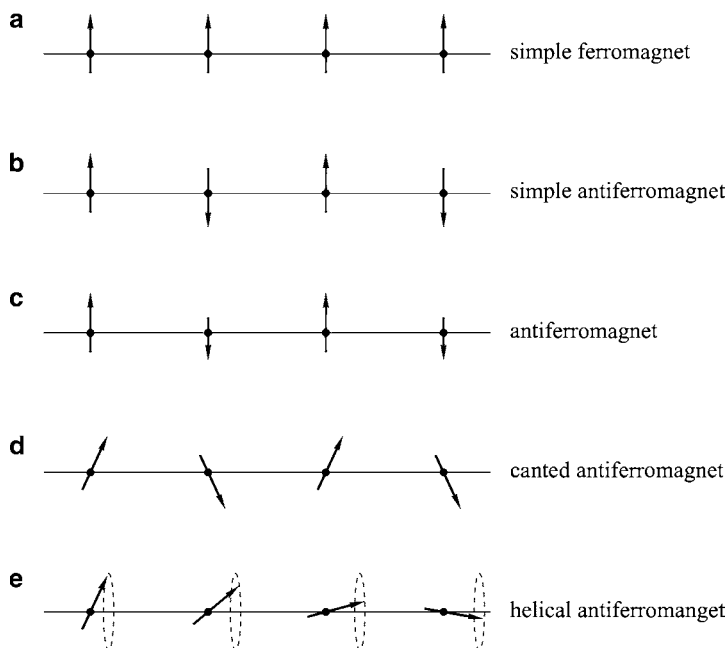


Fig. 20.1. Schematic 1-D presentation of the nonzero atomic magnetic moment, $\mathbf{m}_a$, configurations in various magnetic materials. More complicated configurations do exist

$$\mathbf{m}_t \equiv \sum_d \mathbf{m}_d = 0 \quad (\text{often, but not always}) \quad (20.3)$$

Neighboring magnetic domains (of different orientation of their $\mathbf{m}_d$ s) are separated by the so-called *Bloch* (or *Néel*) *walls* of finite thickness (see the caption of Fig. 20.2); the latter extends over several tens or hundreds of primitive cells, which allow a gradual turn of the $\mathbf{m}_{pc}$ from the value of the one domain to the value of the other domain as shown in Fig. 20.2.

Let us consider a ferromagnet of zero total initial magnetization: $\mathbf{M} = (\sum_d \mathbf{m}_d)/V = 0$; and let us apply an external magnetic field $\mathbf{H}$. As the field $\mathbf{H}$ becomes larger and larger the magnetization keeps increasing through the following physical mechanisms: (a) The Bloch walls move in such a way as to enlarge the domains the magnetization of which happens to be parallel (or almost parallel) to the external field $\mathbf{H}$ at the expense of the other domains; this process is dictated by the minimization of the interaction energy with the external field, which is proportional to $-\sum_d V_d \mu_o \mathbf{M}_d \cdot \mathbf{H}$ (in G-CGS set μ_o equal to 1). The motion of the Bloch walls is reversible for very low values of $\mathbf{H}$ but it becomes irreversible for higher values of $\mathbf{H}$. This irreversibility is due to the fact that the Bloch walls in their continued motion encounter defects, internal strains, boundaries of microcrystallites, etc., which they overcome under the action of $\mathbf{H}$; thus, if the external field is removed,

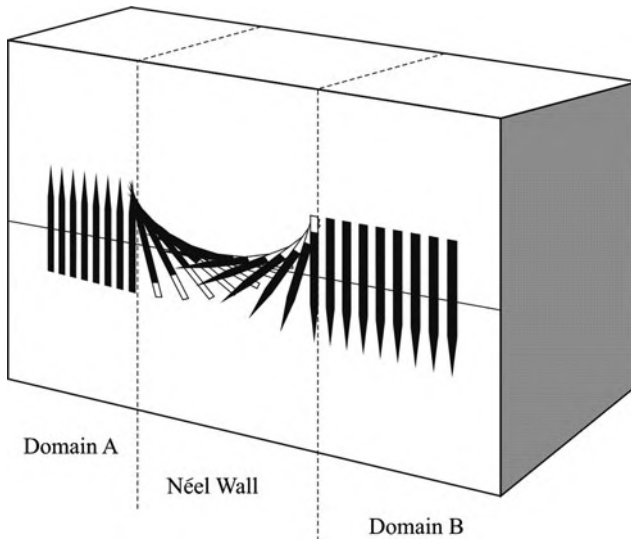


Fig. 20.2. The gradual change of the orientation of the magnetic moments of the primitive magnetic cells takes place within the thickness of a wall, which separates two neighboring magnetic domains. In iron the thickness of this wall is about 300 primitive cells. The term Bloch wall is used when the axis of rotation which changes the magnetization from one domain to the next is in the plane of the wall (an example of Bloch wall is when the magnetization is perpendicular to the wall and of opposite directions in the two neighboring domains); if the axis of rotation is out-of-plane (as in the figure above, where it is perpendicular to the plane of the wall), the term Néel wall is used. For simplicity, from now on we shall use the name Bloch for both types of walls

it is not possible for Bloch walls to surpass the potential barriers associated with defects, strains, etc., (b) At very high fields the magnetic moments $\mathbf{m}_d$ of the energetically unfavorable domains (the volumes V_d of which have been substantially reduced as a result of the Bloch walls movement) rotate to become parallel to $\mathbf{H}$. When this second process is completed, the total magnetization $\mathbf{M} = \mathbf{m}_t/V$ has reached its maximum value, the saturation magnetization. If at this point we start reducing the external field, the magnetization decreases but without following the same dependence on $\mathbf{H}$ as before, because the process is not reversible. This irreversibility leads to the phenomenon of *hysteresis* shown in Fig. 20.3. In this figure we have followed the usual practice of plotting $|\mathbf{B}| \equiv \mu_o |\mathbf{H} + \mathbf{M}|$ vs $|\mathbf{H}|$ instead of $|\mathbf{M}|$ vs $|\mathbf{H}|$ (In G-CGS $\mathbf{B} = \mathbf{H} + 4\pi\mathbf{M}$, $B_s = 4\pi M_s$, and $B_r = 4\pi M_r$, see Fig. 20.3)

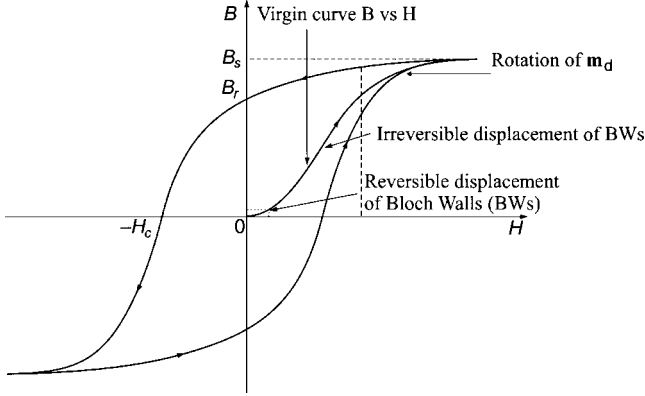


Fig. 20.3. The magnetic field, $|B| \equiv \mu_o |H + M|$ vs the external field $|H|$ in a ferromagnet. The initial curve, which starts from the origin reaches the magnetization saturation value at which $B_s \equiv \mu_o M_s$ plus $\mu_o H$. As the field H is decreasing B follows the upper curve which passes through the point B_r (called *remanence*) for zero H and through the point $-H_c$ (called *coercivity*) at which B becomes zero. Finally, for very negative values of H (i.e., H in the opposite from the initial direction and $|H|$ very large) we reach the saturation value $-M_s$ of M and $B = -\mu_o |H| - B_s$. Then by increasing the value of H (i.e., by making it less negative and eventually positive) we follow the lower curve which is symmetric to the upper one with respect to the origin. The upper and lower curves in this figure define the so-called *hysteresis loop*. The area within the hysteresis loop gives the magnetic energy spent in a full cycle. Small value of H_c implies small area within the hysteresis loop and hence, low magnetic losses. Materials with low H_c are called *soft magnetic materials* and are used in transformers and other applications requiring repeated cycle operation. Large H_c ferromagnets are called *hard magnetic materials* and are used as permanent magnets, since a large H_c implies a large permanent field, B_r .

20.2 Experimental Data for Ferromagnets

20.2.1 Saturation Magnetization vs Temperature for Simple Ferromagnets

In Fig. 20.4 the temperature dependence of M_s of a simple ferromagnet is given. Notice that there is a critical temperature T_c beyond which M_s is zero.

20.2.2 Magnetic Susceptibility of Simple Ferromagnet for $T > T_c$

The magnetic susceptibility, χ_m , which has been defined in App. A (see (A.28), (A.30), (A.32), and (A.34)), obeys the so-called *Curie-Weiss law* in its temperature dependence for $T \gtrsim 1.2T_c$

$$\chi_m = \frac{c_1}{T - T_o}, \quad T \gtrsim 1.2T_c, \quad (20.4)$$

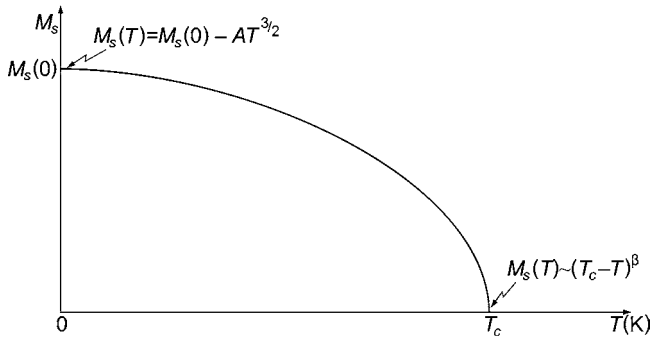


Fig. 20.4. The saturation magnetization M_s decreases monotonically as the absolute temperature T increases and vanishes beyond the critical temperature T_c called *Curie temperature*. The initial decrease of M_s follows the so-called $T^{3/2}$ *Bloch law*. At the critical temperature, a second-order phase transition takes place, where the critical exponent β is about 0.36 for all ferromagnets

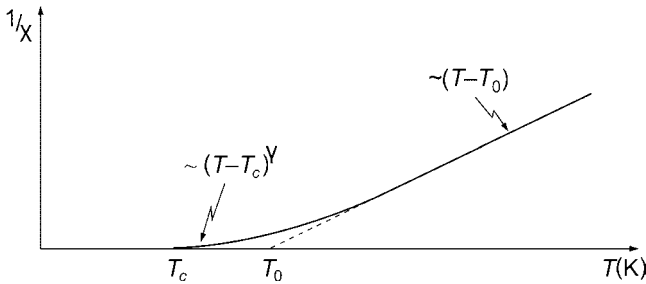


Fig. 20.5. Inverse magnetic susceptibility versus temperature, for a ferromagnet. Notice the behavior near T_c

where c_1 is a constant and T_0 is very close to T_c . Notice that if T_0 were zero, (20.4) would be reduced to the Curie law obtained in (5.105). For T approaching T_c this equation is modified and near T_c takes the following form

$$\chi_m \rightarrow \frac{c_2}{(T - T_c)^\gamma}, \quad T \rightarrow T_c^+ \quad (20.5)$$

where c_2 is another constant; the exponent γ takes the value $\gamma \simeq 4/3$ for almost all ferromagnets. Usually, instead of χ_m , we plot $1/\chi_m$ vs temperature to make the dependence above and near T_c more visible (Fig. 20.5).

20.2.3 Saturation Magnetization vs Temperature for Ferrimagnets

Several ferrimagnets (e.g., the *iron garnets* of chemical formula $5\text{Fe}_2\text{O}_3 \cdot 3\text{M}_2\text{O}_3$ with M being a trivalent metallic ion) exhibit a M_s vs T dependence quite

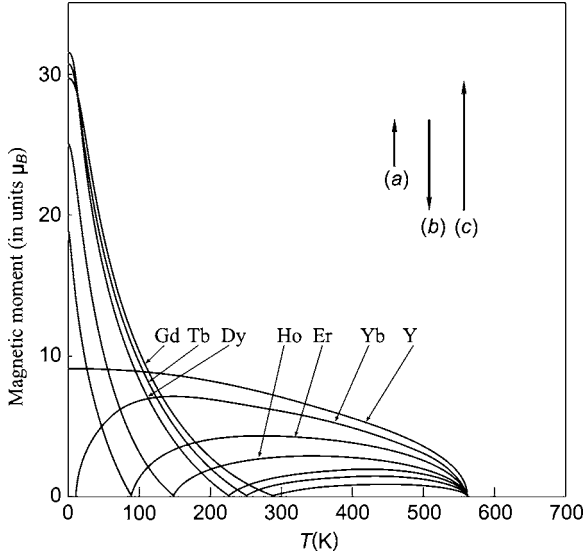


Fig. 20.6. Magnetic moment of the unit $5\text{Fe}_2\text{O}_3 \cdot 3\text{M}_2\text{O}_3$ (where $M = \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Yb}, \text{and Y}$) versus temperature. Notice the so-called *compensation temperature* at which the magnetic moment changes direction passing through zero. There are three contributions to the magnetic moment of the unit $5\text{Fe}_2\text{O}_3 \cdot 3\text{M}_2\text{O}_3$: Four iron cations Fe^{+3} occupy octahedral positions in the unit cell and give contribution (a) pointing up; the other six Fe^{+3} occupy tetrahedral positions and give contribution (b) pointing down; finally the six M^{3+} cations give contribution (c) pointing up (with the exception of Y which gives no contribution). Contribution (c) is larger than the combined iron contributions but it drops much faster with temperature so that at the compensation temperature the combined iron and the M^{3+} contribution cancel each other. For larger temperatures the combined ion contribution wins and eventually dominates until the critical temperature which is common to all garnets, since it is determined by the $5\text{Fe}_2\text{O}_3$ subunit

different from that of Fig. 20.4. In Fig. 20.6 we plot the magnetic moment of the chemical unit $5\text{Fe}_2\text{O}_3 \cdot 3\text{M}_2\text{O}_3$ for several garnets.

20.2.4 Magnetic Susceptibility of Ferrimagnets vs Temperature ($T > T_c$)

Ferrimagnets such as magnetite ($\text{FeO} \cdot \text{Fe}_2\text{O}_3$) exhibit a more complicated temperature dependence than that of the Curie–Weiss law:

$$\chi_m = \frac{c_1 T - c_2}{T^2 - T_c^2}, \quad T \gtrsim 1.1 T_c \quad (20.6)$$

In. Fig. 20.7 experimental data for $1/\chi_m$ vs T for magnetite are shown

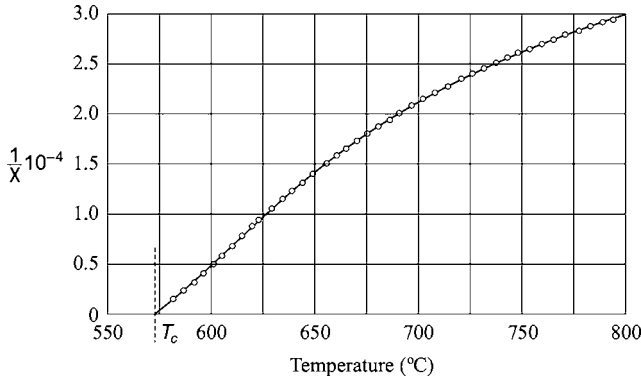


Fig. 20.7. Inverse magnetic susceptibility versus temperature for magnetite. Notice the curvature, which is characteristic for ferrimagnets

20.3 Experimental Data for Antiferromagnets

20.3.1 Determination of the Antiferromagnetic Ordered Structure

The long-range magnetic order in antiferromagnets does not show up macroscopically as in ferromagnets, because the magnetic moment of each primitive magnetic cell is zero. Thus, a probe capable of extracting microscopic information is needed. Such a probe is neutron elastic scattering. Indeed the magnetic moment of each incoming neutron (which is equal to $1.913 \mu_N$, where μ_N is the nuclear magneton) will interact with the magnetic moment $\mathbf{m}_a$ of each atom in the primitive cell of the antiferromagnet and by constructive interference of the scattered neutrons will produce diffracted beams reflecting the periodic antiferromagnetic arrangement of the atomic magnetic moments. To be more specific, consider the schematic antiferromagnetic ordering of Fig. 20.1b; the period is $2a$, where a is the distance between nearest neighbor atoms. For a probe that can distinguish between magnetic moment up and magnetic moment down (as the neutrons can do), the period is $2a$ (which defines the size of the magnetic primitive cell) and the Bragg planes are $G_n = (2\pi/2a)n = \pi n/a$ where n is an integer. On the other hand, for a probe, such as X-rays, that does not see the magnetic moment, the period is a and the Bragg planes are $2\pi n/a$. Hence, neutron scattering “sees” twice as many Bragg planes than X-rays do (and consequently produces twice as many diffracted beams). Instead of using X-rays, we can raise the temperature as to destroy the long-range antiferromagnetic order and repeat the experiment with neutrons, which under those circumstances, would produce the same diffracted beams as the X-rays. A specific realistic example of this unambiguous way of identifying antiferromagnetic long-range order can be found in the book by Kittel [SS74], 8th ed. pp. 340–341.

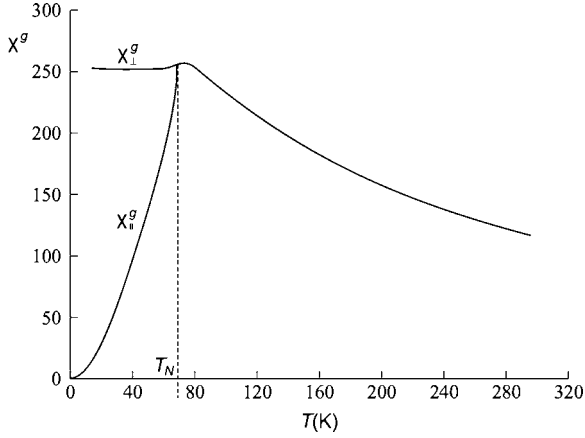


Fig. 20.8. The magnetic susceptibility $\chi_m^g \equiv \chi_m/\rho$ of MnF_2 (in units of $10^{-6} \text{ cm}^3/\text{g}$) vs temperature. The critical Néel temperature, T_N , is 64.34 K. Below T_N , where long-range antiferromagnetic order appears, there are two different susceptibilities depending on whether the direction of the external field is parallel to the axis of symmetry of the crystal or perpendicular to it

20.3.2 Magnetic Susceptibility vs Temperature

In Fig. 20.8 the magnetic susceptibility of the antiferromagnet MnF_2 , is plotted as a function of temperature. At a critical temperature, T_N , called *Néel temperature*, a phase transition takes place: Below T_N there is long-range antiferromagnetic order, while above T_N there is no such order. This phase transition is reflected at the temperature dependence of the susceptibility.

For $T > T_N$ (except of the immediate neighbourhood of T_N) we have the following general expression

$$\chi_m = \frac{c_1}{T + \Theta}, \quad T > T_N \quad (20.7)$$

where Θ is usually comparable but larger than T_N (In case of MnF_2 , $\Theta = 82 \text{ K}$ while $T_N \simeq 64 \text{ K}$ so that $\Theta/T_N \simeq 1.24$). The T dependence of χ_m , for $T < T_N$, is anisotropic and more complicated.

20.4 Materials

20.4.1 Simple Ferromagnetic Materials

This group of materials includes the elemental metals Fe, Co, Ni, Gd, and Dy alloys among them and with other metals or nonmetals, as well as various compounds. The iron(about 20%)/nickel alloy, known as permalloy, is a high permeability, low coercivity ferromagnet with important industrial uses (its

Table 20.1. Data for simple ferromagnetic crystals

Material or chemical unit (C.U.)	Saturation magnetization (Gauss)		Magnetic moment of the C.U. (in μ_B)	Curie temperature (in K)
	295 K	0 K		
Fe	1,701	1,740	2.22	1,043
Co	1,400	1,446	1.72	1,388
Ni	485	510	0.606	627
Gd	0	2,060	7.63	292
Dy	0	2,920	10.2	88
EuO	0	1,920	6.8	69
EuS	0	1,184	—	16.5
CrO ₂	515	—	2.03	386.5
CrBr ₃	0	270	—	32.56
MnAs	670	870	3.4	318
MnBi	620	680	3.52	630
Cu ₂ MnAl	—	726	—	630
Cu ₂ MnIn	—	613	—	500
Au ₂ MnAl	0	323	—	200
Fe _{0.8} Co _{0.2}	—	—	2.42	1,223
Fe _{0.74} Al _{0.26}	—	—	1.40	767
Ni _{0.75} Pt _{0.25}	—	—	0.44	359

Table 20.2. Critical exponents β and γ for simple ferromagnetic materials

Material	β (see Fig. 10.4)	γ (see (20.5))
Fe	0.34 ± 0.04	1.33 ± 0.015
Co	—	1.21 ± 0.04
Ni	0.42 ± 0.07	1.35 ± 0.02
Gd	—	1.39 ± 0.05
Eus	0.33 ± 0.015	—
CrO ₂	—	1.63 ± 0.02
CrBr ₃	0.368 ± 0.005	1.215 ± 0.02

hysteresis loop is reproduced in [SS82], p. 688). In tables 20.1 and 20.2 several quantities pertaining to ferromagnetic materials are presented.

We have seen in section 5.5.3.1 (pp. 135, 137) that the magnetic moment of an ion in paramagnets is given approximately by $2S\mu_B$ for the 3d elements and by $gJ\mu_B$ for the lanthanides, where S is the total spin, J is the total angular momentum and g is the Landé factor (see (5.70)).

It is worthwhile to check whether these relations are valid or not for the ferromagnets. We see that for the 3d ions the experimental value is quite different from $2S$ (with the exception of MnAs and MnBi where the difference

Table 20.3. Values of S , L , J , g , $2S$ and gJ for various magnetic ions together with their experimental value for m/μ_B .

Ion	Fe ²⁺	Fe ³⁺	Co ²⁺	Ni ²⁺	Gd ³⁺	Dy ³⁺	Eu ²⁺ (EuO)	Cr ³⁺ (CrO ₂)	Mn ³⁺ (MnAs)	Mn ³⁺ (MnBi)
S	2	5/2	3/2	1	7/2	5/2	7/2	3/2	2	2
L	2	0	3	3	0	5	0	3	2	2
J	4	5/2	9/2	4	7/2	15/2	7/2	3/2	0	0
$2S$	4	5	3	2	7	5	7	3	4	4
gJ	6	5	6	5	7	10	7	0,6	0	0
m/μ_B (exp)	2.22	2.22	1.72	0.606	7.63	10.2	6.8	2.03	3.4	3.52

is 12%). This indicates that the environment is not magnetically neutral and that it compensates, to some degree, for the magnetic moment of the ion. On the other hand, for the lanthanides the theoretical value of gJ is very close to the experimental value of m/μ_B (Table 20.3).

20.4.2 Ferrimagnetic Materials

Two important classes of materials belong, among others, to the ferrimagnetic category. One such class is the iron garnets already discussed in Subsect. 20.2.3 (see, in particular Fig. 20.6). The zero temperature limit of the magnetic moment of the chemical unit $5\text{Fe}_2\text{O}_3 \cdot 3\text{M}_2\text{O}_3$ is the total magnetic moment of the six M^{3+} ions minus the $6 - 4 = 2$ magnetic moments of the uncompensated Fe^{3+} ions.

Problem 20.1t. Calculate the theoretical value of the magnetic moment of the unit $5\text{Fe}_2\text{O}_3 \times 3\text{M}_2\text{O}_3$ at zero temperature and compare with the corresponding experimental values shown in Fig. 20.6 for various M^{3+} ions.

The other broad class of ferrimagnets is the so-called *ferrites* of the general formula $\text{MO} \cdot \text{Fe}_2\text{O}_3$ where M is a divalent cation ($\text{M} = \text{Zn}, \text{Gd}, \text{Fe}, \text{Ni}, \text{Cu}, \text{Co}, \text{and Mg}$). Magnetite, $\text{FeO} \cdot \text{Fe}_2\text{O}_3$, is a typical representative of this class. Ferrites form a cubic lattice structure known as *spinel*. The unit cell with a lattice constant of about 8 Å has 8 sites of tetrahedral symmetry each one surrounded by four oxygen anions and 16 sites of octahedral symmetry each one surrounded by six oxygen anions. In the *normal* spinel structure the tetrahedral sites are occupied by the divalent cations and the octahedral sites by the trivalent cations. In the *inverse* spinel structure, as e.g., in magnetite, the tetrahedral sites are occupied by divalent ions, while half of the octahedral sites are occupied by the remaining trivalent cations and the other half by the divalent cations. In magnetite the octahedrally located trivalent iron ions have spin “up”, while the tetrahedrally located trivalent iron ions have spin “down”. Thus, the Fe^{3+} ions do not contribute to the magnetic moment of the

Table 20.4. Data for some ferrites.

Chemical unit (C.U.)	Saturation magnetization (Gauss)		Magnetic moment of the C.U. (in μ_B)	Curie temperature (K)
	295 K	0 K		
FeO · Fe ₂ O ₃	480	510	4.1	858
MnO · Fe ₂ O ₃	410	560	5.0	573
NiO · Fe ₂ O ₃	270	300	2.4	858
CuO · Fe ₂ O ₃	135	160	1.3	728
MgO · Fe ₂ O ₃	110	—	1.1	713
CoO · Fe ₂ O ₃	—	475	—	793

unit FeO · Fe₂O₃; the only contribution is essentially this of the divalent ion. The theoretical prediction for the magnetic moment of the unit FeO · Fe₂O₃ is, according to these arguments, $2S = 4$ (in units of μ_B). The experimental data confirm this theoretical value as shown in the Table 20.4.

20.4.3 Antiferromagnetic Materials

Among the elemental solids only Cr and Mn are antiferromagnets. However, there are many compounds that show the phenomenon of antiferromagnetism as shown in Table 20.5

20.5 Thermodynamic Relations

20.5.1 Thermodynamic Potentials

In App. A, we have pointed out that the total energy U_t of a body in a magnetic field $\mathbf{B}(\mathbf{r})$, the external current-density sources of which are $\mathbf{j}_e(\mathbf{r})$, consists of three terms

$$U_t = U_o + U_c + U_b \equiv \tilde{U} + U_b \tag{20.8}$$

where U_o is the energy of the body in the absence of external current-sources, U_c is the work done by external forces to bring the elementary contribution to the current-sources from infinity to their final places, and U_b is the energy supplied by external “batteries” to keep the current in each elementary loop constant as it is moved from infinity to its final place. $\tilde{U}$ is by definition the sum of $U_o + U_c$ ⁶. The infinitesimal changes of U_t and $\tilde{U}$ upon changing the magnetic field $\mathbf{B}$ or the auxiliary magnetic field $\mathbf{H}$ are:

⁶ U_t and $\tilde{U}$ are thus related by some kind of Legendre transform.

Table 20.5. Data for some antiferromagnets

Material	Crystal structure (ignoring magnetic ordering)	Néel temperature T_N (K)	Curie–Weiss temperature Θ (K)	Θ/T_N	$\chi(0)/\chi(T_N)$
Cr	bcc	308	–	–	–
α -Mn	Cubic ⁷	95	–	–	–
MnO	fcc	116	610	5.3	0,66
MnS	fcc	160	528	3.3	0,82
MnTe	hex. layered	307	690	2.25	–
MnF ₂	bc. tetragonal	67	82	1.24	0,76
FeF ₂	bc. tetragonal	79	117	1.48	0,72
FeCl ₂	hex. layered	24	48	2.0	<0,2
FeO	fcc	198	570	2.9	0,8
CoCl ₂	hex. layered	25	38,1	1.53	–
CoO	fcc	291	330	1.14	–
NiCl ₂	hex. layered	50	68,2	1.37	–
NiO	fcc	525	~2000	~4	–
CoF ₂	–	37,7	–	–	–
MnCl ₂	–	2	–	–	–
RbMnF ₃	–	54,3	–	–	–
KMnF ₃	–	88,3	–	–	–
KFeF ₃	–	115	–	–	–
KCoF ₃	–	125	–	–	–
Cr ₂ O ₃	Rhombohedral	307	485	1.58	–
CuCl ₂ ·V ₂ O ₃	Monoclinic	~70 170	109	~1.56	–
VS	–	1040	–	–	–

$$\delta U_t = \int \mathbf{H} \cdot \delta \mathbf{B} dV = \int \mathbf{j}_e \cdot \delta \mathbf{A} dV, \quad \text{SI}^8 \quad (20.9)$$

$$\delta \tilde{U} = - \int \mathbf{B} \cdot \delta \mathbf{H} dV = - \int \mathbf{A} \cdot \delta \mathbf{j}_e dV, \quad \text{SI} \quad (20.10)$$

where $\mathbf{A}$ is the vector potential related to $\mathbf{B}$ by $\mathbf{B} = \nabla \times \mathbf{A}$. It follows from (20.9) that U_t is the thermodynamic potential the natural independent variable of which is $\mathbf{B}$ or $\mathbf{A}$, while $\tilde{U}$ is the thermodynamic potential whose natural independent variable is $\mathbf{H}$ or $\mathbf{j}_e$.

We introduced also the interaction energy between the body and the pre-existing field (*the generalized Zeeman energy*) $\tilde{U}_{\text{int}} \equiv \tilde{U} - U_o - U_c(\mathbf{B}_o)$ where

⁷ The elementary cell is complicated, with 54 atoms.

⁸ In G-CGS $\delta U_t = \frac{1}{c} \int \mathbf{j}_e \cdot \delta \mathbf{A} dV = \frac{1}{4\pi} \int \mathbf{H} \cdot \delta \mathbf{B} dV$.

$U_c(\mathbf{B}_o) = -\frac{1}{2} \int \mathbf{B}_o \cdot \mathbf{H}_o dV$ ($-\frac{1}{8\pi} \int \mathbf{B}_o \cdot \mathbf{H}_o dV$ in G-CGS) and $\mathbf{B}_o, \mathbf{H}_o$ are the fields produced by the current distribution $\mathbf{j}_e(\mathbf{r})$ in the absence of the body. One can show⁹ that the infinitesimal variation of $\tilde{U}_{\text{int}}$ is given by

$$\delta \tilde{U}_{\text{int}} = - \int \mathbf{M} \cdot \delta \mathbf{B}_o dV, \quad \text{SI} \quad (20.11)$$

To avoid carrying the integration over the volume in all intermediate calculations we shall introduce the densities of the various thermodynamic potentials; these densities will be denoted by the corresponding lower case letter. For example, $U_o \equiv \int u_o dV$, where u_o for a ferromagnet is a function of the local magnetization $\mathbf{M}(\mathbf{r})$ (and of the entropy density, particle concentration, etc.). More explicitly we can express $u_o(\mathbf{M})$ as a sum of the terms:

$$u_o(\mathbf{M}) = u_{\text{ex}}(|\mathbf{M}|) + u_a(\mathbf{e}) + u_{\text{m-el}} + u_n \quad (20.12)$$

where the first term, the *exchange interaction*, $u_{\text{ex}}(|\mathbf{M}|)$, depends on the magnitude¹⁰ of the local saturation magnetization within each magnetic domain, $u_a(\mathbf{e})$, the *anisotropy energy-density* (see p. 585) depends on the direction $\mathbf{e} \equiv \mathbf{M}/|\mathbf{M}|$ of the magnetization with respect to the crystal axes, $u_{\text{m-el}}$ is the *interaction of the magnetization with elastic stresses* (or strains) possibly present in the ferromagnetic material, and u_n , the *energy-density of nonuniformity*, is the increase in energy density because of relative disorientation of the primitive cell magnetic moments occurring, e.g., in Bloch walls. Since the saturation magnetization $\mathbf{M}$ is quite large, the effect of the field $\mathbf{H}$ on $\mathbf{M}$ is negligible. Thus, in what follows, $\mathbf{M}$ will be taken as independent of $\mathbf{H}$.

Instead of the energy density, it is more appropriate to consider the Gibbs free energy density, $\tilde{g}$ or g_t , since the minimization of $\tilde{g}$ or g_t , *under constant temperature and pressure* gives the equilibrium state of the system (see (C.18)). In the presence of the magnetic field energy the variation of $\tilde{g}$ or g_t satisfies

$$d\tilde{g} \leq -sdT - \mathbf{B} \cdot d\mathbf{H} + dP + \mu dn, \quad \text{SI} \quad (20.13)$$

or

$$dg_t \leq -sdT + \mathbf{H} \cdot d\mathbf{B} + dP + \mu dn, \quad \text{SI}. \quad (20.14)$$

(In G-CGS $-\mathbf{B} \cdot d\mathbf{H}$ and $\mathbf{H} \cdot d\mathbf{B}$ must be replaced by $-\mathbf{B} \cdot d\mathbf{H}/4\pi$ and $\mathbf{H} \cdot d\mathbf{B}/4\pi$ respectively). Integrating (20.13) and (20.14) under constant T, P, n , and $\mathbf{M}$ (so that, $d\mathbf{B} = \mu_o(d\mathbf{H} + d\mathbf{M}) = \mu_o d\mathbf{H}$) we obtain

$$\tilde{g} = g_o(\mathbf{M}) - \frac{1}{2} \mu_o H^2 - \mu_o \mathbf{M} \cdot \mathbf{H}, \quad \text{SI} \quad (20.15)$$

$$g_t = g_o(\mathbf{M}) + \frac{1}{2} \mu_o H^2 = g_o + \frac{1}{2\mu_o} (\mathbf{B} - \mu_o \mathbf{M})^2 \quad \text{SI}, \quad (20.16)$$

⁹ See Landau and Lifshitz, [E15]. § 32.

¹⁰ This is the main $\mathbf{M}$ dependent contribution to $u_o(\mathbf{M})$; it is a short-range interaction arising as a result of the difference in the Coulomb potential between the parallel and the antiparallel configurations of two neighboring electronic spins (see next chapter).

where $g_o = u_o(\mathbf{M}_s) + P - Ts$ (in G-CGS $\tilde{g} = g_o(\mathbf{M}) - \frac{1}{8\pi}H^2 - \mathbf{M} \cdot \mathbf{H}$ and $g_t = g_o(|\mathbf{M}|) + \frac{1}{8\pi}H^2 = g_o + \frac{1}{8\pi}(B - 4\pi M)^2$); the difference $g_t - \tilde{g} = \mu_o H^2 + \mu_o \mathbf{M} \cdot \mathbf{H} = \mu_o (\mathbf{H} + \mathbf{M}) \cdot \mathbf{H} = \mathbf{B} \cdot \mathbf{H}$. But, according to (A.59) and (20.8), $\mathbf{B} \cdot \mathbf{H} = u_b \equiv u_t - \tilde{u} = g_t - \tilde{g}$, which shows the consistency of our calculations.

20.5.2 Mean Field Approximation (Landau's Approach)

For a ferromagnet, near the critical temperature T_c , the magnetization M is rather small so that we can expand $g_o(\mathbf{M}) \simeq g_{ex}(|\mathbf{M}|)$ in powers of M keeping only even powers (since g_{ex} depends on the magnitude and not on the direction of $\mathbf{M}$). Substituting this expansion in (20.15) we have

$$\tilde{g} \simeq g_o(0) + \frac{1}{2}aM^2 + \frac{1}{4}bM^4 - \mu_o \mathbf{M} \cdot \mathbf{H} - \frac{1}{2}\mu_o H^2, \text{SI} \quad (20.17)$$

Since the dependence of $g_o(\mathbf{M})$ on the direction $\mathbf{e} \equiv \mathbf{M}/|\mathbf{M}|$ has been omitted, the term $\mathbf{M} \cdot \mathbf{H}$ must be equal to $|\mathbf{M}| \cdot |\mathbf{H}| = MH$ in order to minimize $\tilde{g}$ (in other words, $\mathbf{M}$ must be parallel to $\mathbf{H}$). Let us first minimize $\tilde{g}$ in the absence of H ($H = 0$). We have

$$\frac{\partial \tilde{g}}{\partial M} = aM + bM^3 = M(a + bM^2) = 0 \quad (20.18)$$

For $T < T_c$, (20.18) must be satisfied for $M \neq 0$, while for $T > T_c$, (20.18) must be satisfied only for $M = 0$. Furthermore, minimization implies that the second derivative $\partial^2 \tilde{g} / \partial M^2$ must be positive, which in turn means that b is a positive constant. In order for M to satisfy these physical requirement, a must be negative for $T < T_c$ and positive for $T > T_c$. Expanding a in powers of the small quantity $T - T_c$ (i.e., as $T \rightarrow T_c$), we have

$$a = a_1(T - T_c) + \mathcal{O}\left((T - T_c)^3\right) \quad (20.19)$$

Substituting (20.19) in (20.18) we obtain

$$M = \sqrt{\frac{a_1}{b}}(T_c - T)^{1/2}, \quad T < T_c \quad (20.20)$$

$$M = 0, \quad T_c < T \quad (20.21)$$

Thus, the critical exponent β (see Fig. 20.4) is $1/2$ instead of $\beta \simeq 1/3$ found experimentally (see Table 20.2)

Repeating the minimization in the presence of H (but as $H \rightarrow 0$) and for $T > T_c$ and keeping terms linear in H and M we find

$$\frac{\partial \tilde{g}}{\partial M} = aM - \mu_o H = 0, \text{SI},$$

or

$$M = \frac{\mu_o H}{a} \Rightarrow \chi = \frac{\mu_o}{a_1 (T - T_c)}, \quad T > T_c \quad (20.22)$$

(In G-CGS $\chi = 1/a_{1G} (T - T_c)$). Thus, we ended up with the Curie–Weiss law for the susceptibility. Again, the mean field theory produces a value for the critical exponent $\gamma = 1$, instead of $\gamma \simeq 4/3$, which is the experimental result (see Fig. 20.5, (20.5) and Table 20.2).

20.5.3 Why are Magnetic Domains Formed?

The answer to this question, as usually, must be sought in the minimization of the total energy (or Gibbs free energy). As we shall see, the minimization of the term $\frac{1}{2}\mu_o \int H^2 dV$ (in SI; in G-CGS it is $\frac{1}{8\pi} \int H^2 dV$) (see (20.16)) is achieved by forming many magnetic domains of different orientation of the saturation magnetization. On the other hand, the configuration that minimizes $\frac{1}{2}\mu_o \int H^2 dV$ would increase the anisotropy energy $\int u_a(\mathbf{e}) dV$ and the energy of nonuniformity $\int u_n dV$. Hence, what determines the number, size, shape, and orientation of the magnetic domains is the competition between three of the terms contributing to the energy: $\frac{1}{2}\mu_o \int H^2 dV$, $\int u_a(\mathbf{e}) dV$ and $\int u_n dV$. Let us examine each one of them:

- (a) *The auxiliary magnetic field energy density*, $\frac{1}{2}\mu_o H^2$. From Maxwell's equations in the absence of external current sources we have

$$\nabla \cdot \mathbf{B} = 0 \Rightarrow \nabla \cdot \mathbf{H} = -\nabla \cdot \mathbf{M}, \text{ SI} \quad (20.23)$$

$$\nabla \times \mathbf{H} = 0 \quad (20.24)$$

(In G-CGS, $\nabla \cdot \mathbf{H} = -4\pi \nabla \cdot \mathbf{M}$). Thus, the only source of $\mathbf{H}$ is the divergence of the saturation magnetization. Within each magnetic domain, $\mathbf{M}$ is uniform and consequently, $\nabla \cdot \mathbf{M} = 0$. Hence, what is left from $\nabla \cdot \mathbf{M}$ is the discontinuity δM_n of the normal component of the saturation magnetization at the interface between two neighboring magnetic domains and the normal component M_n of $\mathbf{M}$ at the external surface of the ferromagnetic material. Thus, the value and orientation of $\mathbf{H}$ at each point $\mathbf{r}$ depend on the values M_n and δM_n at the external surface and the internal interfaces, respectively. As a result, $\mathbf{H}(\mathbf{r})$ is in general a non-local functional of $\mathbf{M}(\mathbf{r})$. Since it is not possible to have everywhere $M_n = 0$, if the magnetization is uniform over the whole extent of the material or alternately uniform as in Fig. 20.9b, the necessity of different magnetic domains (properly oriented) arises; such a configuration of domains producing everywhere $M_n = \delta M_n = 0$ and known as **magnetic domains of closure** is shown in Fig. 20.9a (for the special case of a ferromagnet whose shape is a rectangular parallelepiped of dimensions $\ell \times w_1 \times w_2$). For closure domains $\nabla \cdot \mathbf{M} = 0$ everywhere and, hence, $\mathbf{H}$ is zero everywhere.

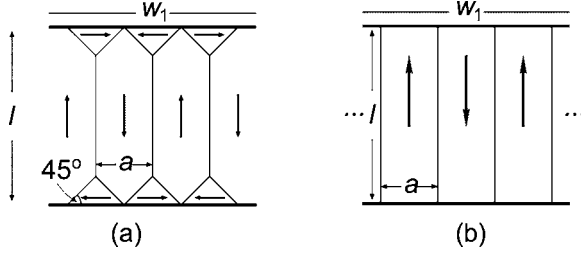


Fig. 20.9. Magnetic domains in a ferromagnet the shape of which is a rectangular parallelepiped of dimensions $\ell \times w_1 \times w_2$ (w_2 is normal to this page and it is not shown). In case (a), known as *magnetic domains of closure* both M_n at the surface and δM_n at the interfaces are zero and, hence, $\mathbf{H} = 0$. In case (b) because of the alternating signs of M_n at each element $a \times w_2$ of the two external surfaces $w_1 \times w_2$ the auxiliary magnetic field $\mathbf{H}$ is of the order of M in a volume extending about $\pm a$ around each of the two external surfaces $w_1 \times w_2$ and zero otherwise. Hence, the magnetic energy $\frac{1}{2}\mu_0 \int H^2 dV$ is of the order $\mu_0 a w_1 w_2 M^2$, while in the absence of magnetic domains it would be of the order of $\frac{1}{2}\mu_0 \ell w_1 w_2 M^2$. Thus, the presence of the magnetic domains as in (b) reduces the magnetic energy by a factor of the order a/ℓ

- (b) *The anisotropy energy density u_a* The anisotropy energy density u_a is mainly due to spin-orbit and to a lesser degree to spin-spin interactions. The former is the interaction between the spin and the local electric field of the lattice; the latter is the long-range magnetic dipole-dipole energy. These interactions, in contrast to the exchange interaction, are of relativistic nature and as such are of the order v^2/c^2 relative to the exchange interaction, where v is typical electronic velocity¹¹. Thus, the anisotropy energy can be expanded in powers of v^2/c^2 . The exact form of each term in this expansion depends on the symmetry properties of the crystal structure. For example, for crystals of uniaxial symmetry the first term in this expansion has the form

$$u_a = \frac{1}{2}\mu_0 C M^2 e_z^2 + \mathcal{O}(v^4/c^4) \quad (20.25)$$

where C is a dimensionless coefficient, the z -axis has been chosen along the symmetry axis, and e_z is the projection of the unit vector parallel to M on the z -axis. If C is negative the z -axis will be the axis of easy magnetization (since then u_a becomes minimum); if C is positive, the axis of easy magnetization will be in the $x - y$ plane¹².

- (c) *The energy density of nonuniformity u_n* . As it was mentioned before, this energy density u_n is the increase of the exchange energy density as a

¹¹ $v/c \simeq \alpha \equiv e^2/\hbar c = 1/137$.

¹² To determine the direction within the $x - y$ plane we need to find the second or even the third term in the expansion in powers of v^2/c^2 .

result of the disorientation of the primitive cell magnetic moments relative to each other along the thickness of the Bloch wall (see Fig. 20.2). The simplest form of u_n appropriate for a cubic crystal is the following

$$u_n = \frac{1}{2} A \mu_o \left[\left(\frac{\partial \mathbf{M}}{\partial x} \right)^2 + \left(\frac{\partial \mathbf{M}}{\partial y} \right)^2 + \left(\frac{\partial \mathbf{M}}{\partial z} \right)^2 \right] \quad (20.26)$$

where A has dimensions of length square. Far from the critical temperature the magnitude $|\mathbf{M}|$ is independent of x, y, z and can be taken out of differentiation symbols leaving inside only the direction unit vector $\mathbf{e}$. Close to the critical temperature the magnitude of $\mathbf{M}$ can also change as its direction is rotated.

20.5.4 How Thick is the Bloch Wall?

Two energy terms determine by their competition the thickness of the Bloch wall: The anisotropy energy, $\int u_a dV$, which favors thin walls, as thin as possible, since it is of the order of $\mu_o C M^2 \delta$ per unit area, where δ is the thickness of the wall; and the nonuniform energy $\int u_n dV$, which is of the order $\mu_o A M^2 \delta (1/\delta^2) \simeq A M^2 / \delta$ per unit area¹³ and hence, it favors as thick a wall as possible. By minimizing the sum of the two terms, we find for the thickness δ

$$\delta \approx \sqrt{A/C} \quad (20.27)$$

while for the energy per unit area $\mu_o \Delta M^2$ we have

$$\Delta \sim \sqrt{AC} \quad (20.28)$$

Problem 20.2ts: Assume that the Bloch wall to be parallel to x, y plane and the axis of easy magnetization to be parallel to the x -axis. Show that the angle $\theta(z)$ of the direction of the magnetic moment at z is given by

$$\theta(z) = \tanh \left(z \sqrt{C/A} \right) \quad (20.29)$$

with boundary conditions $\theta(-\infty) = \pi$ and $\theta(+0) = 0$. Then show that

$$\Delta = 2\sqrt{AC} \quad (20.30)$$

20.5.5 Examples of Magnetic Domains

Let us consider a rectangular parallelepiped ferromagnet such as that shown in Fig. 20.9. The direction of easy magnetization is assumed to be along the direction ℓ . If the magnitude of C in (20.25) is very large the magnetization $\mathbf{M}$ will remain parallel (or antiparallel) to the axis of easy magnetization and the

¹³ The terms $(\partial M / \partial x)^2$ and $(\partial M / \partial y)^2$ is of the order M^2 / δ^2 .

domain structure will be as in Fig. 20.9b. The width a of each magnetic domain will be determined by the competition of magnetic energy $\frac{1}{2}\mu_o \int \hat{H}^2 dV$, which is proportional to $\mu_o a w_1 w_2 M^2$ (and which favors as small a as possible) and the energy of the Bloch walls, which is equal to $\mu_o \Delta M^2 w_2 \ell$ per Bloch wall times the number of Bloch walls, which is equal to w_1/a (this term favors as few Bloch walls as possible thus as large a as possible). Minimizing the sum of these two terms we find

$$a \sim \sqrt{\Delta \ell} \sim \sqrt{C \ell \delta} \quad (20.31)$$

If the magnitude of C in (20.25) is small we expect a configuration of magnetic domains as in Fig. 20.9a. Such a configuration would eliminate the magnetic field energy at the expense of an increase of the anisotropy energy in the regions where $\mathbf{M}$ is parallel to the w_1 direction. The total volume of these regions is on the order of $aw_1 w_2$ so that the anisotropy energy is $\frac{1}{2}\mu_o C M^2 a w_1 w_2$ favoring as small a as possible. The Bloch wall energy is approximately as before, i.e., $2\mu_o \Delta w_2 \ell w_1 M^2/a$, and minimizing the sum of these two terms, we find.

$$a \sim \sqrt{\Delta \ell / C} \sim \sqrt{\delta \ell} \quad (20.32)$$

Equations (20.31) and (20.32) tell us that the thickness of the magnetic domain is proportional to the square root of the thickness of the Bloch wall times the length ℓ of the specimen along the direction of easy magnetization. If the length ℓ exceeds a certain value, each magnetic domain is divided to subdomains near the external surfaces. In the opposite limit of very small ferromagnetic particles, it may be profitable energetically not to form magnetic domains at all. This would happen when the magnetic field energy $\frac{1}{2}\mu_o \int H^2 dV \sim \frac{1}{2}\mu_o M^2 V$ is equal to or smaller than the energy of a single Bloch wall, which is equal $\mu_o \Delta M^2 V^{2/3}$ where $V \sim \ell^3$. Hence, when

$$\ell \lesssim \Delta \sim \sqrt{AC} \quad (20.33)$$

we have a uniformly magnetized particle (also called single-domain particle).

20.5.6 Thermodynamics of Antiferromagnets

In antiferromagnets, the magnetization of the primitive cell for $T < T_N$ consists of two contributions that cancel each other: $\mathbf{M} = \mathbf{M}_1 + \mathbf{M}_2 = 0$. $\mathbf{M}_1 \neq 0$ belongs to sublattice 1 and $\mathbf{M}_2 \neq 0$ to sublattice 2. The magnetic order parameter can be taken either the $\mathbf{M}_1$ or the $\mathbf{M}_2$, although usually we choose

$$\mathbf{L} \equiv \mathbf{M}_1 - \mathbf{M}_2 \quad (20.34)$$

The thermodynamic analysis near the critical temperature T_N proceeds by expanding the Gibbs free energy density in powers of $\mathbf{L}$ up the fourth order

and in powers of the auxiliary magnetic field up to second order. Only even powers will appear in the expansion, since the transformation $\mathbf{L} \rightarrow -\mathbf{L}$ does not change the physics (it simply renames the sublattices); similarly $\mathbf{H} \rightarrow -\mathbf{H}$ corresponds to time reversal, which leaves the physical system unchanged. Thus, the more general expansion for a uniaxial crystal has the following form

$$\begin{aligned} \tilde{g}(\mathbf{L}, \mathbf{H}) = & g_o(0, 0) + aL^2 + bL^4 + \mu_o D (\mathbf{H} \cdot \mathbf{L})^2 + \mu_o D' H^2 L^2 \\ & - \frac{1}{2} \mu_o \chi_p H^2 + \frac{1}{2} b' (L_x^2 + L_y^2) - \frac{1}{2} \mu_o \gamma (H_x^2 + H_y^2) - \frac{1}{2} \mu_o H^2 \end{aligned} \quad (20.35)$$

(In G-CGS $\tilde{g}$ has the same form as (20.35) with μ_o set equal to one except in the last term, where μ_o must be set equal to $1/4\pi$). We assume that b' is positive, which means that the axis of easy sublattice magnetization is along the z -axis and, hence, $L_x = L_y = 0$. Repeating the arguments used in the ferromagnetic case, we conclude that $b > 0$ and that $a = a_1 (T - T_N)$. Furthermore, experimental data show that χ_p, D, D' are all positive. By minimizing $\tilde{g}$ in the absence of $\mathbf{H}$, we obtain

$$L = 0, \quad \text{for } T > T_N \quad \text{and} \quad H = 0 \quad (20.36)$$

$$L = L_z = \left(\frac{a_1}{2b}\right)^{1/2} (T_N - T)^{1/2}, \quad \text{for } T < T_N \quad \text{and} \quad H = 0 \quad (20.37)$$

From (20.13) we have

$$\frac{\partial \tilde{g}}{\partial \mathbf{H}} = -\mathbf{B} = -\mu_o (\mathbf{H} + \mathbf{M}), \quad \text{SI} \quad (20.38)$$

which combined with (20.35) yields

$$\mathbf{M} = \chi_p \mathbf{H} - 2D (\mathbf{H} \cdot \mathbf{L}) \mathbf{L} - 2D' L^2 \mathbf{H} + \gamma (H_x \mathbf{i} + H_y \mathbf{j}) \quad (20.39)$$

Thus, the susceptibility is (taking into account that $\gamma \ll \chi_p$)

$$\chi_x = \chi_y = \chi_p + \gamma \simeq \chi_p, \quad \chi_z = \chi_p, \quad T > T_N \quad (20.40)$$

$$\chi_{\perp} = \chi_p + \gamma - \frac{D' a_1 (T_N - T)}{b}, \quad T < T_N \quad (20.41)$$

$$\chi_{\parallel} = \chi_p - \frac{(D + D') a_1 (T_N - T)}{b}, \quad T < T_N \quad (20.42)$$

20.6 Spintronics

The term Spintronics is used to denote the exploitation of the electronic spin degrees of freedom in solid state systems, mainly in microelectronic devices; it even includes cases of optical manipulation of individual electron spins in

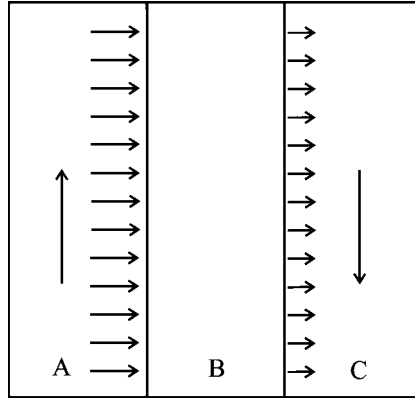


Fig. 20.10. A typical spintronic device (or part of a device) consists of three regions: Region *A* is a source of spin-polarized electrons. Region *B* is a very thin film (a few atomic layers wide) of normal metal or insulator, or simply a depletion interface region acting as tunneling barrier. Region *C* can be a ferromagnetic metal (or more generally a spin-polarized conductor) or an ordinary semiconductor. Current flows from *A* to *B*

quantum dots or doped diamond¹⁴, as a possible quantum bit in the quest for quantum computers.

Electronic spins offer two significant advantages: They can be switched from one state to another much faster than charge can be transported from one point to another in a circuit and they produce less heat; moreover, they retain their polarization. Thus, they may contribute to faster and smaller microelectronic devices and, what is more important, they do not lose information when calculational devices are switched off. On the other hand, their injection and detection is more difficult than that of the charges and much less developed.

Most of the work in Spintronics involves the generic setup shown in Fig. 20.10. In a particular case, *A* and *C* are very thin films of the same ferromagnetic metal (e.g., Fe or Co) but of different (usually opposite) magnetization and *B* is a normal metal such as Cu; the *ABC* structure is repeated several times. The resistance of the device is measured as a function of an applied magnetic field parallel to one of the two magnetizations. As the magnetic field increases the resistance drops and eventually it reaches a saturation value when the magnetizations of *A* and *C* become parallel. The final change in the resistance is quite large and increases with the number of *ABC* units. A. Fert and P. Grunberg were honored with the 2007 Physics Nobel Prize for their discovery (see Baibich et al. [20.1], and Binasch et al. [20.2] respectively) of this strong dependence of the resistance on the magnetic field, which is known as *giant magnetoresistance* (GMR). GMR is quantified as follows

¹⁴ See Awschalom et al. [20.25]

$$\text{GMR} = \frac{R_{\uparrow\downarrow} - R_{\uparrow\uparrow}}{R_{\uparrow\downarrow}} \quad (20.43)$$

where $R_{\uparrow\downarrow}$ ($R_{\uparrow\uparrow}$) is the resistance of the device when the magnetization of A and C are antiparallel (parallel). The GMR depends on the scattering at the interface between A and B and – mainly – on the matching of the wavefunctions at the interface between B and C for each of the independent channels corresponding to spin up and spin down. Actually there is a possibility of mixing of the two channels in B , because of spin-flip due to the spin-orbit coupling; however, the time a polarized electron spends in the region B on its way to the region C is less than the average time required for spin-flip. Devices based on the GMR in ferromagnetic metal/nonmagnetic metal/ferromagnetic metal configuration are used in the hard discs of virtually every computer in the world.

Another important case of the ABC setup of Fig. 20.1, is the one where A and C are ferromagnetic metals, e.g., Fe and B is an insulating material such as Al_2O_3 or MgO . Such devices are known as *magnetic tunnel junctions* (MTJ). Spin-polarized electrons can tunnel through the insulating layer, giving rise to what is called *tunneling magnetoresistance* (TMR); the resistance of this device depends strongly on whether the magnetization of A and C are parallel or antiparallel (Julliere [20.3], Miyazaki [20.4], Moodera [20.5, 20.6]). The TMR is usually quantified as

$$\text{TMR} = \frac{R_{\uparrow\downarrow} - R_{\uparrow\uparrow}}{R_{\uparrow\downarrow}} \quad (20.44)$$

The magnitude of TMR depends strongly on the quality of the A/B and the B/C interfaces. In 2004, Parkin [20.7] and S. Yuasa [20.8] managed to fabricate atomically flat interfaces, and thus, the TMR value was boosted to over 400% (Yuasa [20.9]). The TMR is the basis for the development of a novel type of computer memory called *magnetoresistive random access memory* (MRAM), which has the ability to retain information without requiring any power and thus, it allows instant operation when a computer is turned on.

The full exploitation of the electronic spin degrees of freedom in microelectronics requires the building of a spin-based transistor, a conceptual structure of which was proposed by Datta and Das [20.10] and it is shown schematically in Fig. 20.11.

A realization of such a concept, consistent with the semiconductor domination of the microelectronics, points toward the need to inject polarized carriers into a semiconductor such as GaAs [or/and Si]. The achievement of an appreciable spin-polarized current into the drain required the overcoming of several obstacles:

1. The source of spin-polarized carriers must have a high degree of polarization at room temperature (the latter restriction is imposed by practical requirements concerning device operation). One promising type of materials is the so-called dilute magnetic semiconductors (DMS), i.e.,

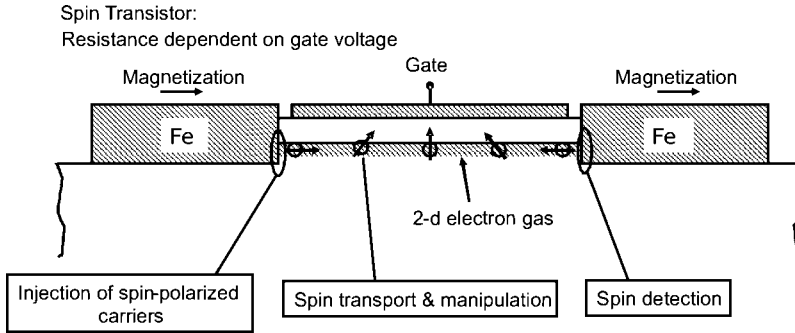


Fig. 20.11. A spin-field effect transistor (SFET) as proposed by Datta and Das [20.10]. Spin-polarized carriers (spin parallel to the current) are injected in the transport channel where the spin direction is manipulated by the gate voltage. The current is large if the spin direction at the drain point is the same as at the source point and small if the direction is reversed

semiconductors such as zinc oxide and gallium nitride doped with magnetic atoms such as manganese or cobalt; with sufficient concentration of dopants, DMS exhibit ferromagnetism well above room temperature. Another possibility for the *A* region material is a ferromagnetic metal. A third broader possibility, which may include the DMS, is the so-called *half-metallic ferromagnets*; these are materials where the spin-up DOS around the Fermi energy exhibits a typical metallic behavior, while the spin-down DOS has a gap around the E_F ; Thus, these materials have 100% spin polarization around the Fermi energy. Examples of half-metallic ferromagnets, besides DMS, are the so-called magnetic Heusler alloys (NiMnSb, etc.) [20.11], CrAs [Akinaza et al. [20.12]] in zinc-blende structure, manganites/perovskites.

2. The interface problem: At the early stages of the field, a spin-polarized medium (DMS or ferromagnetic metals) was deposited directly on a semiconductor resulting in chemical intermixing, strong scattering, and significant reduction of the polarized carriers making it across the interface into the semiconductor. This problem was faced by using a ferromagnetic metal in the *A* region such as to create a Schottky barrier (Rashba [20.13]) and, hence, a depletion layer that acted as an insulating layer in region *B*. Thus, the ferromagnetic metal/semiconductor junction acted as magnetic tunnel junction (MTJ). A further development came in 2003 (Van Dorpe [20.14]) when the Schottky was replaced with a thin insulating layer (creating a structure Ferromagnetic metal/insulating layer/semiconductor). With several improvements [20.14– 20.18], regarding materials and quality of the interfaces, the spin polarization of the injected current from a ferromagnetic metal, into the GaAs semiconductor has reached by the time of this writing (2008) about 40%, at low temperatures [20.19].

3. A major challenge is also the detection of the degree of polarization of the injected current. Several techniques are used. One is optical and is based on the process of polarized electron + hole $\rightleftharpoons$ circularly polarized light (spin-LED). Another is based on the replacement of the ferromagnetic metal by a GMR device that acts as a spin valve.
4. In spite of the significant progress of the period 2001–2008, the DMS approach has not yet produced practical spintronic devices operating at room temperature. On the other hand, the impressive progress achieved in devices based on ferromagnetic metals as a result of remarkable improvement in controlling the interface structure and composition together with theoretical work offers another path for practical spin polarized injection into semiconductor [20.19–20.24].

20.7 Key Points

- Magnetic materials are characterized by nonzero time average magnetic moment of some (or all the) atom(s) in the primitive cell and long-range ordering of these nonzero moments.
- Magnetic materials are classified as simple ferromagnets, ferrimagnets, and antiferromagnets, depending on the relative orientation of the magnetic moment(s) within the magnetic unit cell.
- Simple ferromagnets and ferrimagnets form usually magnetic domains separated by Bloch walls, in order to reduce their total (free) energy. This feature leads to the hysteresis loop.
- The saturation magnetization of ferromagnets (or sublattice magnetization in antiferromagnets) is reduced with increasing temperature and disappears at a critical temperature, T_c , where the long-range magnetic order is destroyed.
- Above the critical temperature (except in a fluctuation-dominated region near that value) the susceptibility χ_m is given by the following formula

$$\chi_m = \frac{c}{T \mp T_o}, \quad T \geq T_o, \quad T_o > T_c$$

where the minus (plus) sign is for simple ferromagnets (antiferromagnets); for the latter instead of T_c , the symbol T_N is used.

- The Gibbs free energy per unit volume is given by

$$\begin{aligned} \tilde{g} &= g_o(\mathbf{M}) - \frac{1}{2}\mu_o H^2 - \mu_o \mathbf{M} \cdot \mathbf{H}, \text{ SI,} \\ \tilde{g} &= g_o(\mathbf{M}) - \frac{1}{8\pi} H^2 - \mathbf{M} \cdot \mathbf{H}, \text{ G-CGS} \end{aligned}$$

where $\mathbf{H}(\mathbf{r})$ is a nonlocal functional of $\mathbf{M}(\mathbf{r})$ and

$$g_o(\mathbf{M}) = u_{\text{ex}}(|\mathbf{M}|) + u_a(\mathbf{e}) + u_{\text{m-el}} + u_n - Ts + P$$

- Landau's mean field theory gives

$$M = \sqrt{a_1/b}(T_c - T)^\beta \quad \text{as } T \rightarrow T_c^- \\ = 0 \quad T > T_c,$$

where $\beta = 1/2$, while experimentally $\beta \simeq 1/3$.

- The thickness δ of the Bloch wall is determined by the competition of the anisotropy energy (characterized by the parameter C) and the nonuniform energy (characterized by the parameter A):

$$\delta \simeq \sqrt{A/C}$$

while the energy of the Bloch wall per unit area is proportional to ΔM^2 , where the length Δ is given by

$$\Delta \simeq \sqrt{AC}$$

- The linear size a of each magnetic domain is determined by the competition of the magnetic energy proportional to aH^2 and the Bloch wall energy proportional to ΔM^2 . For certain simple geometries, the result for the width of the magnetic domain

$$a \sim \sqrt{\ell\delta}$$

where ℓ is the given length of the magnetic domain.

- Landau's analysis can be applied to antiferromagnets as well giving the temperature dependence of the sublattice magnetization and the susceptibility χ_m .
- Sandwiches of the type $(ABC)_n$ where A is a magnetic metal (source of spin polarized electrons), B is a nonmagnetic metal or an insulator, and C a magnetic metal of opposite polarization than that of A exhibit giant magnetoresistance.

20.8 Problems

- 20.1 Taking into account (A.59) to (A.61), prove (20.11) or (A.62).
- 20.2s Prove equations (20.37) to (20.42).
- 20.3 How would equations (20.37) to (20.42) be modified, if b' in (20.35) were negative?
- 20.4 For the ferrites shown in Table 20.4, calculate the magnetic moment of the chemical unit $\text{MO} \cdot \text{Fe}_2\text{O}_3$ and compare it with the corresponding experimental values.
- 20.5s For the ferromagnet of uniaxial symmetry in the presence of a magnetic field $\mathbf{H}$, find the direction of magnetization.

Further Reading

- In Kittel's book [SS74], pp. 322–385, the readers will find further information on magnetic materials.
- The thermodynamics of magnetic materials as well as other related information are presented in the book by Landau and Lifshitz [E15], pp. 130–179.
- An early review of the Spintronic field is given in [20.21].
- The subject of Spintronics is presented also in the books [Ma174] and [Ma175].

Magnetic Materials II: Microscopic View

Summary. The physics behind the parallel or antiparallel orientation of two spins is examined within the framework of two neutral hydrogen atoms at a distance r apart. The exchange interaction, J , is defined and calculated. The question of the appearance or not of ferromagnetism or antiferromagnetism within the JM and its extensions is studied. The same question is also examined within the framework of an extension of the LCAO called Hubbard model. For large values of $U/|V_2|$ the latter can be reduced to a simple version of the Heisenberg model, which is one of the main theoretical tools for studying ground state, the excitation spectrum, and the thermodynamics of ferromagnets and antiferromagnets (usually within the framework of the mean field approximation).

21.1 Introduction

The phenomenon of magnetism requires (a) that at least one atom in the primitive cell has a nonzero magnetic moment and (b) that there is a coupling among nearest neighbors magnetic moments favoring parallel or antiparallel (or even more complicated) relative orientations and leading to a long-range magnetic order. If Bloch states with no electron–electron correlations were true eigenstates, the total spin would be zero everywhere, since each Bloch state would be doubly occupied with one spin up and one spin down. With the spins canceled this way, the requirements for magnetic materials are not satisfied. We conclude that the existence of spontaneous macroscopic magnetization implies the presence of correlations among the electrons due to their mutual interactions. For example, consider a correlation that would force single occupation of each atomic-like orbital; such a correlation in general would create a non-zero local spin and most probably a local magnetic moment. To examine this possibility in the simplest possible system, consider the case of two neutral hydrogen atoms and let us try to find their ground state as a function of the distance, r , between the two protons. According to the LCAO (which implies uncorrelated motion of the two electrons), the ground state is the doubly occupied bonding molecular orbital, which can be re-expressed as

follows:

$$\begin{aligned}
 \Psi(\mathbf{r}_1, \mathbf{r}_2) &= \psi_b(\mathbf{r}_1)\psi_b(\mathbf{r}_2) = c_A^2 [\phi_A(\mathbf{r}_1) + \phi_B(\mathbf{r}_1)] [\phi_A(\mathbf{r}_2) + \phi_B(\mathbf{r}_2)] \\
 &= c_A^2 [\phi_A(\mathbf{r}_1)\phi_A(\mathbf{r}_2) + \phi_B(\mathbf{r}_1)\phi_B(\mathbf{r}_2) + \phi_A(\mathbf{r}_1)\phi_B(\mathbf{r}_2) \\
 &\quad + \phi_B(\mathbf{r}_1)\phi_A(\mathbf{r}_2)] \\
 &= c_A^2 \Psi_I(\mathbf{r}_1, \mathbf{r}_2) + c_A^2 \Psi_{HL}(\mathbf{r}_1, \mathbf{r}_2)
 \end{aligned} \tag{21.1}$$

where c_A^2 is a normalization constant and ϕ_A, ϕ_B are the ground electronic states of atom A and atom B respectively. The ionic-like state $\Psi_I(\mathbf{r}_1, \mathbf{r}_2) \equiv \phi_A(\mathbf{r}_1)\phi_A(\mathbf{r}_2) + \phi_B(\mathbf{r}_1)\phi_B(\mathbf{r}_2)$ places both electrons on the same atom, while the so-called *Heitler–London* state $\Psi_{HL}(\mathbf{r}_1, \mathbf{r}_2) \equiv \phi_A(\mathbf{r}_1)\phi_B(\mathbf{r}_2) + \phi_A(\mathbf{r}_2)\phi_B(\mathbf{r}_1)$ never allows the two electrons to be in the same atom. If we give ourselves the freedom to choose different coefficients in the linear combination of Ψ_I and Ψ_{HL} , i.e., if we try a ground state $\Psi_c(\mathbf{r}_1, \mathbf{r}_2)$ of the following form with an appropriate selection of the ratio c_I/c_{HL}

$$\Psi_c(\mathbf{r}_1, \mathbf{r}_2) = c_I \Psi_I(\mathbf{r}_1, \mathbf{r}_2) + c_{HL} \Psi_{HL}(\mathbf{r}_1, \mathbf{r}_2), \tag{21.2}$$

we expect to obtain a ground state energy lower than that of $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ in (21.1). Indeed, if $r = d$, where d is the bond length of the molecule H_2 , the optimum value of this ratio, which minimizes the total energy, was found to be 0.175 instead of the 1 given by (21.1). Furthermore, as the distance r increases, we expect the ratio c_I/c_{HL} to further decrease and to tend to zero as $r \rightarrow \infty$. The reason is that in the limit of very large r , $V_2 \equiv \langle \phi_A(\mathbf{r}_1) | \hat{H}_1 | \phi_B(\mathbf{r}_1) \rangle$ tends to zero, while the mutual Coulomb repulsion of two electrons in the same atom, $\langle \Psi_I | (e^2/4\pi\epsilon_0 r_{12}) | \Psi_I \rangle / \langle \Psi_I | \Psi_I \rangle$, adds to the total energy an amount U (which for hydrogenic wave function ϕ_A, ϕ_B is equal to $(55/128)(e^2/4\pi\epsilon_0 a_B) = 11.69 \text{ eV}$); thus, the inclusion of Ψ_I in (21.2) in the limit $r \rightarrow \infty$ increases the potential energy substantially without any gain in the kinetic energy, since $V_2 \rightarrow 0$. Hence, in the limit $r \rightarrow \infty$

$$\Psi_c \rightarrow \Psi_{HL}. \tag{21.3}$$

We conclude that in the limit $U/|V_2| \gg 1$ the double occupation is energetically unfavorable, and hence, the total electronic spin at each atom is equal to $1/2$ giving rise to an instantaneous atomic magnetic moment equal to $g_s \mu_B \mathbf{s}$ ($g \simeq 2$). The next question is whether the magnetic moments in the two atoms are “parallel” or “antiparallel”.

The answer involves the Pauli principle, which requires the total wave function of the two electrons (including spin) to be antisymmetric under the exchange, $1 \rightleftharpoons 2$. This total wave function can be written as the product of a spatial part $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ times a spin function, e.g. $X(s_1, s_2)$ if the spin-orbit interactions are neglected. Thus, if the spatial wave function is symmetric under the exchange $\mathbf{r}_1 \rightleftharpoons \mathbf{r}_2$ (as the ones we considered up to now), the spin wave function ought to be antisymmetric, which implies that the total spin $\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2$ must be zero. On the other hand, an antisymmetric spatial

wave function requires a symmetric spin function, which means that the total spin, $S = 1$, with three possible projections $S_z = 1$, $S_z = 0$, and $S_z = -1$. For obvious reasons, the $S = 1$ configuration is called the *triplet state*, while the $S = 0$ is called the *singlet state*. Let us call also singlet, $\Psi_s(\mathbf{r}_1, \mathbf{r}_2)$, the spatial state associated with $S = 0$ and triplet $\Psi_t(\mathbf{r}_1, \mathbf{r}_2)$, the spatial state associated with $S = 1$ and let $\hat{H} = \hat{H}_1 + \hat{H}_2 + e^2/4\pi\epsilon_0 r_{12}$ be the Hamiltonian of the two electrons (without relativistic corrections), where $H_i = (\mathbf{p}_i^2/2m) - (e^2/4\pi\epsilon_0 r_{iA}) - (e^2/4\pi\epsilon_0 r_{iB})$ ($i = 1, 2$). Whether the total spin will be $S = 1$ (triplet) or $S = 0$ (singlet) would depend on whether $\Psi_t(\mathbf{r}_1, \mathbf{r}_2)$ or $\Psi_s(\mathbf{r}_1, \mathbf{r}_2)$ produces the lowest possible energy, or equivalently, on the sign of the difference

$$2J \equiv \left\langle \Psi_{s \min} \left| \hat{H} \right| \Psi_{s \min} \right\rangle - \left\langle \Psi_{t \min} \left| \hat{H} \right| \Psi_{t \min} \right\rangle, \quad (21.4)$$

where the subscript min indicates the singlet or triplet state that produces the minimum energy. J is called the *exchange interaction*. If $J > 0$, then the ground state is triplet ($S = 1$), while, if $J < 0$, the ground state is singlet. Within the Heitler–London approximation we have

$$\Psi_{s \min} \simeq \frac{1}{\sqrt{2(1+\ell^2)}} [\phi_A(\mathbf{r}_1)\phi_B(\mathbf{r}_2) + \phi_A(\mathbf{r}_2)\phi_B(\mathbf{r}_1)], \quad (21.5)$$

$$\Psi_{t \min} \simeq \frac{1}{\sqrt{2(1-\ell^2)}} [\phi_A(\mathbf{r}_1)\phi_B(\mathbf{r}_2) - \phi_A(\mathbf{r}_2)\phi_B(\mathbf{r}_1)], \quad (21.6)$$

where ℓ is the overlap integral $\ell \equiv \langle \phi_A(\mathbf{r}_1) | \phi_B(\mathbf{r}_1) \rangle$ and ϕ_A, ϕ_B are normalized to unity.

Problem 21.1t. Using (21.5) and (21.6), show that

$$2J = \frac{D + E}{1 + \ell^2} - \frac{D - E}{1 - \ell^2}, \quad (21.7)$$

where

$$D \equiv \left\langle \phi_A(\mathbf{r}_1)\phi_B(\mathbf{r}_2) \left| \hat{H} \right| \phi_A(\mathbf{r}_1)\phi_B(\mathbf{r}_2) \right\rangle, \quad (21.8)$$

$$E \equiv \left\langle \phi_A(\mathbf{r}_1)\phi_B(\mathbf{r}_2) \left| \hat{H} \right| \phi_B(\mathbf{r}_1)\phi_A(\mathbf{r}_2) \right\rangle. \quad (21.9)$$

If ϕ_A, ϕ_B were orthogonal, i.e., if $\ell = 0$, then $J = E$, where E is called the *exchange integral*; furthermore, if $\ell = 0$, then

$$J = E = \left\langle \phi_A(\mathbf{r}_1)\phi_B(\mathbf{r}_2) \left| \frac{e^2}{4\pi\epsilon_0 r_{12}} \right| \phi_B(\mathbf{r}_1)\phi_A(\mathbf{r}_2) \right\rangle, \quad (21.10)$$

which means that J is positive and that the triplet state is energetically favorable. This is the physical explanation for the first Hund's rule stating that out of all the electronic configurations with the same L in an atom a term with the highest possible value of the total spin S has the lowest energy.

For hydrogen-like wavefunctions ϕ_A, ϕ_B , the overlap ℓ is not zero and the expression (21.7) becomes for very large r :

$$J \simeq \left\langle \phi_A(\mathbf{r}_1) \phi_B(\mathbf{r}_2) \left| \Delta \hat{H} \right| \phi_B(\mathbf{r}_1) \phi_A(\mathbf{r}_2) \right\rangle, \quad r \rightarrow \infty, \quad (21.11)$$

where

$$\Delta \hat{H} = \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{e^2}{4\pi\epsilon_0 r} - \frac{e^2}{4\pi\epsilon_0 r_{1B}} - \frac{e^2}{4\pi\epsilon_0 r_{2A}}. \quad (21.12)$$

Since $\Delta \hat{H}$ has both positive and negative terms, the sign of J is not obvious a priori. An explicit evaluation of J based on the asymptotic limit of (21.11) and (21.12) gives (in atomic units)

$$J \simeq \left[-\frac{28}{45} + \frac{2\gamma}{15} + \frac{2}{15} \ell n \rho \right] \rho^3 e^{-2\rho}, \quad \rho \equiv \frac{r}{a_B} \gg 1, \quad (21.13)$$

where $\gamma = 0.577215\dots$ is Euler's constant. Equation (21.13) shows that J is negative up to $\rho = 59.7$ and beyond this value becomes positive (if we have used (21.11) instead of its asymptotic value (21.13), the change from negative to positive J will occur at $\rho = 49.5$). An accurate calculation of J , which employs more realistic wave functions than the triplet and singlet H-L ones, shows that J is always negative for the system $H-H$ and that its asymptotic value for very large ρ is as follows (in atomic units).¹

$$J = -0.818 \rho^{5/2} e^{-2\rho} + \mathcal{O}(\rho^2 e^{-2\rho}). \quad (21.14)$$

Problem 21.2t. Show that $\mathbf{s}_1 \cdot \mathbf{s}_2 = 1/4$ for the triplet state and that $\mathbf{s}_1 \cdot \mathbf{s}_2 = -3/4$ for the singlet state

Hint. $\mathbf{S}^2 = \mathbf{s}_1^2 + \mathbf{s}_2^2 + 2\mathbf{s}_1 \cdot \mathbf{s}_2$.

Based on the result of Problem 21.2t, we can write the Hamiltonian $\hat{H}$ in the subspace of the four states $\Psi_{s \min}, \Psi_{t \min, 1}, \Psi_{t \min, 0}$, and $\Psi_{t \min, -1}$ as follows:

$$\hat{H} = \frac{1}{4} E_s + \frac{3}{4} E_t - 2J \mathbf{s}_1 \cdot \mathbf{s}_2, \quad (21.15)$$

where $\hat{H} \Psi_{s \min} = E_s \Psi_{s \min}$ and $\hat{H} \Psi_{t \min} = E_t \Psi_{t \min}$.

The quantity J we calculated for the system $H-H$ is of the type called *direct exchange interaction*, because it is due to the direct overlap of the orbitals of the two neighboring magnetic atoms times the Coulomb interaction. In real materials, more complicated magnetic interactions appear, such as the so-called *superexchange interactions*, where magnetic atoms (or ions) interact not through direct overlap of their orbitals, but through the mediation of a third nonmagnetic atom (or ion), which is placed in between them so that its orbitals overlap with the orbitals of both magnetic atoms (or ions). In other cases, e.g., in lanthanides, the coupling is again indirect but not through a nonmagnetic atom (or ion) but through the conduction electrons, which overlap

¹ See Vol. IIB of the series entitled *Magnetism* ed. by Rado and Suhl [Ma172], p. 68.

with the orbitals of the magnetic atoms (or ions); this kind of coupling is called *indirect exchange interaction* or *RKKY interaction* (from the names of Ruderman, Kittel, Kasuya, Yosida [21.1–21.3]). Of special interest is the case of magnetic 3d materials, e.g., iron, where the 3d electrons responsible for magnetism are, at the same time partially delocalized contributing thus to the conductivity; this phenomenon is known as *itinerant magnetism* and the corresponding effective coupling J is called *itinerant exchange interaction*.

The main conclusion of this introductory section is as follows. When the electron–electron Coulomb repulsion, U , is sufficiently larger than the transfer matrix element $|V_2|$, instantaneous local magnetic moments are formed; at the same time, the Coulomb repulsion, U , in combination with Pauli’s principle (dictating antisymmetric wave functions (including spin)) gives rise to exchange interactions, which couple the local magnetic moments and may lead to macroscopic magnetic order.

We shall test this conclusion in practice by examining the possibility of magnetic phase formation within the framework of the two basic models (JM and LCAO) enriched with the inclusion of Coulomb el-el repulsions.

21.2 Jellium model and el-el Coulomb Repulsion

21.2.1 Is There Ferromagnetic Order in the JM?

Ferromagnetism within the framework of the JM implies that the number of electrons with spin up, N_+ is larger than the number of electrons with spin down, N_- . Let us introduce the quantity $\lambda \equiv (N_+ - N_-)/N_e$, where $N_e = N_+ + N_-$, and the corresponding concentrations $n_+ = N_+/V$, $n_- = N_-/V$ and $n_e = N_e/V$. Then we have

$$N_{\pm} = N_e(1 \pm \lambda)/2, \quad n_{\pm} = n_e(1 \pm \lambda)/2, \quad (21.16)$$

$$\bar{r}_{s\pm} = \left(\frac{3}{4\pi n_{\pm}}\right)^{1/3} \frac{1}{a_B} = \bar{r}_s \left(\frac{2}{1 \pm \lambda}\right)^{1/3}. \quad (21.17)$$

The magnetization, M , can be expressed in terms of λ :

$$M = \mu_B \frac{N_+ - N_-}{V} = \mu_B (n_+ - n_-) = \mu_B n_e \lambda. \quad (21.18)$$

Since both the kinetic energy $\left(E_k \sim \int d^3r \left[n_+^{5/3} + n_-^{5/3}\right]\right)$ and the potential energy (in the framework of the LSDA and the JM $E_p = E_{xc} \sim \int d^3r \left[n_+^{4/3} + n_-^{4/3}\right]$, see p. 219) are additive in the two directions of spin, Eq. (4.40) for the total energy E_t becomes in the current case

$$\frac{E_t}{N_a E_0} = \frac{a}{2\bar{r}_a^2} \left[(1 + \lambda)^{5/3} + (1 - \lambda)^{5/3}\right] - \frac{\gamma}{2\bar{r}_a} \left[(1 + \lambda)^{4/3} + (1 - \lambda)^{4/3}\right]. \quad (21.19)$$

Problem 21.3t. Show that the kinetic energy, E_K , within the framework of the JM is given by

$$E_K = \frac{3(6\pi^2)^{2/3}}{10} \frac{\hbar^2}{m_e} \int d^3r \left[n_+^{5/3} + n_-^{5/3} \right]. \quad (21.20)$$

The minimum of the total energy, given by (21.19) as a function of λ and for *constant* $\bar{r}_a$, is either at $\lambda = 0$ or at $\lambda = 1$. This can be proved by taking the first and the second derivative of E_t with respect to λ and showing that in the range $0 \leq \lambda \leq 1$ there is only one minimum. If $\bar{r}_a$ is less than $2.26a/\gamma$, the minimum of E_t under constant $\bar{r}_a$ occurs at $\lambda = 0$, while if $\bar{r}_a > 2.26a/\gamma$ the minimum occurs at $\lambda = 1$, i.e., when the magnetization has the maximum possible value. The equilibrium value of $\bar{r}_a$ when $\lambda = 0$ is $\bar{r}_a = 2a/\gamma$. Thus if we start from the paramagnetic state $\lambda = 0$ and the corresponding equilibrium value of $\bar{r}_a = 2a/\gamma$ and we continuously increase λ , *keeping $\bar{r}_a$ constant*, the energy $E_t(\lambda)$ would be larger than $E_t(0)$ for all values of λ in the range $0 < \lambda \leq 1$. Based on this picture, one would conclude that the paramagnetic state is the stable one. A reasonable objection to this line of arguing is the following: it is unphysical to keep $\bar{r}_a$ constant as one increases λ from zero; the system at each value of λ would relax and adjust $\bar{r}_a$ to obtain the equilibrium value of $\bar{r}_a(\lambda)$ for each value of λ . We have then that

$$\bar{r}_a(\lambda) = \bar{r}_a(0) \frac{(1+\lambda)^{5/3} + (1-\lambda)^{5/3}}{(1+\lambda)^{4/3} + (1-\lambda)^{4/3}}. \quad (21.21)$$

By substituting (21.21) in (21.19), we obtain

$$E_t(\lambda) = E_t(0) \frac{\left[(1+\lambda)^{4/3} + (1-\lambda)^{4/3} \right]^2}{2 \left[(1+\lambda)^{5/3} + (1-\lambda)^{5/3} \right]}. \quad (21.22)$$

It is easy to see by plotting the expression (21.22) for $E_t(\lambda)$ vs λ that the minima appear at $\lambda = 0$ and $\lambda = 1$ and that they are equal (see Fig. 21.1). This result taken at face value indicates that the question paramagnetic vs fully ferromagnetic state remains undecided within the JM. However, one can argue in favor of the paramagnetic state ($\lambda = 0$). The reasoning is as follows. In the fully ferromagnetic state the total spin state is fully symmetric, which means that the spatial state is fully antisymmetric; as such it has achieved the minimization of el-el Coulomb repulsions and no further reduction seems possible. On the other hand, the uncorrelated paramagnetic state (corresponding to $\lambda = 0$) offers plenty of room for incorporating correlations that will further reduce the el-el Coulomb repulsions. Thus, we expect that a more sophisticated calculation within the JM will lower the paramagnetic total energy relative to the fully ferromagnetic state. In conclusion, we expect that the JM

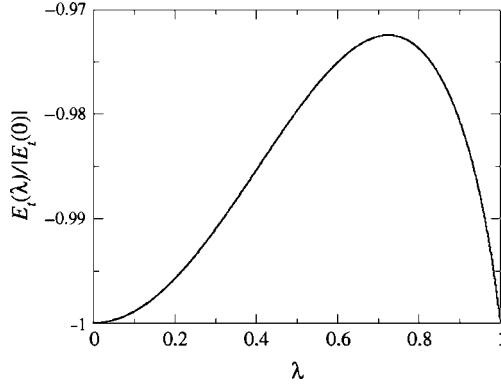


Fig. 21.1. Plot of the reduced total energy $E_t(\lambda)/|E_t(0)|$ of the ferromagnetic state ($\lambda \neq 0$) with magnetization $M = \mu_B n \lambda$ is plotted vs. λ according to (21.22)

will never exhibit ferromagnetism. This conclusion is supported by various calculations² taking into account approximately the role of el-el interactions.

21.2.2 Magnetic Susceptibility Within the JM in the Presence of Electron-Electron Interactions

From (20.16) it follows that in the presence of an auxiliary magnetic field the total energy acquires an extra term

$$E_t(M, H) = E_t(M) + \frac{1}{2} \mu_0 V H^2, \quad \text{SI.} \quad (21.23)$$

(in G-CGS μ_0 must be replaced by $1/4\pi$). At $T = 0$ K and under constant pressure and number of particles, (20.14) gives

$$dE_t(M, H) = V \mathbf{H} d\mathbf{B} = \mu_0 V H dH + \mu_0 V H dM \quad (21.24)$$

(in G-CGS $dE_t(M, H) = V \mathbf{H} d\mathbf{B}/4\pi = V H dH/4\pi + V H dH M$). Comparing the differential of $E_t(M, H)$ obtained from (21.23) with that of (21.24), we have:

$$\mu_0 V H = \frac{\partial E_t(M)}{\partial M}. \quad (21.25)$$

Differentiating once more (21.25) with respect to M we have, taking into account (21.18) and the definition of χ as $\partial M/\partial H$ in the limit $M \sim H \rightarrow 0$

$$\frac{\partial H}{\partial M} \equiv \frac{1}{\chi} = \frac{1}{\mu_0 V} \frac{\partial^2 E_t}{\partial M^2} = \frac{1}{\mu_0 \mu_B^2 n_e} \frac{\partial^2 (E_t/N_e)}{\partial \lambda^2} \quad (21.26)$$

(in G-CGS, $\chi^{-1} = (1/\mu_B^2 n_e) (\partial^2 (E_t/N_e)/\partial \lambda^2)$).

² See, e.g., the book by C. Herring (Ma173): *Exchange Interactions among Itinerant Electrons*, Academic Press, New York.

Problem 21.4t. Show that the energy E_t/N_e (per electron) can be expressed in terms of $\bar{r}_s$ (instead of $\bar{r}_a$) as follows

$$\frac{E_t(0)}{N_e E_0} = \frac{a'}{\bar{r}_s^2} - \frac{\gamma'}{\bar{r}_s}, \quad a' = \frac{a}{\zeta^{5/3}}, \quad \gamma' = \frac{\gamma}{\zeta^{4/3}}, \quad (21.27)$$

Then, using (21.19) and (21.26) and the expressions $\chi_P = 2\mu_0\mu_B^2\rho_F/V$ (in G-CGS set μ_0 equal to one) for the Pauli susceptibility together with the relation, $\rho_{FV} \equiv \rho_F/V = 3n_e/4E_F$, show that

$$\chi = \chi_P \frac{1}{1-\eta}, \quad (21.28)$$

where

$$\eta = \frac{2}{5} \frac{\gamma'}{\bar{r}_s} \frac{\bar{r}_s^2}{a'} = \frac{2}{5} \frac{|\bar{E}_P|}{\bar{E}_k}. \quad (21.29)$$

The last equation in (21.29) was obtained by taking into account that $a'/\bar{r}_s^2$ is the kinetic energy $\bar{E}_k$ (per electron in atomic units) and $\gamma'/\bar{r}_s$ is the absolute value of the potential energy $|\bar{E}_P|$ (per electron in atomic units). At equilibrium, the radius per electron, $\bar{r}_s$, equals $2a'/\gamma'$ and consequently, $\eta = 4/5$; hence, (21.19) in the limit $\lambda \rightarrow 0$ leads to the conclusion that the spin susceptibility in the presence of exchange and correlation energy is five times larger than χ_P .

$$\chi = 5\chi_P, \quad (21.30)$$

no matter what the values of a' and γ' in (21.27) are. The same substantial enhancement of the Pauli susceptibility (by a factor of 5) is obtained by using the alternative expression (21.22) for the total energy in the limit $\lambda \rightarrow 0$.

The fact that the interaction-induced enhancement of the magnetic spin susceptibility does not force χ to blow up indicates that the paramagnetic state of the JM (at least within the approximation (21.19)) is stable against the ferromagnetic phase. The stability of the latter, if it were to be realized, would require η to be larger than, or equal to, one.

Problem 21.5t. Show that η within the JM can be written as follows:

$$\eta = \xi\chi_P = J_P\rho_F = 8|E_P|\rho_F/9N_e = 2|E_P|/3E_F, \quad (21.31)$$

where

$$\xi = \frac{4|E_P|}{9\mu_0\mu_B^2 n_e} = \frac{16}{27} \frac{m_e c^2}{E_0} |\bar{E}_P| \bar{r}_s^3, \quad (21.32)$$

$$\chi_P = 2\mu_0\mu_B^2\rho_{FV} = \frac{9}{8} \frac{E_0}{m_e c^2} \frac{1}{\bar{E}_F} \frac{1}{\bar{r}_s^3}, \quad (21.33)$$

$$J_P = \frac{8}{9} \frac{|\bar{E}_P|}{N_e}, \quad (21.34)$$

J_P is the change in the absolute value of the potential energy per electron, $|E_P|$, by flipping one spin, i.e., by going from state $N_+ = N_- \equiv N/2$ to the state $N_+ = (N/2) + 1$, $N_- = (N/2) - 1$; ρ_F is the DOS at E_F per spin.

In view of (21.31), the magnetic susceptibility given by (21.28) can be re-expressed as follows

$$\chi = \frac{\chi_p}{1 - \xi\chi_p} = \frac{\chi_p}{1 - J_p\rho_F}. \quad (21.35)$$

In the JM and within the expression (21.19) for the energy the denominator of (21.35) does not blow up indicating the stability of the paramagnetic phase against the ferromagnetic one. However, in more realistic cases, where there is non-uniform distribution of the electronic charge, and consequently, stronger el-el repulsion and/or peaks or high values of $\rho(E)$ at E_F , the product $J_p\rho_F$ may exceed one and χ may blow up indicating a transition to the ferromagnetic phase. The inequality

$$\xi\chi_p = J_p\rho_F \geq 1, \quad (21.36)$$

is the so-called *Stoner criterion* for the appearance of ferromagnetism. Transition metals toward the right end of the 3d series are expected to have high el-el interactions and high DOS at E_F (because of the narrow d band); hence, they are the best candidates for ferromagnetic behavior. This expectation is confirmed in nature, since Fe, Co, and Ni are the only elemental solids (together with the lanthanides Gd and Dy) that are ferromagnets.

21.2.3 Is There Antiferromagnetic Order in the JM?

To allow for the possibility of antiferromagnetic (AF) order in the JM (in the presence of el-el interactions), the spin direction must be a periodic function of the position $\mathbf{r}$. Any direction can be determined by two angles θ and ϕ , where θ is the angle between the direction of the spin and a fixed axis, which we shall choose as the z -axis ($0 \leq \theta \leq \pi$) and ϕ determines the direction of the projection of the spin in the $x - y$ plane ($0 \leq \phi < 2\pi$). We shall assume that the angle θ does not depend on the position $\mathbf{r}$, but it is a function of the wave vector $\mathbf{k}$ characterizing each plane wave solution. Translational invariance of $\partial\phi/\partial\mathbf{r}$ implies that the angle ϕ ought to be a linear function of the position vector $\mathbf{r}$: $\phi(\mathbf{r}) = \mathbf{q} \cdot \mathbf{r}$, where $\mathbf{q}$ is an auxiliary wave vector characterizing the rotation angle ϕ . The single-electron eigenfunction, the spin of which has the direction $\theta_{\mathbf{k}}$, $\phi = \mathbf{q} \cdot \mathbf{r}$, is of the form

$$u_+(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k} \cdot \mathbf{r}} \begin{pmatrix} a_+(\mathbf{r}; \mathbf{k}, \mathbf{q}) \\ b_+(\mathbf{r}; \mathbf{k}, \mathbf{q}) \end{pmatrix}, \quad (21.37)$$

where

$$a_+ = e^{-i\mathbf{q} \cdot \mathbf{r}/2} \cos \frac{\theta_{\mathbf{k}}}{2}, \quad (21.38)$$

$$b_+ = e^{i\mathbf{q} \cdot \mathbf{r}/2} \sin \frac{\theta_{\mathbf{k}}}{2}. \quad (21.39)$$

Problem 21.6t. Show that the plane wave (21.37) is an eigenfunction of $\boldsymbol{\sigma} \cdot \mathbf{n}$ with eigenvalue one, where $\mathbf{n} = \hat{\mathbf{x}}_0 \sin \theta_{\mathbf{k}} \cos \phi + \hat{\mathbf{y}} \sin \theta_{\mathbf{k}} \sin \phi + \hat{\mathbf{z}} \cos \theta_{\mathbf{k}}$ and $\boldsymbol{\sigma} = 2\mathbf{s}$ in the vector the components of which are the three Pauli matrices. By replacing $\theta_{\mathbf{k}}$ by $\pi - \theta_{\mathbf{k}}$ and ϕ by $\phi + \pi$, we obtain $u_-(\mathbf{r})$, which is eigenfunction of $\boldsymbol{\sigma} \cdot \mathbf{n}$ with an eigenvalue minus one, i.e., $u_-(\mathbf{r})$ has a spin direction opposite to that of $u_+(\mathbf{r})$. (The Pauli matrices are given in (11.61)).

Notice that for the choice $\theta_{\mathbf{k}} = 0$, $u_{\pm}(\mathbf{r})$ reduces to

$$u_+(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i(\mathbf{k} - \frac{1}{2}\mathbf{q}) \cdot \mathbf{r}} \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad (21.40)$$

$$u_-(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i(\mathbf{k} + \frac{1}{2}\mathbf{q}) \cdot \mathbf{r}} \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \quad (21.41)$$

The functions u_+ , u_- (see (21.37) till (2.39)) are an appropriate basis for describing a helical AF state known as *spin density wave* (SDW). However, working in this basis is lengthy and rather tedious. For this reason, we shall omit the intermediate calculations and proofs and we shall restrict ourselves in quoting (and commenting on) the final results. In Fig. 21.2a and for fixed value³ of $\mathbf{q}$, $|\mathbf{q}| = 2k_F$, we plot the spherical Fermi surfaces in $\mathbf{k}$ -space corresponding to (21.40) (circle at the right) and to (21.41) (circle at the left). We have chosen this value of q , because, usually, it is the one which produces the lowest energy antiferromagnetic SDW state (see below). In Fig. 21.2b we plot the eigenenergy $\varepsilon_+(\mathbf{k})$ corresponding to the state (21.40) (spin up, curve dcb) and $\varepsilon_-(\mathbf{k})$ corresponding to the state (21.41) (spin down, curve $a'b'c'd'$). We shall get exactly the same plot as in Fig. 21.2b, but with a different choice of $\theta_{\mathbf{k}}$: indeed, if in $u_+(\mathbf{r}; \theta_{\mathbf{k}}, \phi)$ and $u_-(\mathbf{r}; \theta_{\mathbf{k}}, \phi)$ we choose $\theta_{\mathbf{k}} = 0$ (for $\mathbf{k} \cdot \mathbf{q} > 0$), $\theta_{\mathbf{k}} = \pi$ ($\mathbf{k} \cdot \mathbf{q} < 0$), and $\theta_{\mathbf{k}} = \pi/2$ (for $\mathbf{k} \cdot \mathbf{q} = 0$), we get the same plot, but now the correspondence between $u_{\pm}$ and spin direction for $\mathbf{k} \cdot \mathbf{q} < 0$, (i.e., for $k_{\parallel} < 0$), changes, because now u_+ is associated with spin down and u_- with spin up (see (21.38) and (21.39)); on the otherhand for $\mathbf{k} \cdot \mathbf{q} > 0$, (i.e. for $k_{\parallel} > 0$), the correspondence remains as before. Hence, with the new choice of $\theta_{\mathbf{k}}$, ε_+ is now associated with the lower branch $a'b'cc'b$ and ε_- is now associated with the upper branch $dc'cd'$.

We assume that the upper branch in Fig. 21.2(b, c) is empty, so that it does not contribute to the total energy E_t , which is obtained by summing up all occupied $\mathbf{k}'$ s in the lower branch. The angle $\theta_{\mathbf{k}}$ in the general case will be neither zero nor π , but it will be allowed to vary with $\mathbf{k}$ as shown in Fig. 21.2c. This variation, as well as the size of q , will be determined by the minimization

³ The value $|\mathbf{q}| = 2k_F$ corresponds also to the well - known phenomenon of the Kohn anomalies, and also to the “nesting - condition” of two opposite tangential planes of a k_F - sphere.

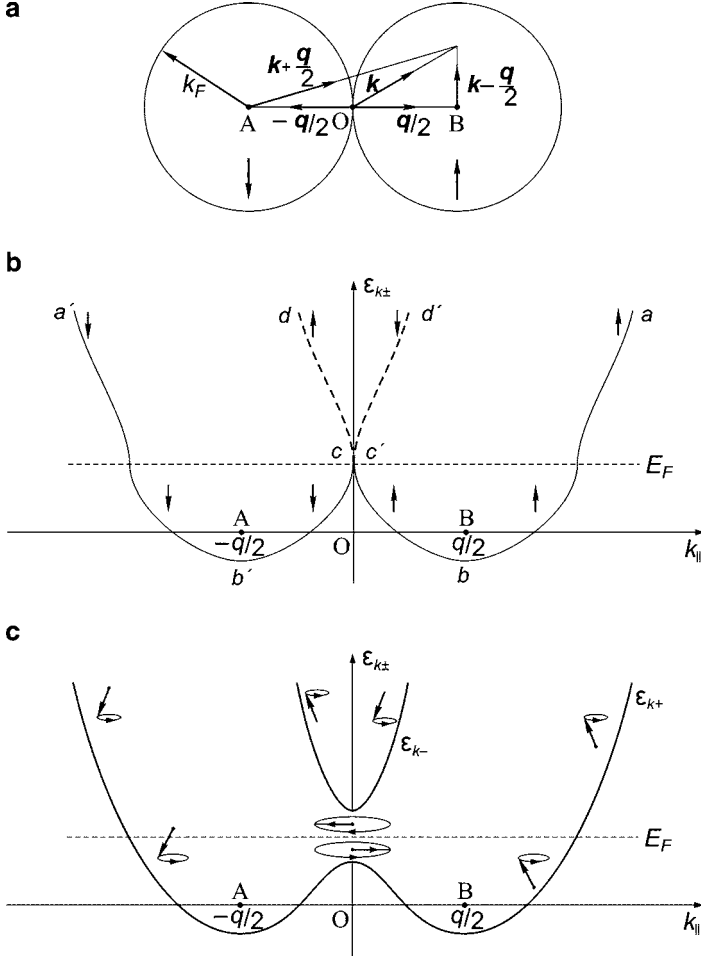


Fig. 21.2. (a) The Fermi surfaces corresponding to (21.40) (spin up circle at the right) and (21.41) (spin down, circle at the left) respectively; q was chosen equal $2k_F$ because this value is usually favorable for SDW order. (b) Plot of the eigenenergies ϵ_+ (line $dcba$), and ϵ_- (line $a'b'c'd'$) vs $k_{\parallel}$ where $k_{\parallel} \equiv \mathbf{k} \cdot \mathbf{q} / |\mathbf{q}|$; ϵ_+ and ϵ_- correspond to fixed direction of the spin either parallel or antiparallel to the z -axis, i.e., to the states (21.40) and (21.41) respectively; on the other hand, a different choice of $\theta_{\mathbf{k}}$ ($\theta_{\mathbf{k}} = 0$ for $k_{\parallel}$ positive and $\theta_{\mathbf{k}} = \pi$ for $k_{\parallel}$ negative) gives the same overall plot but associates the lower branch (continuous line $a'b'c'ba$) with ϵ_+ and the upper branch (dashed line $dcc'd'$) with ϵ_- . This association makes more transparent how the transition to the SDW may take place. (c) If the SDW is lower in energy, a gap will open up between the lower and the upper branch at $k_{\parallel} = 0$ and $\theta_{\mathbf{k}}$ would be neither 0 nor π but will vary with $k_{\parallel}$ in the two branches as shown by the arrows. This variation will be such as to minimize the total energy

of the total energy,⁴ E_t . By implementing this minimization with respect to q and θ_k , we end up with the following equation for the AF gap, Δ , at $k = 0$ (in atomic units)

$$\Delta = \tilde{v} \int \frac{d^3k}{(2\pi)^3} n_{k+} \frac{\Delta}{\sqrt{\Delta^2 + k_{\parallel}^2 q^2}}, \quad (21.42)$$

where Δ is a function of $\mathbf{q}$, which minimizes E_t , and $\tilde{v}$ is the strength of the el-el repulsion assumed to be of the simple form $v(\mathbf{r} - \mathbf{r}') = \tilde{v} \delta(\mathbf{r} - \mathbf{r}')$. The $\Delta = 0$ solution of (21.42) corresponds to the paramagnetic state. On the other hand, if there is a nonzero Δ solution of (21.42), it can be proved that $\Delta(\mathbf{q})$ is equal to $(\tilde{v}/\mu_B) \tilde{M}_x(\mathbf{q})$, where $\tilde{M}_x(\mathbf{q})$ is the only nonzero Fourier component of the magnetization $M_x(\mathbf{r})$ (see Problem 21.4). Thus a nonzero Δ implies an AF magnetization; furthermore, the nonzero Δ solution to (21.42), if any, has a lower total energy than the paramagnetic one (at least in the limit of small $\tilde{v}$). Hence, if a $\Delta > 0$ solution of (21.42) exists, the paramagnetic state is unstable against the competition with the SDW AF state. We shall examine whether Δ is zero or nonzero in the limit of very small $\tilde{v}$. From (21.42) we have, assuming $\Delta \neq 0$

$$\frac{1}{\tilde{v}} = \int \frac{d^3k}{(2\pi)^3} \frac{1}{\sqrt{\Delta^2 + k_{\parallel}^2 q^2}} \leq \int \frac{d^3k}{(2\pi)^3} \frac{1}{k_{\parallel} q}, \quad (21.43)$$

where minimization of energy leads, under certain conditions, to $q = 2k_F$; $\mathbf{k}$ is restricted in the interior of the two touching Fermi spheres shown in Fig. 21.2a. The last integral in (21.43) can be calculated analytically and the result is finite and equal to $k_F/2\pi^2$ (in atomic units). Hence, the assumption $\Delta \neq 0$ led to inconsistency, since the lhs of (21.43) tends to infinity as $\tilde{v} \rightarrow 0$, while the rhs is finite and less than $k_F/2\pi^2$. It is worthwhile to point out that the analog of (21.43) in 1D has a nonzero Δ for all values of $\tilde{v}$. Indeed, we have

$$\frac{1}{\tilde{v}} = \frac{1}{\pi q} \int_0^{k_0} \frac{dk}{\sqrt{(\Delta/q)^2 + k^2}} = \frac{1}{\pi q} \sinh^{-1} \left(\frac{k_0 q}{\Delta} \right), \quad (21.44)$$

where $k_0 = 2k_F$ since $\sum_{|k| < k_0} 1 = N \Rightarrow k_0 = \pi N/L = 2k_F$. Solving (21.44) for Δ , we obtain

$$\Delta = \frac{k_0 q}{\sinh(\pi q/\tilde{v})} \xrightarrow{\tilde{v} \rightarrow 0} 2k_0 q \exp\left(-\frac{\pi q}{\tilde{v}}\right). \quad (21.45)$$

The different result in 3D vs 1D is due to phase space: in 3D, in contrast to the 1D, the integral $\int d^3k/|k_{\parallel}|$ (obtained for $\Delta = 0$) is finite because the factor

⁴ The eigenenergy ε_+ (and ε_-) is the sum of two parts: the kinetic part, $\varepsilon_+^{(k)}$, and the potential part, $\varepsilon_+^{(p)}$. To avoid double counting of the el-el interaction, the total energy is of the form $E_t = \sum_k n_{k+} \varepsilon_{k+}^{(k)} + \frac{1}{2} \sum_k n_{k+} \varepsilon_{k+}^{(p)}$.

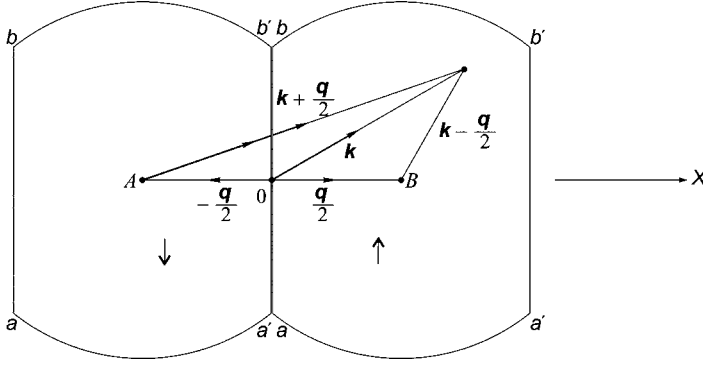


Fig. 21.3. The idealized identical two touching Fermi surfaces $abb'a'$ (one for spin up and the other for spin down) exhibit nesting between the two plane pieces ab and $a'b'$, so that parallel translation by the vector q (normal to both ab and $b'a'$) brings the two pieces to coincidence

k^2 in $d^3k = -k^2 d\phi d(\cos\theta)$ eliminates the singularity in the denominator of the integrand as $k \rightarrow 0$. Notice that such a logarithmic singularity may appear in 3D solids, if the unperturbed Fermi surface exhibits nesting as in Cr (see Fig. 15.8). For simplicity, consider an idealized Fermi surface that has two parallel plane pieces symmetric with respect to its center; then, instead of the shape shown in Fig. 21.2a (two touching spheres), we shall have a shape as in Fig. 21.3, where the touching of the spin-up and spin-down Fermi surfaces is along this plane piece. Then we have

$$\int \frac{d^3k}{|k_{\parallel}|} = 2 \int dk_y dk_z \int_0^q \frac{dk_x}{k_x} = 2S \int_0^q \frac{dk_x}{k_x} + S_0, \quad (21.46)$$

where S is the area of the plane piece and S_0 is finite. Hence, when nesting is present, a logarithmic singularity appears in the integral $\int d^3k/|k_{\parallel}|$, which in turn allows a nonzero value of $\Delta(q)$, where $q = k_0$; k_0 is the vector in k -space that brings the two nesting pieces of the Fermi surface in coincidence (see Fig. 15.8).

21.3 The Hubbard Model

The Hubbard model extends the LCAO by incorporating an extra repulsion term in the Hamiltonian. Thus, it includes the essential competition between kinetic energy, which dictates spreading of the electronic states over the whole extent of the material and el-el interactions, which try to keep the electrons apart from each other.

The simplest version of the Hubbard model consists of the simplest LCAO Hamiltonian (6.11) and (6.12) plus an on-site el-el interaction of the form

$U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$, where $\hat{n}_{i\sigma}$ is the operator of the number of electrons at the atomic site i with spin σ ($\sigma = 1$ means spin up, while $\sigma = -1$ means spin down); the eigenvalues of $\hat{n}_{i\sigma}$ are 1 or 0:

$$\hat{H} = \varepsilon \sum_{i=1}^{N_a} \sum_{\sigma=1, \bar{1}} |i\sigma\rangle \langle i\sigma| + V_2 \sum_i \sum_j' \sum_{\sigma} |i\sigma\rangle \langle j\sigma| + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}. \quad (21.47)$$

The first term in the rhs of (21.47) can be eliminated (without loss of generality) by choosing the zero of energy at the diagonal element, ε . Then, the important parameter in (21.47) is the dimensionless ratio U/V_2 , where V_2 tells the electrons to spread over all N_a atoms uniformly, while U tells them to avoid each other. Equally important for the electrons in choosing the optimum course under these competing “instructions” is their number ζ per atom: $\zeta \equiv N_e/N_a$. The dimensionality, D , of the lattice $\{i\}$ is a third important parameter with the lattice type playing usually a minor role.

The model shown in (21.47), in spite of its simplicity, does not allow exact solutions. Here, we shall employ mean field approximation to compare the total energies of the three simple configurations shown in Fig. 21.4.

The mean field approximation is as follows:

$$\begin{aligned} U \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} &\simeq \varepsilon_{i\uparrow} \hat{n}_{i\uparrow}; & \varepsilon_{i\uparrow} &= U \langle \hat{n}_{i\downarrow} \rangle \\ &\simeq \varepsilon_{i\downarrow} \hat{n}_{i\downarrow}; & \varepsilon_{i\downarrow} &= U \langle \hat{n}_{i\uparrow} \rangle, \end{aligned} \quad (21.48)$$

where the quantities $\langle \hat{n}_{i\uparrow} \rangle$ and $\langle \hat{n}_{i\downarrow} \rangle$ must be determined self-consistently within the mean field approximation. The sum $\langle \hat{n}_{i\uparrow} \rangle + \langle \hat{n}_{i\downarrow} \rangle$ for all the three

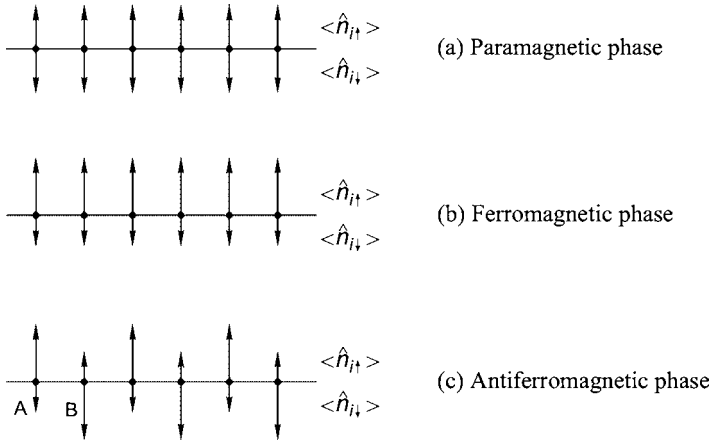


Fig. 21.4. Schematic configuration of the average values $\langle \hat{n}_{i\uparrow} \rangle$ and $\langle \hat{n}_{i\downarrow} \rangle$, of the number of electrons at the site i with spin up or down for the three simple possible phases of the Hubbard model

configurations is assumed to be the same for all sites i (no charge fluctuation) and, consequently,

$$\langle \hat{n}_{i\uparrow} \rangle + \langle \hat{n}_{i\downarrow} \rangle = \frac{N_e}{N_a} = \zeta. \quad (21.49)$$

The difference m , where

$$m = \langle \hat{n}_{i\uparrow} \rangle - \langle \hat{n}_{i\downarrow} \rangle, \quad i = A, \quad (21.50)$$

is proportional to the magnetic moment $m' = g_s \mu_B m / 2$. The quantities $\langle \hat{n}_{i\uparrow} \rangle$ and $\langle \hat{n}_{i\downarrow} \rangle$ can be expressed in terms of m and the known quantity, ζ . We have the following relations by referring to Fig. 21.4 and taking into account (21.48)–(21.50):

$$\langle \hat{n}_{i\uparrow} \rangle_{i=A} = \frac{\zeta + m}{2}, \quad (21.51)$$

$$\langle \hat{n}_{i\downarrow} \rangle_{i=A} = \frac{\zeta - m}{2}, \quad (21.52)$$

$$\varepsilon_{i\uparrow} = \varepsilon_{i\downarrow} = \frac{1}{2} U \zeta, \text{ case (a)}, \quad (21.53)$$

since in case (a) $m = 0$

$$\begin{aligned} \varepsilon_{i\uparrow} &= \frac{1}{2} U (\zeta - m) \\ \varepsilon_{i\downarrow} &= \frac{1}{2} U (\zeta + m) \end{aligned}, \text{ case (b)} \quad (21.54)$$

and

$$\begin{aligned} \varepsilon_{i\uparrow, i=A} &= \varepsilon_{i\downarrow, i=B} = \frac{1}{2} U (\zeta - m) \\ \varepsilon_{i\downarrow, i=A} &= \varepsilon_{i\uparrow, i=B} = \frac{1}{2} U (\zeta + m) \end{aligned}, \text{ case (c)}. \quad (21.55)$$

Having now the periodic Hamiltonians $\hat{H}_{\uparrow}$ and $\hat{H}_{\downarrow}$,

$$\hat{H}_{\sigma} = \sum_i \varepsilon_{i\sigma} |i\sigma\rangle \langle i\sigma| + V_2 \sum_i \sum_j' |i\sigma\rangle \langle j\sigma|, \quad \sigma = \uparrow, \downarrow, \quad (21.56)$$

we can determine the DOS, $\rho_{i\sigma}(E)$, at the site i and for spin σ by generalizing the formula in Problem 10.2s:

$$\rho_{i\sigma}(E) = -\frac{V}{\pi} \text{Im} \int \frac{d^3 k}{(2\pi)^3} \frac{|\langle i\sigma | \mathbf{k} \sigma \rangle|^2}{E + i\epsilon - E_{\sigma}(\mathbf{k})}, \quad (21.57)$$

where $|\mathbf{k} \sigma\rangle$ is the normalized eigenfunction of $\hat{H}_{\sigma}$. The Fermi energy is determined by the relation

$$\int^{E_F} \rho(E) dE = N_e \Rightarrow \int_{E_{G\uparrow}}^{E_F} \rho_{i\uparrow}(E) dE + \int_{E_{G\downarrow}}^{E_F} \rho_{i\downarrow}(E) dE = \zeta. \quad (21.58)$$

All, quantities $\varepsilon_{i\sigma}$, $\rho_{i\sigma}$, $\varepsilon_{G\sigma}$, and E_F depend on m . Finally, the quantity m is determined from (21.50), which gives the self-consistency relation:

$$m = \int_{E_{G\uparrow}}^{E_F} dE \rho_{i\uparrow}(E) - \int_{E_{G\downarrow}}^{E_F} dE \rho_{i\downarrow}(E); \quad i = A. \quad (21.59)$$

The energy per atom is

$$\frac{\langle \hat{H} \rangle}{N_a} = \sum_{\sigma} \int_{E_{G\sigma}}^{E_F} dE \rho_{i\sigma}(E) E - U \langle \hat{n}_{i\uparrow} \rangle \langle \hat{n}_{i\downarrow} \rangle, \quad (21.60)$$

where the last term $-U \langle \hat{n}_{i\uparrow} \rangle \langle \hat{n}_{i\downarrow} \rangle = \frac{1}{4}U(\zeta^2 - m^2)$ corrects the double counting of the el-el interaction in both $\hat{H}_{\uparrow}$ and $\hat{H}_{\downarrow}$.

To implement the approximate scheme defined by (21.48)–(21.60), we need an explicit expression for $\rho_{i\sigma}(E)$. We have obtained in (6.25) such an expression for cases (a) and (b) and for a 1D lattice. In other cases, we have to do the integral in (21.57) numerically. To avoid this trouble, we approximate the 3D DOS for cases (a) and (b) by the following simple relation

$$\rho_{i\sigma}(E) = \frac{2}{\pi B^2} \sqrt{B^2 - (E - \varepsilon + \sigma x)^2}, \quad \sigma = \pm 1, \quad (21.61)$$

where $\varepsilon = \frac{1}{2}U\zeta$, $B = Z|V_2|$, $x = \frac{1}{2}Um$, and Z is the coordination number (the number of nearest neighbor sites) (see also Problem 18.4s).

Problem 21.7t. In the limit $\zeta \ll 1$, compare the energy of the ferromagnetic phase with that of the paramagnetic case using the 3D DOS given by (6.61) or the 1D DOS (6.25) (in (6.25) and for the ferromagnetic case $\varepsilon \rightarrow \varepsilon - \sigma x$).

Hint. Since $\zeta \ll 1$, E_F is close to the lower band edges, $E_{G\sigma}$; hence, $\rho_{i\sigma}$ can be approximated by its limit as $E \rightarrow E_{G\sigma}$.

In Fig. 21.5, we show the phase diagram of the simple Hubbard model obtained in the framework of the mean field approximation (21.48) with the approximate DOS (21.61). In regions P, F, AF cases (a), (b), (c) respectively have the lowest energy among the three. We expect, in the framework of a more accurate theory, that the region P will expand mainly at the expense of the region F and to a lesser degree of the region AF. The argument in support of this expectation is the same as the one presented in Sect. 21.2.1 in the framework of the JM; it is even possible that the region F may disappear altogether. For large values of U/B ($U/B \gtrsim 5$), where $B \equiv Z|V_2|$, and in the region to the right of F/AF solid line, up to the dashed line, the plot of $\langle \hat{H} \rangle$ vs ζ has a negative second derivative indicating an instability toward a two-phase state (similar to the Maxwell construction in the van der Waals equation of state in non-ideal atomic or molecular gases). One of the two phases is the AF one, case (c), which is the only one as $\zeta \rightarrow 1$ (at least for U/B above a certain critical value). In Fig. 21.6, we plot the calculated size of the quantity m vs

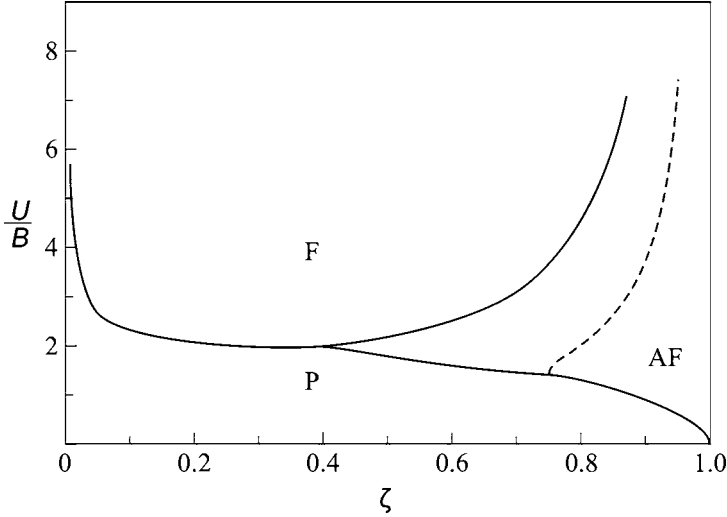


Fig. 21.5. Phase diagram of the simple Hubbard model (21.47) within the framework of the mean field approximation and approximate 3D DOS (21.61) ($B \equiv Z|V_2|$). The continuous lines separate the $\zeta, U/B$ plane into three regions: in region P the paramagnetic case (a) has lower energy than both the ferromagnetic (F) case (b), and the AF case (c); in region F, case (b) has the lower energy among the three and in region AF, case (c) has the lower energy among the three. In view of the approximations used and our restriction to only three configurations we cannot conclude that this phase diagram is correct. Actually we expect that the P region will expand at the expense of region F, which may disappear altogether. The AF region may remain to the right of the dashed line. The results for ζ and for $2 - \zeta$ are the same

U/B keeping $\zeta = 1$. For $U/B \simeq 2$, m is close to the maximum possible value of $m = 1$.

The mean field approximation to the simple Hubbard model allows also a rough estimate of the indirect exchange interaction J in the $\zeta = 1$ AF case by flipping one spin and calculating the corresponding change $\delta \langle \hat{H} \rangle$ of the energy. We have then according to the definition (21.4) of J that

$$2ZJ = -\delta \langle \hat{H} \rangle. \quad (21.62)$$

Problem 21.8t. Assuming $N_a = N_e = 2$ and $|V_2|/U \ll 1$ so that $m = 1$, show that the ground state energy of the Hubbard AF state within the mean field approximation is equal to $-2V_2^2/U$, while the exact energy in this limit is equal to $-4V_2^2/U$. The ground state energy for the ferromagnetic state is equal to zero for both the exact and mean field case.

Hint. The Hamiltonian for the mean field AF case is that for the ionic diatomic molecule with $\varepsilon_1 = 0$ and $\varepsilon_2 = U$ for both spin up and the spin down

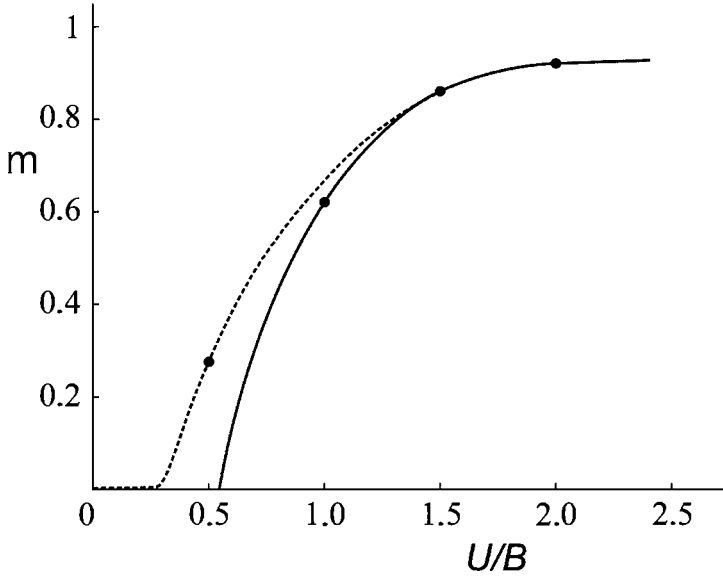


Fig. 21.6. The reduced magnetic moment $m = 2m'/g_s\mu_B$ (see (21.50)) vs. the dimensionless on-site repulsion U/B for $\zeta = 1$ in the framework of the simple Hubbard model and within the mean field approximation (21.48). The dotted line is for an approximate 3D DOS, while the continuous line (indicating a critical value of U/B below which $m = 0$) has been obtained by employing the simple cubic DOS

(see (F.26)). For the exact Hubbard case and for $N_a = N_e = 2$, there are three spatial symmetric states associated with $S = 0$: $\psi_1(\mathbf{r}_1)\psi_1(\mathbf{r}_2)$, $\psi_2(\mathbf{r}_1)\psi_2(\mathbf{r}_2)$, and $\frac{1}{\sqrt{2}}[\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) + \psi_1(\mathbf{r}_2)\psi_2(\mathbf{r}_1)]$. The diagonal elements of the Hamiltonian on the basis of these three states are U , U , and 0 , respectively. The off-diagonal between the first two is zero and the rest are equal to $\sqrt{2}V_2$. Diagonalize this 3×3 matrix and then take the limit, $|V_2|/U \rightarrow 0$.

In Fig. 21.7, we plot J vs U/B for $\zeta = 1$ for the simple Hubbard model approximated by the mean field approach and for an approximate 3D DOS. It is worthwhile to point out that the simple Hubbard model (21.47) in the limit of $|V_2|/U \rightarrow 0$ can be expressed in terms of spin operators as follows:

$$\hat{H} = -J \sum_{i \neq j}^l \mathbf{s}_i \cdot \mathbf{s}_j + C, \quad |V_2|/U \rightarrow 0, \quad (21.63)$$

where $J = -2V_2^2/U$, $C = -N_a Z V_2^2/2U$, and the prime in the summation means that i and j are nearest neighbors.

Concluding this section, we mention that there are several extensions of the simple Hubbard model as to make it more realistic. For example, terms may be added describing direct exchange interactions of the form, $-\sum_{i \neq j} J_{i-j} \mathbf{s}_i \cdot \mathbf{s}_j$,

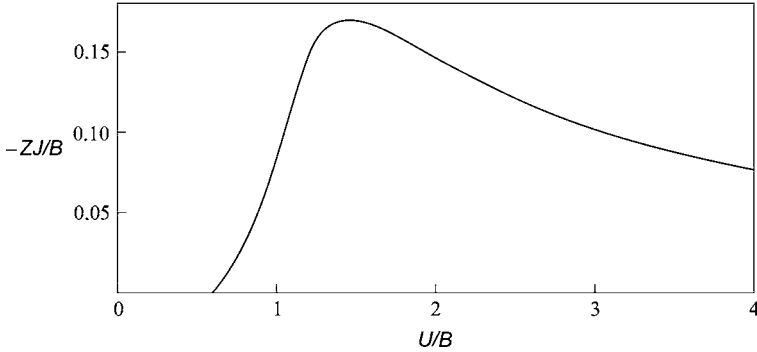


Fig. 21.7. The normalized indirect exchange interaction $-ZJ/B$ vs U/B for the $\zeta = 1$ antiferromagnet phase ($B = Z|V_2|$, and Z is the number of nearest neighbor sites) of the simple Hubbard model within the mean field approximation

or terms where the transfer matrix element V_2 depends on the occupation of the sites between which the transfer takes place. Another important extension of the simple Hubbard model is obtained by allowing more than one orbital per site. This extra orbital allows two electrons with parallel spins to occupy the same atom; then, in the limit of $|V_2|/U \rightarrow 0$, the triplet state can reduce its energy by a process as in Problem 21.8t, and the indirect exchange coupling in this limit will become

$$J = \frac{2V_2^2}{U''} - \frac{2V_2^2}{U'}, \quad (21.64)$$

where U' and U'' are the el-el repulsions of two electrons in the same atom but at different orbitals with $S = 0$ and 1 respectively. Since it is reasonable to expect that $U'' < U' < U$, it is quite possible that the presence of more than one orbital per atom may reverse the sign of the indirect exchange coupling to positive, i.e., to one favoring ferromagnetism. Thus, it may be no coincidence that the ferromagnetic elemental materials are transition metals (or lanthanides), where both d and s orbitals are involved (in lanthanides f orbitals as well).

21.4 The Heisenberg Model

21.4.1 The Hamiltonian

We have seen in Sects. 21.1 and 21.3 and in (21.15) and (21.63) that the interactions responsible for the appearance of long-range magnetic ordering can be re-expressed in terms of various types of spin-spin coupling. The Heisenberg model by recognizing and extending this idea has become the main tool for the microscopic theoretical study of magnetism. Its Hamiltonian is as follows:

$$\hat{H} = - \sum_{i=1}^{N_a} \sum_{j=1}^{N_a} J_{ij} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j, \quad J_{ii} = 0, \quad J_{ij} = J_{ji}, \quad (21.65)$$

where $\hat{\mathbf{S}}_i$ can be the total spin of atom i , or total angular momentum (both spin and orbital), depending on each particular case; thus in general, $S_i = n/2$ where n is a natural number. N_a is the total number of magnetic atoms in the solid. In a periodic system $J_{ij} = J_{|i-j|}$. Quite often, we assume only nearest neighbor (nn) coupling: $J_{ij} = J$ for nn, and zero otherwise. If all the J_{ij} are positive, the simple ferromagnetic phase is favored. In the simple case of a single negative J and a bipartite lattice,⁵ an AF phase is favored. There are of course more complicated cases, e.g., when the signs and the magnitudes of J_{ij} are random; then, we expect that each particular spin would receive different “instructions” by its neighbors regarding its orientation. This conflicting character of the interactions, known as *frustration*, fails to produce macroscopic magnetization, because the orientation of each spin is random but correlated with the orientation of all others, so that rotating one tends to rotate by the same angle all the others. This configuration known as *spin glass* appears in alloys where the percentage of magnetic atoms is low, e.g., 1–2% and randomly distributed within the non-magnetic host. This randomness in the position leads to randomness in the sign and size of J_{ij} (see (12.24)).

There are simpler versions of Heisenberg-like interactions. In one of them, only the x and y components of each $\mathbf{S}_i$ are retained. The corresponding Hamiltonian

$$\hat{H} = - \sum_{i \neq j} J_{ij} \left(\hat{S}_{ix} \hat{S}_{jx} + \hat{S}_{iy} \hat{S}_{jy} \right), \quad (21.66)$$

defines the so-called **x, y model**. In the so-called *Ising model*, only the z component of the spin is retained:

$$\hat{H} = - \sum_{i \neq j} J_{ij} \hat{S}_{iz} \hat{S}_{jz}. \quad (21.67)$$

One reason for introducing these less realistic models (less realistic as far as magnetic systems are concerned)⁶ is that they allow exact solutions where the Heisenberg Hamiltonian fails to do so. One famous example is the exact calculation of thermodynamic properties of the 2D Ising model by Onsager [21.4], who showed for the first time that interactions lead to a phase transition (of second order) without imposing it by assuming such a possibility a priori. We shall conclude our remarks regarding the possible modifications of (21.65) by pointing out that several energy terms mentioned in Chap. 20 can be easily incorporated in the Heisenberg Hamiltonian. For example, the anisotropy part may have the following form:

⁵ A bipartite lattice is one consisting of two interpenetrating sublattices such that the partners of all nearest neighbor pairs belong to different sublattices.

⁶ Notice that the Ising model describes also binary non-magnetic systems such as binary alloys, the so-called lattice-gas, etc.

$$\hat{H}_a = D \sum_i \hat{S}_{iz}^2, \quad (21.68)$$

where $D > 0$ implies that the easy magnetization is in the $x - y$ plane, while $D < 0$ gives the easy magnetization along the z -axis.

In working with angular momenta operators, the readers must recall the basic commutation relation

$$[\hat{S}_{ix}, \hat{S}_{jy}] = i\delta_{ij} \hat{S}_{iz}, \quad (21.69)$$

(and cyclic permutations of the indices x, y, z) as well as the definitions

$$\hat{S}_{i\pm} \equiv \hat{S}_{ix} \pm i\hat{S}_{iy}. \quad (21.70)$$

From (21.69) and (21.70), we obtain the following relations:

$$[\hat{S}_{iz}, \hat{S}_{j+}] = \delta_{ij} \hat{S}_{i+}, \quad [\hat{S}_{iz}, \hat{S}_{j-}] = -\delta_{ij} \hat{S}_{i-}, \quad (21.71)$$

$$[\hat{S}_{i+}, \hat{S}_{j-}] = 2\delta_{ij} \hat{S}_{iz}, \quad (21.72)$$

$$\hat{S}_{i\pm} |S_{iz} \rangle = \sqrt{(S \mp S_{iz})(S + 1 \pm S_{iz})} |S_{iz} \pm 1 \rangle. \quad (21.73)$$

Taking into account that $J_{ij} = J_{ji}$ and $J_{ii} = 0$, we can recast the first two terms in (21.65) as follows:

$$\sum_{ij} J_{ij} (\hat{S}_{ix} \hat{S}_{jx} + \hat{S}_{iy} \hat{S}_{jy}) = \sum_{ij} J_{ij} \hat{S}_{i-} \hat{S}_{j+} = \sum_{ij} J_{ij} \hat{S}_{i+} \hat{S}_{j-}. \quad (21.74)$$

21.4.2 Mean Field Approximation

The Hamiltonian $\hat{H}_i$ felt by the spin $\mathbf{S}_i$ in the presence of an external field $\mathbf{B}$ is

$$\hat{H}_i = -2\hat{\mathbf{S}}_i \cdot \left[\sum_j J_{ij} \hat{\mathbf{S}}_j - \frac{1}{2} g\mu_B \mathbf{B} \right], \quad (21.75)$$

which in the mean field approximation becomes

$$\hat{H}_i \simeq -\hat{\mathbf{S}}_i \cdot \left[2 \sum_j J_{ij} \langle \hat{\mathbf{S}}_j \rangle - g\mu_B \mathbf{B} \right] = g\mu_B \hat{\mathbf{S}}_i \cdot \mathbf{B}_e, \quad (21.76)$$

where the effective $\mathbf{B}_e$ is by definition

$$\mathbf{B}_e \equiv \mathbf{B} - \frac{2}{g\mu_B} \sum_j J_{ij} \langle \hat{\mathbf{S}}_j \rangle = \mathbf{B} + \frac{2}{(g\mu_B)^2} \langle \hat{\mathbf{m}}_j \rangle \sum_j J_{ij}. \quad (21.77)$$

From the Hamiltonian (21.76), we can calculate the average value, $\langle \hat{\mathbf{S}}_i \rangle$, or equivalently, the average value $\langle \hat{\mathbf{m}}_i \rangle = -g\mu_B \langle \hat{\mathbf{S}}_i \rangle$ of the magnetic moment,

by the relation $\langle \hat{\mathbf{m}}_i \rangle = -\partial F_i / \partial B_e$ as in Sect. 5.5.3.1 by using (5.102) and (5.103). Then, by substituting in the result, $\mathbf{B}_e$ from (21.77) and taking into account that translational symmetry implies that $\langle \hat{\mathbf{m}}_i \rangle = \langle \hat{\mathbf{m}}_j \rangle$, we obtain the following equation from $\langle \hat{\mathbf{m}}_i \rangle$.

$$\langle \hat{\mathbf{m}}_i \rangle \left[1 - \frac{2}{3} \frac{S(S+1)}{k_B T} \sum_j J_{ij} \right] = \frac{1}{3} \frac{(g\mu_B)^2}{k_B T} S(S+1) \mathbf{B}. \quad (21.78)$$

From (21.78), the susceptibility χ can be calculated easily, since $\mathbf{M} = N_a \langle \hat{\mathbf{m}}_i \rangle / V$ and $\mathbf{M} = \chi \mathbf{B} / \mu_0$:

$$\chi = \frac{\chi_0}{1 - (T_c/T)}; \quad T > T_c, \quad (21.79)$$

where

$$T_c = \frac{2}{3} S(S+1) J_0 / k_B; \quad J_0 \equiv \sum_j J_{ij}, \quad (21.80)$$

is the critical temperature above which the magnetization, in the absence of an external field, is zero; χ_0 is given by (5.105). If we want to find the value of $\langle \hat{\mathbf{m}}_i \rangle$ for $T < T_c$, we must abandon the approximate calculation of $\sum_i \exp(-\beta E_i)$ in (5.104) and do the sum exactly (this can be done, since it is essentially a geometric sum).

Problem 21.9t. Show that the average magnetic moment, $\langle m_i \rangle$, is given by

$$|\langle \hat{m}_i \rangle| = g\mu_B \left\{ \left(S + \frac{1}{2} \right) \coth \left[\beta g\mu_B B_e \left(S + \frac{1}{2} \right) \right] - \frac{1}{2} \coth \left[\frac{\beta g\mu_B B_e}{2} \right] \right\}. \quad (21.81)$$

In (21.81), use the expansion $\coth x = x^{-1} + \frac{1}{3}x - \frac{1}{45}x^3 + \dots$ and replace B_e from (21.77). Show then that the resulting expression for $\langle m_i \rangle$ is of the form $\langle \hat{m}_i \rangle = (T_c/T) \langle \hat{m}_i \rangle - A^2 \langle \hat{m}_i \rangle^3 + \dots$ and that the nonzero value of $\langle m_i \rangle$ is given by the following expression

$$\langle \hat{m}_i \rangle = \frac{1}{A} \left(\frac{T_c}{T} - 1 \right)^{1/2}, \quad T < T_c, \quad (21.82)$$

where

$$A^{-1} = \sqrt{\frac{5}{3}} \frac{S(S+1)}{\sqrt{S^2 + S + \frac{1}{2}}} g\mu_B \left(\frac{T}{T_c} \right)^{3/2}. \quad (21.83)$$

Equation (21.82) is valid for T less than T_c but close to it. For $T \rightarrow 0$, (21.81) gives the expected result: $|\langle \hat{m}_i \rangle| = g\mu_B S$. Notice that the critical exponents for χ and $\langle m_i \rangle$ have the mean field expected values of 1 and 1/2 respectively instead of the values 1.33 ± 0.05 and 0.33 ± 0.03 respectively obtained by more sophisticated methods and numerical simulations.

21.4.3 The Ferromagnetic Case, ($J_{ij} > 0$) and its spin waves

The exact ground state $|G\rangle$ of (21.65) in this case is the one with all spins pointing the same direction (which we choose as the z -axis)

$$|G\rangle = |S_{1z} = S, S_{2z} = S, \dots, S_{N_a z} = S\rangle, \quad (21.84)$$

and the corresponding exact ground state energy is

$$E_G = -N_a J_0 S^2. \quad (21.85)$$

To prove these statements, act on $|G\rangle$ by $\hat{H}$, take into account (21.74) and (21.73) (the latter shows that $\hat{S}_{i+}|S_{iz} = S\rangle = 0$) and end up with $\hat{S}_{iz}\hat{S}_{jz}$ acting on $|G\rangle$ and giving $S^2|G\rangle$. Thus, (2.85) follows⁷ with $J_0 \equiv \Sigma_i J_{ij}$.

To find a possible excited state of $\hat{H}$, we consider the minimum reduction of the total S_{tz} from $N_a S$ to $N_a S - 1$. This reduction can take place at a single spin located, let us say, at the site ℓ . The resulting state (normalized to one) can be written according to (21.73) as

$$|\ell\rangle \equiv \frac{\hat{S}_{\ell-}|G\rangle}{\sqrt{2S}}. \quad (21.86)$$

There are N_a such states depending on which site this minimum reduction took place. Any linear combination $\Sigma_\ell c_\ell |\ell\rangle$ describes also a minimum reduction of the total S_z from $N_a S$ to $N_a S - 1$ but spreads over all sites for which $c_\ell \neq 0$. It is rather obvious from Bloch's theorem that periodicity (together with normalization) implies that

$$c_\ell = \frac{\exp(i\mathbf{k} \cdot \ell)}{\sqrt{N_a}}. \quad (21.87)$$

Problem 21.10t. Show the following:

$$\hat{S}_{i-}\hat{S}_{j+}|\ell\rangle = \sqrt{2S}\delta_{j\ell}\hat{S}_{i-}|G\rangle = 2S\delta_{j\ell}|i\rangle, \quad (21.88)$$

$$S_{iz}S_{jz}|\ell\rangle = (S - \delta_{j\ell})(S - \delta_{i\ell})|\ell\rangle, \quad (21.89)$$

and

$$\hat{H} \sum_\ell c_\ell |\ell\rangle = (-N_a J_0 S^2 + \varepsilon(\mathbf{k})) \sum_\ell c_\ell |\ell\rangle, \quad (21.90)$$

where

$$\varepsilon(\mathbf{k}) = 2S \sum_{\mathbf{n}} J_{\mathbf{n}} (1 - e^{i\mathbf{k} \cdot \mathbf{n}}), \quad (21.91)$$

is the excitation energy; c_ℓ is given by (21.87) and $J_{ij} = J_{i,i+n}$ does not depend on i (only on n) because of the periodicity.

⁷ To actually complete the proof, one must show that $\langle \Phi | \hat{H} | \Phi \rangle$ is larger or equal to E_G as given by (21.85), where $|\Phi\rangle$ is any state. For the proof of this see [SS75], p. 703.



Fig. 21.8. Graphical representation of the state $|\mathbf{k}\rangle$ showing the phase advance as the wave moves from site to site. The projection of all spins on the z -axis is $S - 1$. This *does not* mean that the total S_{tz} is $N_a S - N_a$; it means that the total S_{tz} is $N_a S - 1$ and that this single spin reduction may occur at any site ℓ with probability $1/N_a$. If $S = \frac{1}{2}$ the minimum reduction is equivalent to a single spin flip

Equation (21.90) shows that the one-spin reduction state $|\mathbf{k}\rangle = \sum_{\ell} c_{\ell} |\ell\rangle$, where c_{ℓ} is given by (21.87) and $|\ell\rangle$ by (21.86), is an exact eigenstates of $\hat{H}$; its eigenenergy is by an amount $\varepsilon(\mathbf{k})$ above the ground state energy, where $\varepsilon(\mathbf{k})$ is given by (21.91). The eigenstate $|\mathbf{k}\rangle$ is a *spin wave* state where the single spin reduction of $S_{\ell z}$ by one can take place at any site ℓ with probability $1/N_a$. In Fig. 21.8, a pictorial representation of the classical analogue of $|\mathbf{k}\rangle$ is given.

The eigenstates $|\mathbf{k}\rangle$ is what is called in general an elementary excitation and in particular a magnetic elementary excitation or a *magnon*. The energy, $\varepsilon(\mathbf{k})$, of a magnon of crystal momentum $\hbar\mathbf{k}$ is fixed and is given by (21.91). In this sense, the magnon can be considered as the quantum of the magnetization in a similar way that the phonon is the quantum of the lattice vibration. Several such quanta $|\mathbf{k}_1\rangle, |\mathbf{k}_2\rangle, \dots$ can be thought of as making up a more general excited state of the system of energy $\varepsilon(\mathbf{k}_1) + \varepsilon(\mathbf{k}_2) + \dots$. Actually, this is only approximately true, because two or more magnons interact with each other; if the concentration of magnons is low, we expect this interaction to be a small correction (to the sum of their energies), which to a first approximation can be neglected. As the temperature is raised from the absolute zero, more magnons are created in analogy with what happens with phonons. The average number, $\langle n_{\mathbf{k}} \rangle$, of magnons of wavevector $\mathbf{k}$ is given by Bose–Einstein distribution (see (C.71)), if their interactions are neglected. The average magnetization per site is

$$\langle \hat{n}_i \rangle = g\mu_B \langle \hat{S}_{iz} \rangle = g\mu_B (S - \langle \hat{n}_i \rangle), \quad (21.92)$$

where the average number of magnons per site $\langle n_i \rangle$ is given by

$$\langle \hat{n}_i \rangle = \frac{1}{N_a} \sum_{\mathbf{k}} \langle \hat{n}_{\mathbf{k}} \rangle = \frac{1}{N_a} \sum_{\mathbf{k}} \frac{1}{e^{\beta\varepsilon(\mathbf{k})} - 1} = \frac{1}{N_a} \int \frac{d\varepsilon \rho(\varepsilon)}{e^{\beta\varepsilon} - 1} \quad (21.93)$$

Having the dispersion relation $\varepsilon(\mathbf{k})$ for magnons in (21.91), we can find the corresponding DOS by the usual procedure. For low temperatures (i.e., high values of $\beta = 1/k_B T$), only small values of ε contribute to the last integral in (21.93); the small values of ε correspond to small values of $|\mathbf{k}|$ for which $\varepsilon(\mathbf{k})$ can be approximated as follows:

$$\varepsilon(k) \simeq \frac{\hbar^2 k^2}{2m^*}; \quad m^* = \frac{\hbar^2}{4SJ a^2}, \quad (21.94)$$

where in (21.94) it was assumed that J_{ij} is equal to J for nearest neighbors and zero otherwise and that the lattice is **sc** with lattice constant a . In view of (21.94), the DOS $\rho(\varepsilon)$ is as in (4.15) with $\varepsilon_G = 0$ and the mass m replaced by m^* . Hence, the last integral in (21.93) becomes, by changing variables from ε to $x = \beta\varepsilon$ and extending the integration to infinity without appreciable error:

$$\langle \hat{n}_i \rangle = \frac{(k_B T)^{3/2}}{4\pi^2 (2SJ)^{3/2}} \int_0^\infty \frac{x^{1/2} dx}{e^x - 1} = 0.0586 \left(\frac{k_B T}{2SJ} \right)^{3/2}. \quad (21.95)$$

In obtaining (21.95), we took into account that $V/N_a = a^3$ for **sc** lattice. Combining (21.92) (multiplied by V/N_a) with (21.95), we have for the low-temperature magnetization $M(T)$

$$\frac{M(T)}{M(0)} = 1 - \frac{0.0586}{S} \left(\frac{k_B T}{2SJ} \right)^{3/2}. \quad (21.96)$$

Equation (21.96), valid for $k_B T \ll 2SJ$, is in agreement with the corresponding experimental data (see Fig. 20.4), and it is known as the $T^{3/2}$ *Bloch law*.

If we attempt to calculate the last integral in (21.93) for a 2D Heisenberg model (for which the DOS goes to constant as $\varepsilon \rightarrow 0$) or for a 1D Heisenberg model (where the DOS goes to $\varepsilon^{-1/2}$ as $\varepsilon \rightarrow 0$), we shall find that the integral diverges. This unphysical behavior indicates that the quantum fluctuations in 2D and 1D systems are so large that the assumed spontaneous magnetization is destroyed at any nonzero temperature, no matter how small. Mermin and Wagner [21.5] proved rigorously within the Heisenberg model that the spontaneous magnetization $M(T)$ for any $T > 0$ and for 1D and 2D systems is zero.

21.4.4 The AF Case

The AF case is considerably more complicated than the ferromagnetic one. Neither the ground state nor a single elementary excitation is rigorously known (except in special cases such as the 1D with $S = 1/2$). Nevertheless, one can introduce (by a series of transformations) approximate spin-wave excitations. Here we quote the results of such an approximate theory: if the interactions among these excitations are neglected, the Heisenberg Hamiltonian in a bipartite lattice (with $J_{ij} = J < 0$, for nearest neighbors and zero otherwise) can be approximated as follows

$$\hat{H} \simeq -E_0 + \sum_k \varepsilon(\mathbf{k}) \hat{n}_k, \quad (21.97)$$

where the approximate ground state energy is given by

$$-E_0 = -N_a S^2 Z |J| - SZ |J| \sum_{\mathbf{k}} \left[1 - \sqrt{1 - \gamma_{\mathbf{k}}^2} \right], \quad (21.98)$$

the approximate energy of a single elementary excitation $\varepsilon(\mathbf{k})$ is

$$\varepsilon(\mathbf{k}) = 2SZ|J|\sqrt{1 - \gamma_{\mathbf{k}}^2}, \quad (21.99)$$

and $\hat{n}_{\mathbf{k}}$ is the operator for the number of elementary excitations called again quanta of spin-waves or *magnons*. Z is the number of nearest neighbors and

$$\gamma_{\mathbf{k}} = \frac{1}{Z} \sum_{i=1}^Z e^{i\mathbf{k} \cdot \delta_i}. \quad (21.100)$$

Notice the following:

1. The approximate ground state energy $-E_0$ is lower than the corresponding classical one, $-E_{0,\text{cl}} = -N_{\text{a}}S^2Z|J|$. This is to be expected, since in the case of $N_{\text{a}} = 2$, where the exact result for $2\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2$ is known, $(2\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 = \hat{S}^2 - \hat{S}_1^2 - \hat{S}_2^2)$ we obtain for the ground state energy of the AF case, $\hat{S}_t = 0$, $-2|J|S(S+1)$, which is lower than the classical result $-2|J|S^2$. The quantum correction $-\delta E_0$ to the classical result $-E_{0,\text{cl}}$ is

$$\frac{\delta E_0}{E_{0,\text{cl}}} = \frac{1}{N_{\text{a}}S} \sum_{\mathbf{k}} \left[1 - \sqrt{1 - \gamma_{\mathbf{k}}^2} \right], \quad (21.101)$$

For the 1D case for which $\gamma_{\mathbf{k}} = \cos ka$, the result is

$$\frac{\delta E_0}{E_{0,\text{cl}}} = \frac{1}{S} \left(1 - \frac{2}{\pi} \right) = \frac{0.363}{S} \underset{S=1/2}{=} 0.727, \quad (21.102)$$

while the corresponding exact result for the 1D case and $S = 1/2$ is $4 \ln 2 - 2 = 0.7726$. Such a small error (only 2.6%) between the approximate and the exact result in the 1D case and for $S = 1/2$ is very encouraging, since the 1D, $S = 1/2$ case is expected to be the most severe test of (21.101), because the quantum fluctuations in this case have a bigger role. This is seen by comparing (21.102) with the corresponding results in higher dimensions.

$$\frac{\delta E_0}{E_{0,\text{cl}}} = \frac{0.158}{S}, \quad \text{for the 2D square lattices,} \quad (21.103)$$

$$\frac{\delta E_0}{E_{0,\text{cl}}} = \frac{0.097}{S}, \quad \text{for the 3D sc lattices.} \quad (21.104)$$

For higher dimensions and/or higher S , the role of quantum fluctuations is reduced.

2. For small $\mathbf{k}$, the dispersion relation $\varepsilon(\mathbf{k})$ given by (21.99) can be approximated

$$\varepsilon(\mathbf{k}) \rightarrow \sqrt{8Z}Sa|J||\mathbf{k}|, \quad (21.105)$$

where a is the lattice constant. In the 1D case and for integer S , (21.105) fails: Haldane and other authors [21.6–21.9] have shown that the excitation spectrum in this case is separated from the ground state by a gap known as the Haldane gap.

The approximations that led to (21.97) allow us to calculate the staggered magnetization $\mathbf{L}$ defined in (20.34):

$$L = \frac{g\mu_B}{V} \left[\sum_{i,1} \langle S_{iz} \rangle - \sum_{i,2} \langle S_{iz} \rangle \right]. \quad (21.106)$$

The final result involves three terms

$$L = L_0 + L_c + L_{\mathbf{T}}, \quad (21.107)$$

where L_0 is the classical result for $T = 0$ K:

$$L_0 = \frac{N_a}{V} g\mu_B S, \quad (21.108)$$

L_c is due to quantum corrections at $T = 0$ K

$$L_c = -\frac{g\mu_B}{2V} \sum_{\mathbf{k}} \left[\frac{1}{\sqrt{1-\gamma_k^2}} - 1 \right], \quad (21.109)$$

and $L_{\mathbf{T}}$ is due to the finite temperature contribution

$$L_{\mathbf{T}} = -\frac{g\mu_B 2Z |J| S}{V} \sum_{\mathbf{k}} \frac{1}{\varepsilon(\mathbf{k})} \frac{1}{e^{\beta\varepsilon(\mathbf{k})} - 1}. \quad (21.110)$$

In the last term at low temperatures, the approximation (21.105) can be used, which will produce a $\rho(\varepsilon) \sim \varepsilon^2$ for 3D lattices (while in 2D, $\rho(\varepsilon) \sim \varepsilon$, and in 1D, $\rho(\varepsilon) \rightarrow \text{constant}$ for low ε). Thus, the temperature term $L_{\mathbf{T}}$ is proportional to T^2 for the 3D case, while it blows up for the 2D and the 1D cases if $T > 0$. This indicates that the spontaneous magnetization is destroyed for 2D and 1D systems at any nonzero temperature no matter how small. For the 1D case, even at $T = 0$ K, we expect the spontaneous magnetization to be zero, since L_c blows up for 1D. This expectation is confirmed by the exact solution of $S = 1/2$ for 1D. For the approximate quantum corrections at $T = 0$ K, one finds the following results by numerical integration of (21.109).

$$\frac{L_c}{L_0} = -\frac{0.197}{S}, \quad \text{2D square lattice,} \quad (21.111)$$

$$\frac{L_c}{L_0} = -\frac{0.078}{S}, \quad \text{3D sc lattice.} \quad (21.112)$$

21.5 Key Points

- The exchange interaction, J , is defined as follows:

$$2J \equiv \langle \Psi_{\text{s min}} | \hat{H} | \Psi_{\text{s min}} \rangle - \langle \Psi_{\text{t min}} | \hat{H} | \Psi_{\text{t min}} \rangle,$$

where the subscripts denote singlet and triplet states, respectively; positive J favors parallel orientation of the magnetic moments, while negative J favors the antiparallel configuration.

- In the framework of a jellium type model (where the energy is of the form $(a'/r_s^2) - (\gamma'/r_s)$), the magnetic susceptibility is given by

$$\chi = \chi_{\text{p}} \frac{1}{1 - \eta},$$

where

$$\eta = \frac{2}{5} \frac{E_{\text{p}}}{E_{\text{k}}} = \frac{4}{5}.$$

From the relation $\eta = \frac{4}{5}$ as well as from direct calculation of the energy, it is expected that there will be no ferromagnetism in the JM or the RJM.

- For more general models, η is given by

$$\eta = \xi \chi_{\text{p}} = J_{\text{p}} \rho_{\text{F}}.$$

If $\eta = 1$, χ blows up, indicating the instability of the paramagnetic state, and the onset of ferromagnetism. The relation $\eta \geq 1$ is the Stoner criterion for the appearance of ferromagnetism.

- A state called SDW is a plane wave, $\exp(i\mathbf{k} \cdot \mathbf{r})$, with a spin direction determined by the angles $\theta_{\mathbf{k}}$ and $\phi_{\mathbf{q}} = \mathbf{q} \cdot \mathbf{r}$. Such a state is a candidate for antiferromagnetism within the jellium type of models. The result is that this antiferromagnetism is not favored energetically in 3D, unless the Fermi surface exhibits nesting as in Cr.
- The Hubbard model, in its simplest version, is a simple tight-binding model (one orbital per site, only nearest neighbors V_2) plus an intraatomic Coulomb repulsion of the form $U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$. The model incorporates the essential competition between kinetic energy (as represented by $|V_2|$) and Coulomb repulsion (as represented by U). Besides the ratio $U/|V_2|$, another important parameter is the number, ζ , of electrons per atom.
- Within a mean field approximation of the Hubbard model, the ζ , $U/|V_2|$ plane is divided into three regions: P, F, AF; in the region P, the paramagnetic state has lower energy than the ferromagnetic (F) or the antiferromagnetic (AF) one, etc. Going beyond the mean field approximation, the region F will be probably eliminated and the region AF will survive around the $\zeta = 1$ line and for $U \gg |V_2|$.

- Within the mean field approximation of the Hubbard model and for $\zeta = 1$, one can calculate the size of the magnetic moment, m_i , per site and the coupling, J , vs the ratio, $U/|V_2|$.
- The Hubbard model for $\zeta = 1$ and $U/|V_2| \rightarrow \infty$ reduces to a simple version of the well-known and extensively studied Heisenberg model

$$\hat{H} = -J \sum_{i \neq j} \hat{\mathbf{s}}_i \cdot \hat{\mathbf{s}}_j + \text{const.},$$

where $J = -2V_2^2/U$. Generally, the Heisenberg model has couplings J_{ij} ($i \neq j$), which can be positive (leading to ferromagnetism) or negative (which may lead to antiferromagnetism).

- For positive J_{ij} s, long-range ferromagnetic order is established for $T < T_c$ where

$$T_c \simeq \frac{2}{3} S(S+1) J_0 / k_B, \quad J_0 = \sum_j J_{ij}.$$

The excitations are Bose quasi-particles known as magnons, each one of which corresponds to a state with total spin along the z -axis equal to $N_a S - 1$ spread as a Bloch wave over all sites. The energy of a magnon of wavevector $\mathbf{k}$ is

$$\varepsilon(\mathbf{k}) = 2S \sum_{\mathbf{n}} J_{\mathbf{n}} (1 - e^{i\mathbf{k} \cdot \mathbf{n}}) \underset{k \rightarrow 0}{\sim} k^2; \quad \mathbf{n} = \mathbf{i} - \mathbf{j}.$$

- For low temperatures ($T \ll T_c$), the magnetization follows the $T^{3/2}$ Bloch law

$$\frac{M(T)}{M(0)} = 1 - \frac{0.0586}{S} \left(\frac{k_B T}{2SJ} \right)^{3/2}.$$

- For the AF case ($J_{ij} = J < 0$ for i, j nearest neighbors), the Hamiltonian can be approximated as follows:

$$\hat{H} = -E_0 + \sum_{\mathbf{k}} \varepsilon(\mathbf{k}) \hat{n}_{\mathbf{k}},$$

where

$$\begin{aligned} -E_0 &= -N_a S^2 Z |J| - S Z |J| \sum_{\mathbf{k}} \left[1 - \sqrt{1 - \gamma_{\mathbf{k}}^2} \right], \\ \varepsilon(\mathbf{k}) &\simeq 2S Z |J| \sqrt{1 - \gamma_{\mathbf{k}}^2} \sim k, \quad \text{as } k \rightarrow 0, \\ \gamma_{\mathbf{k}} &= \frac{1}{Z} \sum_{i=1}^Z \exp(i\mathbf{k} \cdot \boldsymbol{\delta}_i). \end{aligned}$$

- The staggered magnetization $\mathbf{L}$ can also be calculated in terms of the AF magnons.

21.6 Problems

- 21.1s Prove (21.11) and (21.12).
- 21.2 Prove (21.21) and (21.22).
- 21.3 Show that (21.22) in combination with (21.26) leads to (21.30).
- 21.4 Show that $\Delta(\mathbf{q})$ is equal to $(\tilde{v}/\mu_B)\tilde{\mathbf{M}}_x(\mathbf{q})$.
- 21.5s Prove (21.63).
- 21.6 Starting from the 3×3 matrix of Problem 21.8t, obtain the result $E_G = -4V_1^2/U$, valid for $N_e = N_a = 2$, $S = 0$, and $|V_2| \ll U$, by perturbation theory.
- 21.7s Starting from (21.69) and (21.70), prove (21.71)–(21.74).
- 21.8 Obtain the temperature-dependent term, L_T , of the staggered magnetization at very low temperatures.

Further Reading

- See the Ashcroft and Mermin book [SS75], pp. 672–691 and 701–724.
- A detailed advanced theory of magnetic materials can be found in the books [Ma168] to [Ma173] and [Ma175], [Ma176], [Ma178].
- There is an extensive literature on the Hubbard model [21.10]. A small sample follows: [21.11–21.19].

Superconductivity, I: Phenomenology

Abstract Materials becoming superconductors as they are cooled below the critical temperature T_c are mentioned; the main properties of the superconducting state are briefly reviewed. The role of the magnetic field in squeezing a superconductor and increasing its energy is shown. London equation and its non-local generalization by Pippard connecting the current density $\mathbf{j}(\mathbf{r})$ to the vector potential $\mathbf{A}(\mathbf{r})$, are presented; these phenomenological equations embody the basic superconducting properties. The Ginzburg–Landau theory, which encompasses, among other things, type II superconductors, is also presented.

We mentioned in Chap. 8, Sect. 8.5.2, that the main characteristics of the superconductive state of matter are the absence of magnetic field inside a superconductor (Meissner–Ochsenfeld effect [22.1]; perfect diamagnetism) and the zero DC resistivity [22.2]. Superconductivity occurs for several elemental metals and many compounds below the critical temperature T_c , which depends on the material; superconductivity can be destroyed by the application of a sufficiently strong external magnetic field.

22.1 Materials

In Table 22.1 the elemental metals that are capable of making the transition to the superconducting state under normal pressure are shaded. Several other elemental solids that become superconducting under pressure are also indicated. Besides elemental solids, several compounds become superconductors. In Chap. 15, Sect. 15.6 we discussed the so-called high T_c superconducting materials [22.3] and the compounds of Nb or V that crystallize in the so-called A15 structure. Also in Chap. 19, Sect. 19.4, we discussed fullerene-based superconductors of the type M_3C_{60} or $M_2M'C_{60}$, where M, M' are alkalis [22.4]. Some other categories of superconductors are as follows:

- (a) *Heavy fermion superconductors*, which are based on atoms with non-completed f orbitals (either 4f in lanthanides or 5f in actinides). These orbitals are responsible for a sharp peak in the DOS at $E = E_F$, and hence,

Table 22.1. Superconducting transition temperature, T_c (in K.), critical magnetic field, B_c (in Gauss for $T < T_c$) and coefficient of the electronic specific heat, γ_c (in mJ/mol K in the normal state). Asterisk (*) denotes superconductivity only under pressure (in Kbar)[†]

Li	Be	Nb						B	C	N	O	F	Ne					
	0.026 1.35	9.25 2026 7.80	$\leftarrow T_c$ $\leftarrow B_c$ $\leftarrow \gamma_c$					Al	Si	P	S	Cl	Ar					
Na	Mg							1.75 105 1.35	6.7-7.1* (120-130)	5.8* (170)								
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se II	Br	Kr	
			0.40 56 3.3	5.4 1408 9.82							0.85 54 0.66	1.083 58.3 0.6	5.35* (115)	0.31-0.5* (220-140)	6.7-6.9* (~130)			
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn (w)	Sb	Te IV	I	Xe	
		1.7-2.5* (110-160)	0.61 47 2.77	9.25 2060 7.80	0.915 96 1.83	7.8 1410 6.28	0.49 69 2.8	0.0003 0.049			0.517 28 0.69	3.404 282 1.672	3.722 305 1.78	2.6-2.7* (pt. 120)	4.72* (63)			
Cs V -1.5* (>125)	Ba IV 4.5-5.4* (144-190)	La β	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg (c)	Tl	Pb	Bi VI	Po	At	Rn	
		6.00 1096 11.3	0.128 829 12.7	4.47 829 6.15	0.0154 1.15 0.9	1.697 200 2.35	0.66 70 2.35	0.1125 16 3.19			4.154 411 1.81	2.38 178 1.47	7.196 803 3.1	8.55* (90-101)				
Fr	Ra	Ac	Ce (α)			Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
			1.9*															0.1 350
			Th	Pa	U (c)	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		
			1.38 160 4.32	1.4 1.4	2.4* (10)													

† Values from the
Handbook of Chemistry
and Physics, 60th
edition, CRC (1979).

[†] Values from the *Handbook of Chemistry and Physics*, 60th edition, CRC (1979).

to a very large effective mass m^* (justifying the name heavy fermions). Typical examples of this category are the uranium compounds UPd_2Al_3 , UBe_{13} , and UPt_3 .

- (b) *Organic superconductors*, such as $(\text{TMTSF})_2X$, where X can be PF_6 , or ClO_4 , or FSO_3 , or AsF_6 and the acronym TMTSF denotes a specific complicated organic molecule [22.5].
- (c) Another complicated organic molecule, denoted by DEDT-TTF combined with $X' = \text{I}_3$, or $\text{Cu}(\text{NCS})_2$, or SF_5CH_2 , etc. makes compounds of the form $(\text{DEDT-TTF})_2X'$, which become superconductors at low temperature.
- (d) *Borocarbides and boronitrides* of the form $\text{RTBC}(N)$, where $R = \text{Y}$ or Lu and $T = \text{Ni}$, or Pd , or Pt ; typical examples are as follows: $\text{Y}_{1-x}\text{Pt}_x\text{N}_2\text{B}_2\text{C}$ ($x = 0$ or 0.2), $\text{LuNi}_2\text{B}_2\text{C}$ and $\text{YNi}_2\text{B}_2\text{C}$.
- (e) *Oxides with perovskite structure* such as Sr_2RuO_4 , or $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$, or $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ (with $T_c \simeq 30$ K).
- (f) The *layered material* MgB_2 with its unexpectedly high T_c of 38.2 K, observed in 2001 [22.6].
- (g) The *iron-based* compound $\text{RE}[\text{O}_{1-x}\text{F}_x]\text{FeAs}$ ($x = 0.05 - 0.12$), where RE is rare earth exhibiting superconductivity with T_c as high as 55 K [22.7].
- (h) In Fig. 22.1 we plot the highest observed T_c vs. time of first observation (see also superconductors.org).

22.2 Properties of Superconductors

22.2.1 Zero DC Resistivity

In Fig. 22.2 the temperature dependence of the resistivities along the three principal axes of the crystal $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is shown. All the three resistivities drop precipitously to zero at the critical superconducting transition temperature of $T_c \simeq 92$ K.

22.2.2 Expulsion of the Magnetic Field B from the Interior of a Superconductor

Directly related with the zero DC resistivity of the superconducting state is the Meissner effect according to which such a state does not allow a magnetic field in its interior. If a superconductor is placed in an external magnetic field, surface¹ currents will spontaneously circulate;² their unique distribution will be such as to create a magnetic field $\mathbf{B}_{\text{ind}}$ that will cancel exactly the external field $\mathbf{B}_0$ in the interior of superconductor. This is analogous to what happens

¹ Actually, these currents circulate in a thin surface layer, the thickness of which is characterized by the *penetration depth* of typical size of 10^{-5} cm.

² Because of the zero resistivity, these currents, even if they are macroscopic, do not suffer from ohmic losses; hence, they are maintained for “ever”.

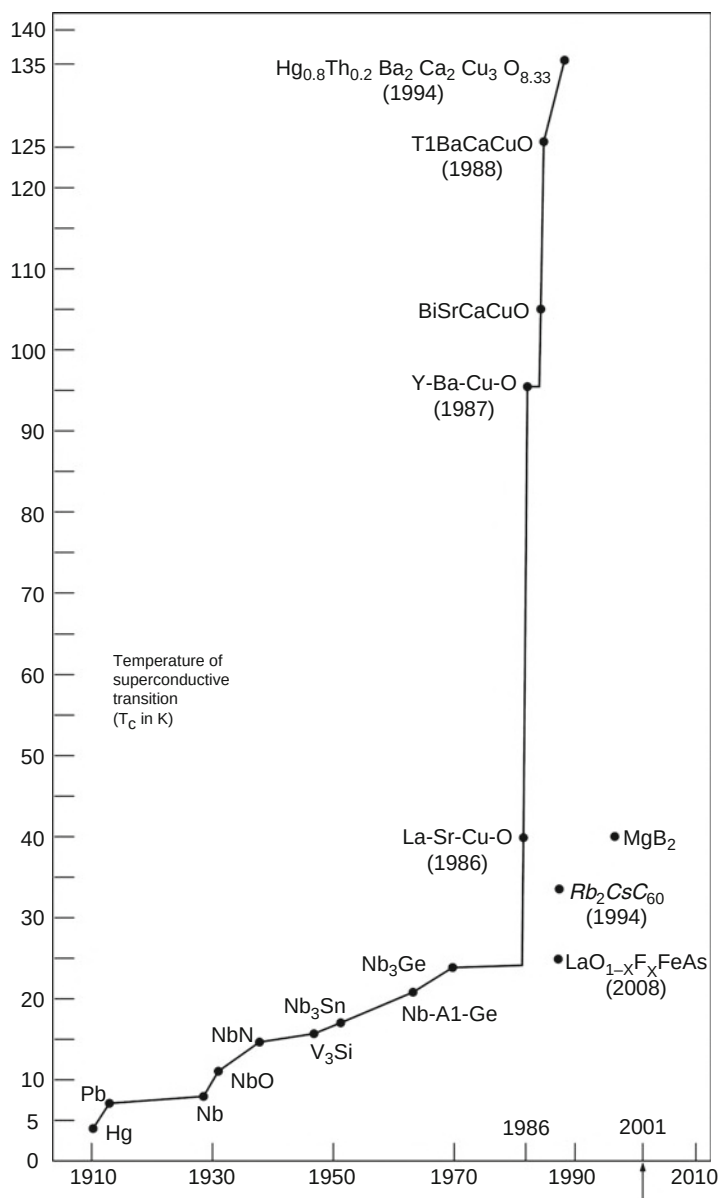


Fig. 22.1. Evolution of the record T_c , vs. time of first observation and the record-holding (at that time) materials. The interesting cases of $M_2M'C_{60}$ (M, M' alkalis), MgB_2 and $LaO_{1-x}F_xFeAs$ are also shown. Claims appear (2008) for T_c exceeding 200 K in In-doped $Sn_6Ba_4Ca_2Cu_{10}O_y$

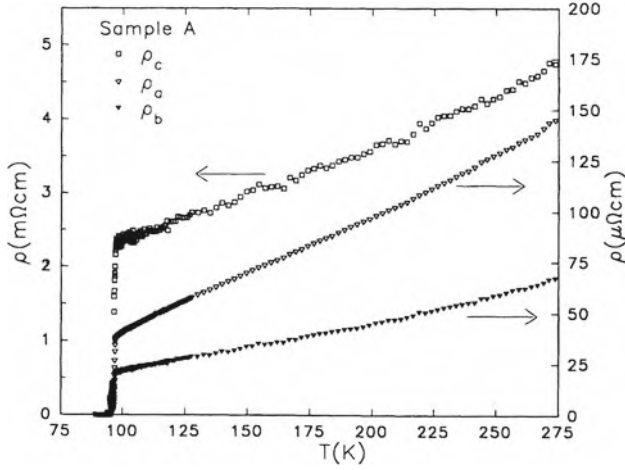


Fig. 22.2. The principal values of the resistivity tensor for a sample of the anisotropic crystal of $YBa_2Cu_3O_{7-\delta}$ vs. temperature. Notice the onset of superconductivity at $T_c \simeq 92$ K by the drop of the resistivities to zero (after [22.8])

if a conductor is placed in an external static electric field. Surface charges are set up that create an induced electric field, canceling the external field in the interior of the conductor.

Problem 22.1ts. Consider a superconducting sphere placed in a uniform external magnetic field $\mathbf{B}_0$. Calculate (a) the total magnetic field $\mathbf{B}(\mathbf{r}) = \mathbf{B}_0 + \mathbf{B}_{\text{ind}}(\mathbf{r})$ outside the sphere, (b) the induced magnetic moment of the sphere $\mathbf{m}$, and (c) the surface-current density $\mathbf{g}$. $|\mathbf{B}|$ is less than the critical value $\mu_0 H_{c1}$.

Hint. Show that $\nabla \times \mathbf{B} = 0$ both inside and outside the sphere; then $\mathbf{B}$ can be written as $-\nabla\phi$, where $\nabla^2\phi = 0$ and $\partial\phi/\partial n = 0$ at the surface. Define formally an auxiliary magnetization $\mathbf{M} \equiv \mathbf{m}/V$. (See Sects. 53 and 54 in [E15]). Take into account that $\mathbf{m}$ is necessarily proportional to $\mathbf{B}_0$, and then use the continuity of parallel to the surface component of $\mathbf{H}$; $\mathbf{g}$ can be obtained from (A.11).

22.2.3 Critical Value of the Magnetic Field Beyond Which Superconductivity Disappears

Consider a thin and long cylindrical superconductor placed in a uniform, static external magnetic field $\mathbf{B}_0 = \mu_0 \mathbf{H}_0$ ($\mathbf{B}_0 = \mathbf{H}_0$ in G-CGS) parallel to its axis. As the magnitude of $\mathbf{B}_0$ increases, a critical value $B_c = \mu_0 H_c$ is reached beyond which the superconductivity disappears and the cylinder makes a transition to its normal state. In the elemental pure solids (where the mean free path of the electrons in the normal state is long enough), the

transition from the superconducting to the normal state occurs abruptly over the whole extent of the cylinder when $H_0 = H_c$. Materials exhibiting such a transition are called *type I superconductors*. In alloys and compounds (where the electronic mean free path is rather short) the transition to the normal state, as the magnetic field $\mathbf{H}_0$ increases, is gradual and it evolves two critical fields H_{c1} and H_{c2} . For H_0 less than H_{c1} , the entire volume of the material is in the superconducting state. For H_0 between H_{c1} and H_{c2} , parts of the material are in the superconducting state and parts in the normal state;³ as the upper critical field H_{c2} is approached, the normal parts expand at the expense of the superconducting parts; at $H_0 \geq H_{c2}$, the entire material is the normal state. The superconducting materials for which the transition to the normal state is gradual and involves two critical fields H_{c1} and H_{c2} are called *type II superconductors*. For the geometry we consider in this subsection, the mixed state between H_{c1} and H_{c2} consists of many tiny cylinders (along the length of the material) being in the normal state, while the surrounding material is still in the superconducting state (see Fig. 22.3). Notice that the superconducting part is connected so that the DC resistivity is still zero in the mixed state between H_{c1} and H_{c2} . On the other hand, the spatial average, $\langle H \rangle$, of the magnetic field inside the cylindrical superconductor increases from zero at $H_0 = H_{c1}$ to H_{c2} at $H_0 = H_{c2}$. At the interface⁴ between each tiny normal-state cylinder and the surrounding superconducting material, surface-currents normal to $\mathbf{H}_0$ and of density $g = H_0$, $[(c/4\pi) H_0$ in G-CGS] circulate counterclockwise to create a field equal to $\mathbf{H}_0$. For this reason, the mixed state between H_{c1} and H_{c2} is called *vortex state*. An equal size surface current, but of clockwise direction, circulates at the external surface, which creates a field equal to $-\mathbf{H}_0$; this field cancels the external field $\mathbf{H}_0$ in the region among the tiny normal-state cylinders. Each of these circulating currents creates a magnetic moment $\mathbf{m} = \mp V \mathbf{H}_0$ ($\mp (V/4\pi) \mathbf{H}_0$ in G-CGS) where V is the volume enclosed by each current and the upper (lower) sign refers to clockwise (counterclockwise) direction of the flux of the current. By adding all the magnetic moments (including the one due to the current at the external surface), we define the total magnetic moment $\mathbf{m}_t$ and the average formal auxiliary magnetization $\langle \mathbf{M} \rangle = \mathbf{m}_t/V_t$, where V_t is the total volume of the material. It is

³ A mixed state, partly superconducting and partly normal, appears also in type I superconductors for purely geometrical reasons. Indeed, the total field $\mathbf{H} = \mathbf{H}_o + \mathbf{H}_{\text{ind}}$ is not uniform in general, even if $\mathbf{H}_o$ is uniform (except for the long thin cylindrical geometry chosen in the present subsection, where $\mathbf{H}_{\text{ind}} \simeq 0$). Thus, the points $\mathbf{r}$ such that $H(\mathbf{r}) = \mu_o H_c$ define the interface (or the interfaces) between superconducting the normal states. This geometrical mixed state is called *intermediate state*.

⁴ Actually the interface is not sharp but it has a thickness of the order of the penetration length; over this thickness the magnetic field changes from B_o at the center of each tiny cylinder to zero outside.

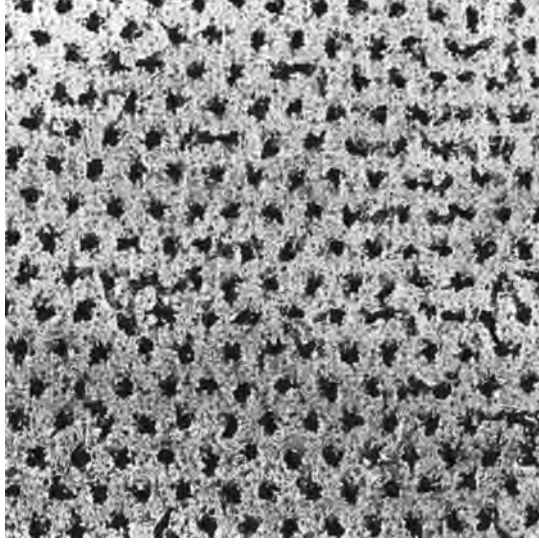


Fig. 22.3. Experimental imaging (black dots) of the tiny cylinders (consisting of material in the normal state), as they are seen at the base of the cylindrical superconductor for $H_{c1} < H_0 < H_{c2}$. The imaging is based upon the non-zero magnetic field penetration inside each tiny normal-state cylinder; this non-zero field attracts a powder of iron particles at the base of the material. Notice that the tiny cylinders are periodically arranged in a triangular lattice (H. Träuble and, U. Essmann, J. Appl. Phys. **39**, 4052 (1968))

easy to see that $\langle \mathbf{M} \rangle = -(\mathbf{H}_0)(V_s/V_t) [-\mathbf{H}_0(V_s/4\pi V_t)]$ (in G-CGS), where V_s is the fraction of the volume where the superconducting state is maintained. In Fig. 22.4 we plot $-\langle M \rangle$ vs. H_0 for type I and type II superconductors.

In Fig. 22.5 we plot the temperature variation of H_c , H_{c1} and H_{c2} . This variation of the critical field H_c (and H_{c2}) can be approximated by the relation

$$H_c(T) = H_c(0) \left[1 - \frac{T^2}{T_c^2} \right]. \quad (22.1)$$

Notice that the flow of strong electric current through a superconductor creates high magnetic fields, which may reach the critical value H_{c2} . This is one reason that there is a critical value j_c of the current-density beyond which superconductivity is destroyed. Another mechanism contributing to the critical current density j_c is the possibility of the vortices to be moved by the action of the strong current. Thus, there are three critical quantities T_c , H_c (or H_{c2}) and j_c , each one of which is a function of either B and j , or T and j , or T and B_0 respectively; in other words, for each superconductor there is a critical surface $f_c(T, B_0, j) = 0$ in the space of temperature, magnetic field and current-density beyond which superconductivity is destroyed.

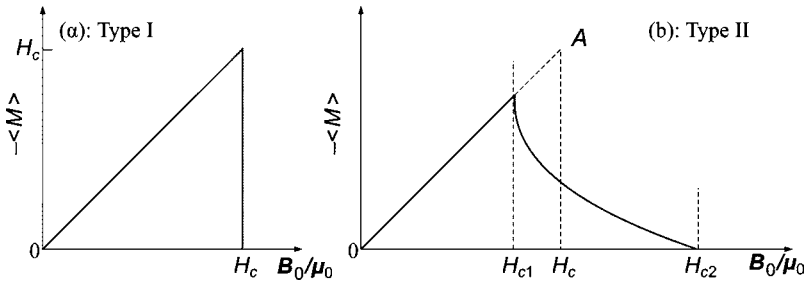


Fig. 22.4. Average auxiliary magnetization $-\langle M \rangle$ vs. external field $H_0 = B_0/\mu_0$ parallel to a long thin cylindrical superconductor and for $T \rightarrow 0$ K. In type I superconductors the transition to the normal state takes place abruptly over the whole volume when $H_0 = H_c$ (and the average magnetization drops abruptly to zero since $V_s = 0$). In contrast, in type II superconductors up to H_{c1} the whole volume is in the superconducting state. In the regime between H_{c1} and H_{c2} the vortex state appears to incorporate parallel to the axis many tiny cylinders, which are in the normal state, arranged in the triangular lattice so that the superconducting volume V_s is reduced gradually until it disappears completely at $H_0 = H_{c2}$ and beyond. In type II superconductors, (b), we define H_c in such a way that the area of the triangle OH_cA is equal to the area under the continuous line in Fig. 22.4b

22.2.4 Specific Heat and Other Thermodynamic Quantities

In Fig. 22.6 experimental results for the *electronic* contribution to the Helmholtz free energy, the entropy, and the specific heat of a type I superconductor vs. temperature are presented (for $T \lesssim T_c$). Both the superconducting and the corresponding normal state results are shown. (The normal state results are obtained by the application of a magnetic field higher than H_c ; such a field destroys the superconductivity.)

The main points drawn from these results for the superconducting state are as follows:

1. At very low temperature ($T \ll T_c$), we have that

$$A_s(T) = A_s(0) + f(T) \exp\left(-\frac{E_g}{2k_B T}\right); \quad A_s = F_s, \text{ or } S_s, \text{ or } C_s, \quad (22.2)$$

where $f(T)$ depends weakly on temperature so that the exponential dependence dominates. Equation (22.2) suggests that in the superconducting state a gap E_g appears in the electronic excitation spectrum, which is reduced with increasing temperature and vanishes at $T = T_c$ and beyond. Thus, the quantity $\Delta \equiv E_g/2$ characterizes the superconducting state and it can be considered as its *order parameter*.

2. The Helmholtz free energy of the superconducting state is lower than that of the normal state over the whole range of temperatures $0 < T < T_c$; this, of course, was expected given the stability of the superconducting

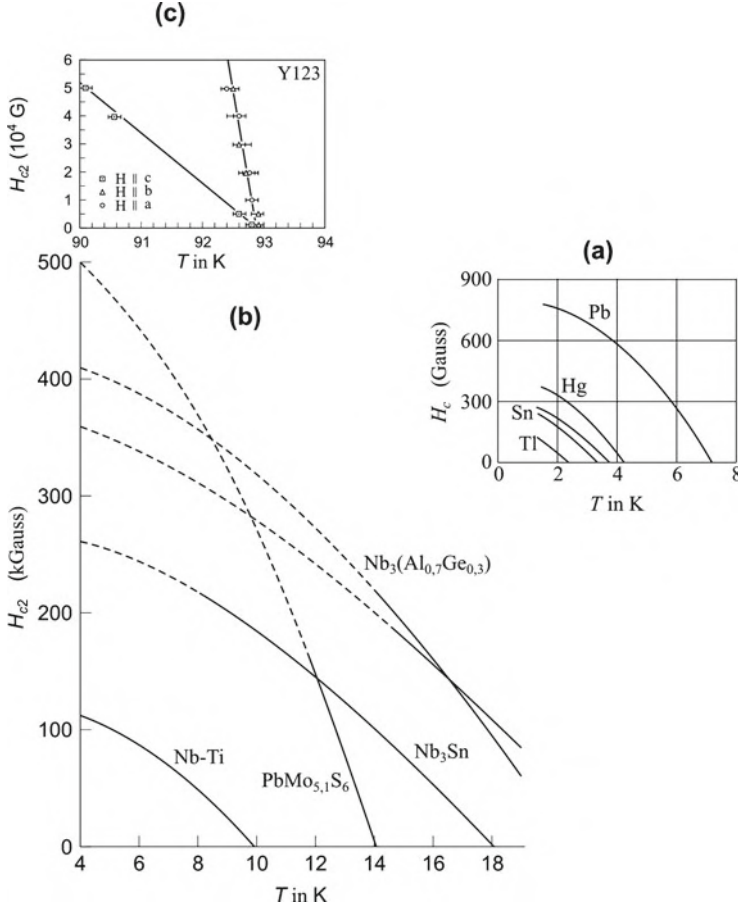


Fig. 22.5. Temperature variation of H_c ((a) for type I) and H_{c2} ((b) and (c) for type II) superconductors. Notice that H_{c2} (in type II) can be thousand times larger than H_c (in type I) superconductors. In high- T_c superconductors (c), the $T \rightarrow 0$ K value of H_{c2} is so large that it is difficult to be measured; this is why it is measured near T_c . The layer structure of these materials leads to strong anisotropies in H_{c2}

state. The non-zero difference between F_N and F_S for $T < T_c$ suggests that a phase transition to the normal state for $T < T_c$ (in the presence of a magnetic field) is a first-order phase transition. On the other hand, the transition to the normal state at $T = T_c$ (in the absence of a magnetic field) is a *second-order* phase transition, which is characterized by the continuity of F and S and the discontinuity of the specific heat.

- Given the shape of S_s vs. T shown in Fig. 22.6b, and taking into account that $C = T(\partial S/\partial T)$, we conclude that $C_s(T_c) > C_N(T_c)$, as shown in Fig. 22.6c.

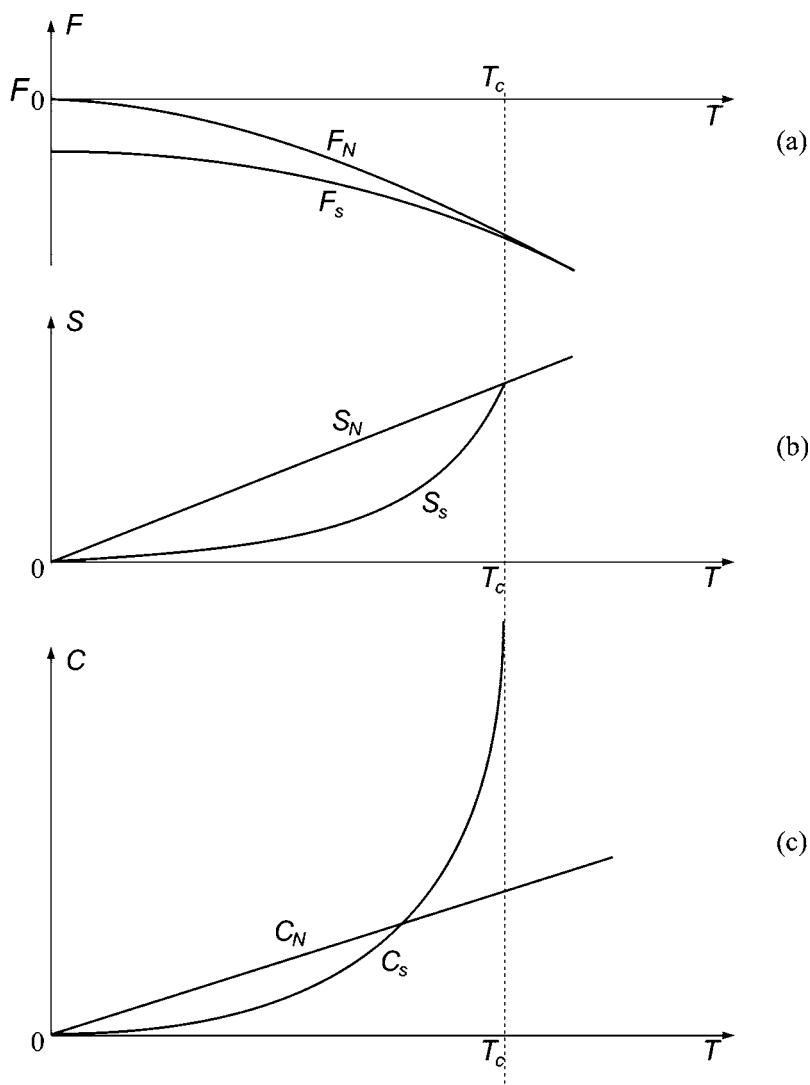


Fig. 22.6. Temperature dependence of the electronic contribution to the Helmholtz free energy (a); to the entropy (b); and to the specific heat (c) for aluminum ($T_c = 1.18\text{ K}$), for both the normal (subscript N) and the superconducting (subscript s) state

22.2.5 Response to Microwave or Far Infrared EM Radiation

The low-temperature thermodynamic data suggested the appearance of a gap $E_g = 2\Delta$ in the superconducting state. A direct verification of this can be obtained by an EM transmission experiment. As in semiconductors we expect

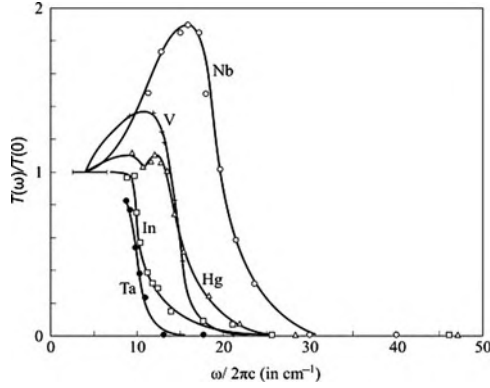


Fig. 22.7. The relative EM transmission coefficient $T(\omega)/T(0)$ vs. $\omega/2\pi c$ at $T = 1.3$ K for various superconductors: indium with $T_c = 3.4$ K, and $E_g(0)/2\pi\hbar c = 8.5 \text{ cm}^{-1}$; niobium with $T_c = 9.25$ K, and $E_g(0)/2\pi\hbar c = 25 \text{ cm}^{-1}$; tantalum with $T_c = 4.47$ K, and $E_g(0)/2\pi\hbar c = 11.3 \text{ cm}^{-1}$; vanadium with $T_c = 5.4$ K, and $E_g(0)/2\pi\hbar c = 12.9 \text{ cm}^{-1}$; and Hg with $T_c = 4.15$ K and $E_g(0)/2\pi\hbar c = 13.3 \text{ cm}^{-1}$

that there will be easy transmission as long as $\hbar\omega < E_g$ and no transmission for $\hbar\omega > E_g = 2\Delta$ (because of absorption). This is what is happening as shown in Fig. 22.7.

22.2.6 Ultrasound Attenuation

In normal metals, a sound wave decays, since part of the wave energy is transferred to the electrons, which are excited from just below to just above the Fermi energy. In superconductors such a process cannot take place as long as $\hbar\omega$ is below the gap $E_g = 2\Delta$. Hence, in superconductors the decay of ultrasound waves is expected to be substantially lower than in normal metals as long as $\hbar\omega < 2\Delta$. Experimental data confirm this prediction providing thus another independent indication for the existence of the gap.

22.2.7 Tunneling Current in Metal/Insulator/Superconductor Junctions

The most direct measurement of the superconducting gap is through the I -vs.- V characteristic of a Metal/Insulator/Superconductor (M/I/S) junction; we expect no current I until the voltage V reaches the value $\Delta/|e|$, as shown in Fig. 22.8a. In Fig. 22.8b the explanation for this behavior is offered.

22.2.8 Temperature Dependence of the Superconducting Gap

In Fig. 22.9 experimental data for the temperature dependence of the superconducting gap in three different superconductors are shown together with

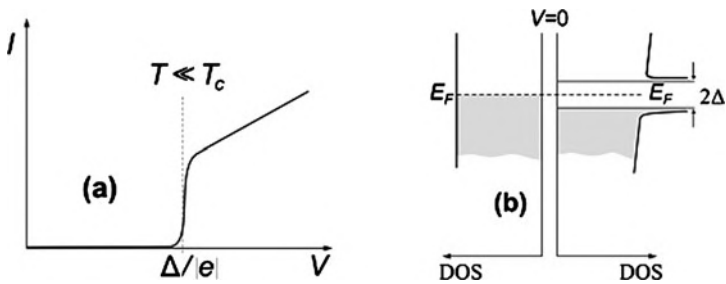


Fig. 22.8. (a) The I vs. V characteristic for a M/I/S junction. (b) The DOS in the normal metal and the superconductor vs. energy. The application of voltage V on the metal side will lower (raise) the metal Fermi level by $|eV|$, if V is positive (negative). If $|eV|$ is less than Δ , no current can flow, since there are no states in the superconductor side at $E_F \pm eV$ for the electrons to use. If $|eV|$ exceeds Δ , electrons will be transferred from the occupied levels of the superconductor to the levels above the metal Fermi level (if $V > 0$) or electrons will be transferred from the occupied levels of the metal to the empty levels of the superconductor (if $V < 0$). In either case the I vs. V will be as in (a)

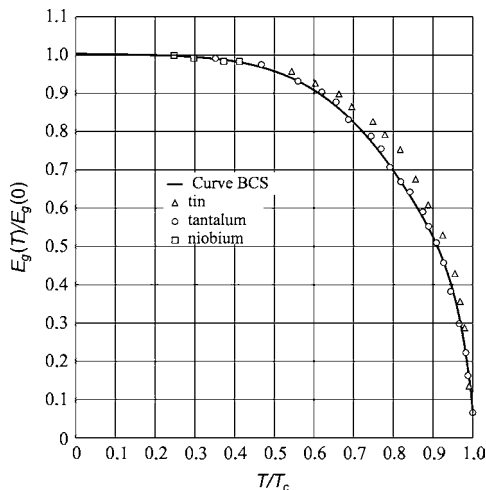


Fig. 22.9. Temperature dependence of $E_g(T) = 2\Delta(T)$ for Sn, Ta, and Nb. The continuous line is the BCS theoretical result, which is of the form, $\Delta(T)/\Delta(0) = \tanh [T_c\Delta(T)/T\Delta(0)]$

the result based on the so-called BCS theory (to be presented in the next chapter). The BCS result for $T \rightarrow T_c$ is as follows:

$$\frac{\Delta(T)}{\Delta(0)} = \sqrt{3} \left(1 - \frac{T}{T_c} \right)^\beta ; \quad T \rightarrow T_c^- . \tag{22.3}$$

Table 22.2. Experimental values of the superconducting gap $E_g(0) \equiv 2\Delta(0)$ (in meV) and of the critical temperature T_c (in K) as well as the ratio $2\Delta(0)/k_B T$ are given

Superconductor	$E_g(0) \equiv 2\Delta(0)/k_B T$ (in meV)	T_c (in K)	$2\Delta(0)/k_B T_c$
La (fcc)	1.9	6	3.7
V	1.6	5.4	3.4
Nb	3.05	9.25	3.8
Ta	1.4	4.47	3.6
Mo	0.27	0.915	3.4
Zn	0.24	0.85	3.2
Cd	0.15	0.517	3.2
Hg (a)	1.65	4.154	4.6
Al	0.34	1.75	3.3
Ga	0.33	1.08	3.5
In	1.05	3.4	3.6
Tl	0.745	2.38	3.57
Sn (w)	1.15	3.72	3.5
Pb	2.73	7.2	4.38

It exhibits the exponent $\beta = 1/2$, characteristic for mean field theory. The zero temperature value $\Delta(0)$ is related to the critical temperature T_c as follows:

$$\frac{2\Delta(0)}{k_B T} = c_1, \quad (22.4)$$

where $c_1 = 3.53$ according to the BCS theory. In Table 22.2 the experimental values of $E_g(0) \equiv 2\Delta(0)$ and T_c are given.

22.2.9 Isotope Effect

If in elemental or compound superconductors, one constituent element is replaced (partly or fully) by one of its isotopes so that the mass (or the average mass) M of this element will change, the critical temperature changes too according to the following empirical relation

$$T_c \sim M^{-a}, \quad (22.5)$$

where the exponent a is usually between 0 and 0.6. Positive value of a implies that increase of the isotopic mass leads to reduction of T_c . There are exceptions: e.g., if in PdH (with $T_c \simeq 9$ K) the hydrogen is replaced by deuterium, we obtain PdD (with $T_c = 11$ K). For most superconductors not containing transition or rare earth elements, the value of a is close to $1/2$ indicating that the eigenfrequencies of the lattice vibrations (which are proportional to

Table 22.3. Values of the exponent a (see (22.5)) for various superconductors

Superconductors	Values of a
Zn	0.45 ± 0.05
Cd	0.32 ± 0.07
Sn	0.47 ± 0.02
Hg	0.50 ± 0.03
Pb	0.49 ± 0.02
Tl	0.61 ± 0.1
Ru	0.00 ± 0.05
Os	0.15 ± 0.05
Mo	0.33
Zr	0.00 ± 0.05
Nb ₃ Sn	0.08 ± 0.02
Mo ₃ Ir	0.33 ± 0.03
YBa ₂ Cu ₃ O _{7-x} (YBCO or Y123)	0.02 ± 0.03
Ba _{0.6} K _{0.4} BiO ₃	$\simeq 0.5$

$1/\sqrt{M} = M^{-1/2}$) may play a role in the phenomenon of superconductivity.⁵ In Table 22.3 values of the exponent a are given for various superconductors.

22.2.10 Relaxation Times for Nuclear Spin

In Chap. 5, Sect. 494, we have seen that the nuclear-spin component I_z (i.e., the one parallel to the external magnetic field $\mathbf{B}$) is proportional to the eigenenergy ε_{I_z} and hence, it is conserved. In reality, there are various interactions that drive the value of I_z back to its thermal equilibrium value I_0 . The simplest way to describe such a process is through a phenomenological relaxation time denoted in the present case by T_1

$$\frac{dI_z}{dt} = -\frac{I_z - I_0}{T_1}. \quad (22.6)$$

(This is the analog of $(G \cdot 2)$.) The relaxation time T_{1s} in the superconducting state is lower than the normal state value T_{1N} , at the same temperature.

22.2.11 Thermoelectric Coefficients

One would naively expect the electronic thermal conductivity K_e in superconductors to be very high (remember the Wiedemann and Franz “law”,

⁵ No mechanism other than the lattice vibrations can create an appreciable isotope mass dependence. The direct influence of the isotope mass on the electronic states is either through the ratio m_e/M or through the interaction of the nucleus magnetic moment with the electronic angular momentum. Both of these effects are tiny, of the order of m_e/M , to produce an appreciable isotope effect.

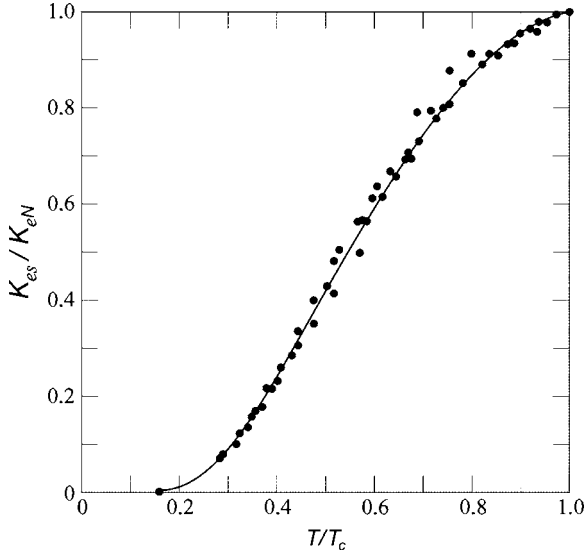


Fig. 22.10. Temperature dependence of the electronic thermal conductivity, in the superconducting state (over that of normal state), for aluminum. Both the experimental points and the BCS theoretical results (solid continuous line) are shown

$K_e \sim T\sigma$). Actually, the opposite is true: K_{es} is much smaller than K_{eN} , the normal state one, as shown in Fig. 22.10.

A possible interpretation of this unexpected result may be that, in a superconductor, only a fraction of the electrons are carriers of entropy, and hence,⁶ of heat. This fraction is decreasing as the temperature is decreasing and goes to zero as $T \rightarrow 0$ K. The rest of the electrons do not carry entropy. Through this interpretation, we were led to a picture of two categories of electrons in the superconducting state. The first one consists of normal electrons, which are entropy carriers; the second one consists of electrons that do not carry entropy and that are not subject to friction forces, i.e., they are the ones responsible for superconductivity.

22.3 Thermodynamic Relations

Taking into account that the infinitesimal change in the interaction energy of a magnetic moment $\mathbf{m}$ due to the infinitesimal change $d\mathbf{B}_0$ of an external field $\mathbf{B}_0$ is given by⁷ $-\mathbf{m} \cdot d\mathbf{B}_0$, and that in a superconductor $\mathbf{m} = -(V/\mu_0) \mathbf{B}_0$ (in SI; in G-CGS, we simply get $\mathbf{m} = -V\mathbf{H}_0/4\pi$), we can write the change

⁶ The thermal energy-current density $\mathbf{j}_E$ is related to the entropy-current density $\mathbf{j}_S$ as follows: $\mathbf{j}_E = T\mathbf{j}_S$.

⁷ See (A.62) and take $\delta\mathbf{B}_0$ out of the integral, since it is uniform; $\mathbf{m} = \int \mathbf{M} dV$.

in Helmholtz free energy of a thin long cylindrical superconductor parallel to an external static uniform field $\mathbf{B}_0$, as follows

$$dF_s = -SdT - \mathbf{m} \cdot d\mathbf{B}_0 = -SdT + \frac{V}{\mu_0} \mathbf{B}_0 d\mathbf{B}_0, \text{ SI.} \quad (22.7)$$

Integrating with respect to $\mathbf{B}_0$, we find

$$F_s = F_{s0}(V, T) + \frac{V}{2\mu_0} B_0^2, \text{ SI.}^8 \quad (22.8)$$

The pressure is obtained from (22.8) as follows (see (C.21)):

$$P = -\left(\frac{\partial F_s}{\partial V}\right)_{T, B_0} = P_0(V, T) - \frac{B_0^2}{2\mu_0}, \quad \text{SI.} \quad (22.9)$$

Equation (22.9) means that the volume $V(P, T)$ of a superconductor in the presence of the field $\mathbf{B}_0$ is the same as the one in the absence of the field $\mathbf{B}_0$, but under a pressure $P + (B_0^2/2\mu_0)$. Hence, the field $\mathbf{B}_0$ leads to a compression of the superconductor.⁹ The Gibbs free energy is given by (C.3), which in the present case becomes (taking into account (22.8) and (22.9))

$$\begin{aligned} G_s(P, T, B_0) &= F_s(P, T, B_0) + PV = F_{s0}(V, T) + VP_0 \\ &= G_{s0}\left(P + \frac{B_0^2}{2\mu_0}, T\right) \simeq G_{s0}(P, T) + V_{s0}(P, T) \frac{B_0^2}{2\mu_0}, \end{aligned} \quad (22.10)$$

where $G_{s0}(P, T)$ is the Gibbs free energy in the absence of $\mathbf{B}_0$; the last relation was obtained by expanding G_{s0} in the small parameter $B_0^2/2\mu_0$ and taking into account that $\partial G_{s0}/\partial P = V_{s0}$ (in G-CGS $B_0^2/2\mu_0$ must be replaced by $B_0^2/8\pi$).

By equating $G_s(P, T, B_0)$ to the normal-state Gibbs free energy $G_N(P, T)$, we can obtain T_c vs. B_0 or H_c vs. T . The physical meaning of the equation

$$G_{s0}(P, T) + \frac{1}{2} V_{s0}(P, T) \mu_0 H_c^2 \simeq G_N(P, T), \quad \text{SI,} \quad (22.11)$$

is that the expulsion of the magnetic field $\mathbf{B}_0$ from the interior of a superconductor increases its Gibbs free energy by $V_{s0}(P, T) B_0^2/2\mu_0 = V_{s0}(P, T) \mu_0 H_0^2/2$ ($V_{s0}(P, T) H_0^2/8\pi$ in G-CGS). As $|\mathbf{H}_0|$ keeps increasing it reaches a critical value H_c such that the quantity $V_{s0}(P, T) \mu_0 H_0^2/2$ becomes equal to the difference $G_N(P, T) - G_s(P, T)$ and the material makes a transition to its normal state, since for $H_0 > H_c$, $G_N(P, T)$ is lower than $G_s(P, T, B_0)$. This description is valid for type I superconductors. For type II and $H_0 > H_{c1}$ the mixed vortex state has lower Gibbs free energy than both G_N and the uniform superconducting state. More specifically, for $H_{c1} < H_0 < H_c$ we

⁸ In G-CGS $(V/2\mu_0) B_0^2$ is replaced by $VB_0^2/8\pi = VH_0^2/8\pi$.

⁹ In fact, this is part of the Maxwellian stress tensor.

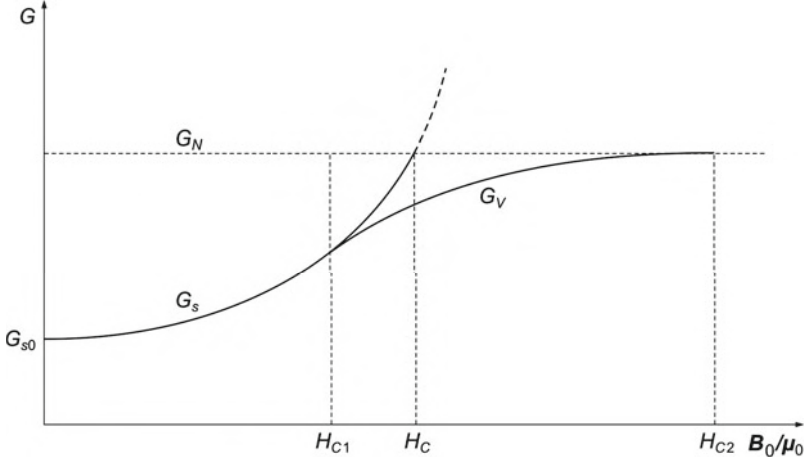


Fig. 22.11. The Gibbs free energy, for the normal state (G_N), the uniform superconducting state (G_s) and the mixed vortex state (G_V), for a type II superconductor vs. the external field $H_0 = B_0/\mu_0$ under constant pressure and temperature $T (< T_c)$. In view of (22.7) and (22.10) the difference between G_N and G_{s0} is equal to the area of the triangle OH_cA in Fig. 22.4b multiplied by $\mu_0 V$ (by $V/4\pi$ in G-CGS); the difference between $G_V(B_0)$ and G_{s0} for every value of H_0 less than H_{c2} is equal to the area under the continuous line in Fig. 22.4b multiplied by $\mu_0 V$. Since $G_s(H_c) = G_N = G_V(H_{c2})$, it follows that the area of the triangle OH_cA in Fig. 22.4b is equal to the area under the continuous line from 0 up to H_{c2} .

have the inequalities $G_V < G_s < G_N$, while for $H_c < H_0 < H_{c2}$ we have $G_V < G_N < G_s$; finally for $H_0 > H_{c2}$ the normal state G_N is lower than both G_V and G_s . This situation is shown in Fig. 22.11. For a more extended treatment of the thermodynamic properties of the superconductors, the readers are referred to the book [E15], Sect. 22.55.

22.4 London Equation

The experimental results presented in the previous subsection suggest that the mobile electrons are grouped in two categories: the normal ones of concentration $n_N(T)$ and the “superconducting” ones of concentration $n_s(T)$ (where $n = n_N + n_s$). The electrons of the latter category carry no entropy and are subject to no friction forces; hence, under the action of an electric field $\mathbf{E}$, their acceleration dv_s/dt is equal to $-e\mathbf{E}/m$. Since $\mathbf{j} = -en_v\mathbf{v}_s$, we obtain

$$\frac{\partial \mathbf{j}}{\partial t} = \frac{e^2 n_s}{m} \mathbf{E}. \quad (22.12)$$

If we substitute the electric field $\mathbf{E}$ from (22.12) to the second Maxwell equation (A.18) we have

$$\frac{\partial}{\partial t} \left[\nabla \times \mathbf{j} + \frac{e^2 n_s}{mc} \mathbf{B} \right] = 0, \text{ G-CGS, }^{10} \quad (22.13)$$

which means that the quantity in brackets in (22.13) is a constant as far as time is concerned. Since it is reasonable to assume that at some initial time both $\mathbf{j}$ and $\mathbf{B}$ were zero, it is natural to set this constant equal to zero as F. London and H. London [22.9] did:

$$\nabla \times \mathbf{j} + \frac{e^2 n_s}{mc} \mathbf{B} = 0. \quad (22.14)$$

Problem 22.2t. Taking into account that there is no charge accumulation within a superconductor and the validity of (22.14), show that

$$\frac{\partial \mathbf{j}}{\partial t} = \frac{e^2 n_s}{m} \mathbf{E}, \quad (22.15)$$

$$\nabla^2 \mathbf{B} = \frac{4\pi n_s e^2}{c^2 m} \mathbf{B}, \text{ G-CGS, }^{10} \quad (22.16)$$

$$\mathbf{j} = -\frac{e^2 n_s}{mc} \mathbf{A}, \text{ G-CGS. }^{11} \quad (22.17)$$

Hints. If both $\nabla \cdot \mathbf{D}$ and $\nabla \times \mathbf{D}$ of any vector field $\mathbf{D}$ are zero everywhere, then $\mathbf{D}$ is zero. To prove (22.15) take the time derivative of (22.14) and (A.18), as well as the relations $\nabla \cdot \mathbf{E} = 0$ and $\nabla \cdot \mathbf{j} = 0$. To prove (22.16), combine (22.14) with (A.20) assuming that $\partial \mathbf{D} / \partial t$ is negligible. To prove (22.17), use (22.14) and (A.22) and chose the gauge $\nabla \cdot \mathbf{A} = 0$.

Equation (22.17) is the most common form of London equation, since from it (22.14) till (22.16) follow in a more direct way. Notice that London's equation cannot be exact, since $\mathbf{j}$ is gauge invariant, whereas the vector potential $\mathbf{A}$ does depend on the choice of the gauge. However, a microscopic theory such as the one to be presented in the next chapter can produce a result resembling (22.17) (See (23.62) and [Su181]; in the latter, the question of gauge invariance is treated).

Problem 22.3t. Consider a semi-infinite superconductor occupying the semi-space $x > 0$. Show then that the solution of (22.16) is

$$B_j(x) = B_j(0) \exp\left(-\frac{x}{\lambda_L}\right), \quad j = y, z, \quad (22.18)$$

where

$$\lambda_L = \left(\frac{m c^2}{4\pi n_s e^2} \right)^{1/2}, \text{ G-CGS} \quad ; \quad \lambda_L = \left(\frac{\varepsilon_0 m c^2}{n_s e^2} \right)^{1/2}, \text{ SI.} \quad (22.19)$$

¹⁰ In SI set $c = 1$ in (22.13, 22.14); replace the combination $4\pi/c^2$ in (22.16) by $\mu_0 = 1/\epsilon_0 c^2$.

¹¹ In SI, $\mathbf{j} = -(e^2 n_s / m) \mathbf{A}$.

The numerical value of λ_L , called the *London penetration depth*, is (in Å)

$$\lambda_L \simeq 42 \bar{r}_s^{3/2} \left[\frac{n_s(0)}{n_s(T)} \right]^{1/2} \text{ Å}, \quad (22.20)$$

i.e., about 200 Å at $T \ll T_c$ and reaching over 1,000 Å for T close to T_c .

To get a first idea of the physical mechanism behind London equation, (22.17), let us consider the current-density $\mathbf{j} = \sum_i \mathbf{j}_i$, where the summation is over all mobile electrons and $\mathbf{j}_i$ is the current-density for one electron given by (B.70) (for $T = 0$ K). For a non-magnetic material, the magnetic current $\mathbf{j}_{iM} = c \nabla \times \mathbf{M}_{si}$ is zero, so that the total current density is given by

$$\mathbf{j} = \sum_i \mathbf{j}_{ip} - \frac{e^2 n}{mc} \mathbf{A}, \quad \text{G-CGS}, \quad (22.21)$$

where $\mathbf{j}_{ip}$ is the single-particle paramagnetic contribution (the first term in the rhs of (B.70)), and the last term in (22.21) is the total diamagnetic contribution, which was obtained by taking into account that for a uniform system $\Psi^* \Psi = 1/V$, $\sum_i e^2/m = Ne^2m$, and $n = N/V$. One way to obtain (22.17) (for $T = 0$ K, where $n_s = n$), starting from the general expression (22.21), we simply need to set the paramagnetic contribution $\sum_i \mathbf{j}_{ip}$ equal to zero for superconductors at $T = 0$ K and for the gauge $\nabla \cdot \mathbf{A} = 0$. To see why $\sum_i \mathbf{j}_{ip}$ may be zero (under these conditions) for superconductors and not for normal metals, we must recall that the eigenfunction Ψ , entering the paramagnetic term is not the unperturbed Ψ_0 (i.e., the one corresponding to $\mathbf{A} = 0$), but the perturbed one¹² $\Psi = \Psi_0 + \Psi_1$, where the perturbed part Ψ_1 is non-zero because of the presence of the electromagnetic vector potential $\mathbf{A}$. Since the conductivity is related by definition to the linear response of the system (linear in $\mathbf{A}$), we need Ψ up to first order in $\mathbf{A}$, which is given by (B.53):

$$|\Psi\rangle = |\Psi_0\rangle + \sum_n \frac{\langle \Psi_{0n} | \hat{H}_1 | \Psi_0 \rangle}{E_0 - E_{0n}} |\Psi_{0n}\rangle, \quad (22.22)$$

where $\hat{H}_1 = \sum_i (e/mc) \mathbf{A}_i \cdot \mathbf{p}_i$ according to (B.69), $|\Psi_{0n}\rangle$ are the unperturbed (i.e., the ones corresponding to $\mathbf{A} = 0$) excited eigenstates of the system and E_{0n} the corresponding unperturbed eigenenergies. The denominators in (22.22) may offer the clue for understanding what distinguishes the normal state from the superconducting one: In the former, the difference $E_{0n} - E_0$ may be as small as possible, i.e., $E_{0n} - E_0 \geq 0$, while in the superconducting state, because of the non-zero gap E_g , we have $E_{0n} - E_0 \geq E_g$. In view of $E_{0n} - E_n$ being equal to or larger than E_g , it is not unreasonable to suspect that for superconductors the summation in (22.22) may be zero, and, hence,

¹² In the diamagnetic term we do not need to keep the perturbed part in Ψ , because this would give a contribution of second order in $\mathbf{A}$, since Ψ_1 is of first order.

$|\Psi\rangle = |\Psi_0\rangle$. If this is true, the paramagnetic current is zero, since the equality $|\Psi\rangle = |\Psi_0\rangle$ implies the effective absence of the field and hence, no current. On the contrary, in the normal state, the correction $|\Psi_1\rangle$ is not zero, and as a result, the paramagnetic and the diamagnetic contributions partially cancel each other. Indeed, in the Kubo–Greenwood [18.45, 18.50, 18.52] expression for $\sigma(\omega)$ (see Chap. 18 footnote in p. 519),

$$\sigma(\omega) = \lim_{s \rightarrow 0^+} \frac{i}{\omega + is} \left[\frac{e^2 n}{m} - \frac{e^2}{Vm^2} \sum_{a\beta} |\langle a | \hat{p}_x | \beta \rangle|^2 \frac{f_a - f_\beta}{\hbar\omega_{\beta a}} \right] - \lim_{s \rightarrow 0^+} \frac{ie^2}{Vm^2} \sum_{a\beta} |\langle a | \hat{p}_x | \beta \rangle|^2 \frac{f_a - f_\beta}{\hbar\omega_{\beta a}} \frac{1}{\omega_{\beta a} - \omega - is}, \quad (22.23)$$

$ie^2 n/m\omega$ is the diamagnetic term (remember (A.21), according to which $\mathbf{E} = +i\omega\mathbf{A}/c$) and all the rest is the paramagnetic contribution. In the normal state, the terms in the brackets cancel each other¹³ and what remains is the part of the paramagnetic contribution shown in the second line of (22.23). On the other hand, for a perfect conductor with periodic boundary conditions, the eigenstates $|a\rangle, |\beta\rangle$ are eigenstates of the momentum as well, so that $\langle a | \hat{p}_x | \beta \rangle = 0$, and consequently, only the diamagnetic contribution survives.

22.5 Pippard's Generalization

We have mentioned on several occasions that the relation between the current-density $\mathbf{j}$ and the electric field $\mathbf{E}$ is in general non-local, but until now we have not given an explicit formula for such a relation. In studying the *anomalous skin effect* (i.e., the penetration of an AC EM field in a metal for a depth δ such that $\delta \lesssim \ell$) we obviously need a non-local $\mathbf{j}$ -vs.- $\mathbf{E}$ relation that has the form

$$\mathbf{j}(\mathbf{r}) = \frac{3\sigma}{4\pi\ell} \int d^3r' \frac{\mathbf{R}(\mathbf{R} \cdot \mathbf{E}(\mathbf{r}'))}{R^4} e^{-R/\ell}, \quad \mathbf{R} = \mathbf{r} - \mathbf{r}', \quad (22.24)$$

which reduces to $\mathbf{j} = \sigma\mathbf{E}$, if $\mathbf{E}$ is constant over a range larger than the mean free path ℓ . In analogy with (22.24), Pippard [22.10] generalized London's equation to a non-local one to cover cases where the vector potential varies appreciably over a characteristic length ξ_p (which is the analog of the mean free path ℓ in (22.24)):

$$\mathbf{j}(\mathbf{r}) = -\frac{3}{4\pi\xi_0} \frac{e^2 n_s}{mc} \int d^3r' \frac{\mathbf{R}(\mathbf{R} \cdot \mathbf{A}(\mathbf{r}'))}{R^4} e^{-R/\xi_p}, \quad \mathbf{R} \equiv \mathbf{r} - \mathbf{r}', \quad (22.25)$$

where

¹³ See, E.N. Economou, *Green's Function in Quantum Physics*, 3rd ed., Springer-Verlag, 2006, §8.2.3, pp. 178–180.

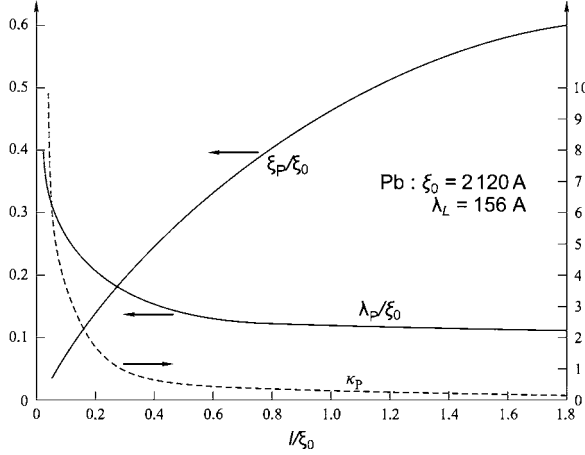


Fig. 22.12. The ratio ξ_P/ξ_0 , λ_P/ξ_0 and $\kappa_P \equiv \lambda_P/\xi_P$ vs. the ratio ℓ/ξ_0 for Pb, based on Pippard's approach and the following values: $v_F = 1.38 \times 10^6$ m/s, $\Delta(0) = 1.37$ meV, $r_s = 1.27$ Å, $n_s(0) = n$. The quantity κ_P is very important because it determines whether a superconductor is type I (if $\kappa_P \ll 1$) or type II (if $\kappa_P \gg 1$)

$$\xi_0 = \frac{\hbar v_F}{\pi \Delta(0)}; \quad \frac{1}{\xi_P} = \frac{1}{\xi_0} + \frac{1}{a\ell}. \quad (22.26)$$

Equation (22.25) reduces to (22.17), if $\mathbf{A}(\mathbf{r}')$ is constant over a range larger than ξ_P and $\ell \gg \xi_0$. The length ξ_0 is called *intrinsic coherence length* and the constant a is about 0.8. If ℓ is much smaller than ξ_0 (i.e., if we have dirty samples), then $\xi_P \simeq \ell$, while in the opposite case where $\xi_0 \ll \ell$ (clean samples) we have $\xi_P \simeq \xi_0$.

Pippard's relation (22.25) combined with Maxwell's equation $\nabla \times \mathbf{H} = \mathbf{j}$ for a semi-infinite superconductor allows us to find the penetration depth λ_P according to Pippard, which is a complicated function of λ_L , ξ_0 , ℓ . In some limited cases, we have simple formulas for λ_P :

$$\lambda_P = \lambda_L \left(\frac{\xi_0}{\xi_P} \right)^{1/2}, \quad \xi_P \ll \lambda_P, \quad (22.27)$$

$$\lambda_P = 0.65 (\xi_0 \lambda_L^2)^{1/3}, \quad \lambda_P \ll \xi_P. \quad (22.28)$$

In Fig. 22.12 we plot the dimensionless ratios ξ_P/ξ_0 , λ_P/ξ_0 and $\lambda_P/\xi_P \equiv \kappa_P$ vs. the ratio ℓ/ξ_0 for Pb.

22.6 Ginzburg–Landau Theory

This is a phenomenological mean field theory in the spirit of expanding the Gibbs free energy in a power series of the order parameter, which in the

present case is taken as the half energy gap Δ . However, there is a very significant difference between the superconducting state and the magnetic state outlined in Sect. 20.5.2. In order to describe the mixed vortex state in type II superconductors a position dependent $\Delta = \Delta(\mathbf{r})$ is needed; on the other hand, to allow for type I superconductors (or type II for $H < H_{c1}$), a term in the free energy is required that will favor a position independent Δ . Ginzburg and Landau [22.11] chose for this additional term a form similar to the kinetic energy in Schrödinger equation; because of this choice, it is only natural to let Δ be a complex quantity in analogy with the wavefunction in the Schrödinger case. Thus, the Gibbs free energy G_s for the superconducting state (including its interaction with a preexisting field $\mathbf{A}$) has the following form according to Ginzburg and Landau:

$$G_s = G_N - a_1 \int d^3r \Delta^*(\mathbf{r}) \left[\nabla + i \left(\frac{2e}{c \hbar} \right) \mathbf{A} \right]^2 \Delta(\mathbf{r}) - a_2 \int d^3r |\Delta(\mathbf{r})|^2 + \frac{1}{2} a_3 \int d^3r |\Delta(\mathbf{r})|^4, \quad \text{G-CGS, (in SI delete } c). \quad (22.29)$$

The Gibbs free energies G_s , G_N are equal to $U' + PV - TS$, where U' is defined as $U_0 + U_{\text{int}}$ in App. A for either the superconducting or the normal state. In (22.29) the terms proportional to $|\Delta(\mathbf{r})|^2$ and $|\Delta(\mathbf{r})|^4$ are the analogs of the terms proportional to M^2 and M^4 respectively for the magnetic case (see (20.17)). The second term on the r.h.s. of (22.29) is the same as the average kinetic energy $\frac{1}{2} m \mathbf{v}^2$ in QM with the wave function $\Psi(\mathbf{r})$ replaced by $\Delta(\mathbf{r})$ and $\hbar^2/2m$ replaced by a_1 . Notice that the term proportional to the vector potential $\mathbf{A}$ is multiplied by $2e \equiv 2|e|$ and not by e as in (B.69). This is so because what enters in superconductivity, and hence, in Δ is the Cooper pairs (of charge $-2e$) and not the individual electrons. To determine the constants a_1, a_2, a_3 , we consider some limiting cases; we examine first the $\mathbf{A} = 0$, $T < T_c$, and *uniform* Δ case, where the minimization of G_s with respect to Δ leads to the relation $|\Delta|^2 = a_2/a_3$ and $G_s - G_N = -V a_2^2/2a_3$. However, in this case, by the definition of H_c , we have that $G_s - G_N = -V \mu_0 H_c^2/2$. Solving with respect to a_2 and a_3 the relation $|\Delta|^2 = a_2/a_3$ and $V a_2^2/2a_3 = V \mu_0 H_c^2/2$ we obtain:

$$a_2 = \mu_0 H_c^2 / \Delta^2; \quad a_3 = \mu_0 H_c^2 / \Delta^4, \quad \text{SI}^{14} \quad (22.30)$$

To express a_1 in terms of familiar quantities, we must find the total current-density, $\mathbf{j}$, which can be obtained from (22.29) as follows

$$\mathbf{j}(\mathbf{r}) = -c \frac{\delta G_s}{\delta \mathbf{A}(\mathbf{r})} = -2 \frac{a_1}{c} \left(\frac{2e}{\hbar} \right)^2 \Delta^2 \mathbf{A}(\mathbf{r}). \quad (22.31)$$

¹⁴ In G-CGS replace μ_0 by $1/4\pi$.

The last expression in (22.31) is valid for the uniform case, where Δ does not depend on $\mathbf{r}$ and for $A(\mathbf{r})$ practically constant within the intrinsic coherence length¹⁵ ξ_0 (in SI delete c).

Problem 22.4t. Prove that $\mathbf{j}(\mathbf{r}) = -c \delta G_s / \delta \mathbf{A}(\mathbf{r})$, where G_s is the total Gibbs free energy.

Hint: Start with (A.62) and take into account that $\delta \mathbf{B}_0 = \nabla \times \delta \mathbf{A}$ and $\mathbf{j} = \nabla \times \mathbf{M}$ (in SI) as well as the identity $\nabla \cdot (\mathbf{M} \times \delta \mathbf{A}) = \delta \mathbf{A} \cdot (\nabla \times \mathbf{M}) - \mathbf{M} \cdot (\nabla \times \delta \mathbf{A})$; then apply the analog of (A.63).

Equation (22.31) is of the form of (22.17). Hence, by comparing the coefficients of (22.31) and (22.17), we obtain

$$a_1 = \frac{e^2 n_s \Phi_0^2}{2(2\pi)^2 \Delta^2 m} = \frac{\Phi_0^2}{2(2\pi)^2 \mu_0 \lambda_L^2 \Delta^2}, \quad \text{SI}, \quad (22.32)$$

where $\Phi_0 = h/2e$ ($hc/2e$ in G-CGS) is the quantum of magnetic flux [in G-CGS $a_1 = \Phi_0^2/4(2\pi)^3 \lambda_L^2 \Delta^2$]. The quantity λ_L is given by (22.19), when $\ell \gg \xi_0$ (otherwise, λ'_L , a more complicated function of λ_L , ξ_0 , and L must replace λ_L). The corrected London length λ'_L is defined in general by the local relation

$$\mathbf{j} = -\frac{1}{\mu_0 \lambda_L'^2} \mathbf{A}, \quad \text{SI}. \quad (22.33)$$

(in G-CGS, replace μ_0 by $c/4\pi$). For simplicity, in what follows, we shall assume that $\ell \gg \xi_0$, so that $\lambda'_L = \lambda_L$. Furthermore, to stress the analogy with Schrödinger equation, we introduce a Cooper pair “wave function” $\Psi(\mathbf{r})$ proportional to $\Delta(\mathbf{r})$ with the proportionality constant being equal to $\sqrt{n_c}/\Delta$, where $n_c = n_s/2$ and Δ are the concentration of Cooper pairs and the gap respectively in the case of the uniform superconducting state. The constant $\sqrt{n_c}/\Delta$ has been chosen so that $|\Psi|^2 = n_c = n_s/2$ in the uniform case. Replacing $\Delta(\mathbf{r})$ by $\Delta/\sqrt{n_c}\Psi(\mathbf{r})$ in (22.29) we obtain the Gibbs free energy in terms of $\Psi(\mathbf{r})$:

$$G_s - G_N = -\frac{\hbar^2}{4m} \int d^3r \Psi^*(\mathbf{r}) \left[\nabla + \frac{2ie}{\hbar c} \mathbf{A}(\mathbf{r}) \right]^2 \Psi(\mathbf{r}) - b_2 \int d^3r |\Psi(\mathbf{r})|^2 + \frac{1}{2} b_3 \int d^3r |\Psi(\mathbf{r})|^4, \quad \ell \gg \xi_0, \quad \text{G-CGS (in SI delete } c), \quad (22.34)$$

where

$$b_2 = \frac{\mu_0 H_c^2}{n_c} = \frac{2\mu_0 H_c^2}{n_s}; \quad b_3 = \frac{\mu_0 H_c^2}{n_c^2} = \frac{4\mu_0 H_c^2}{n_s^2}, \quad \text{SI} \quad (22.35)$$

¹⁵ In the opposite case where $\mathbf{A}(\mathbf{r})$ varies substantially within ξ_0 , the order parameter must be a function of both $\mathbf{r}$ (the center of mass of the Cooper pair) and $\delta\mathbf{r} \equiv \mathbf{r}_1 - \mathbf{r}_2$, the relative vector of the two electrons making up the pair. G-L theory omits the $\delta\mathbf{r}$ dependence of Δ under the assumption that $\mathbf{A}(\mathbf{r})$ is practically constant within the scale ξ_0 .

(in G-CGS, replace μ_0 in (22.35) by $1/4\pi$). Minimizing G_s with respect to $\Psi^*(\mathbf{r})$ by setting $\delta G_s / \delta \Psi^* = 0$ we obtain a nonlinear differential equation for $\Psi(\mathbf{r})$ that is capable of determining the spatial variation of $\Psi(\mathbf{r})$, or equivalently, of $\Delta(\mathbf{r})$:

$$\frac{1}{4m} [-i\hbar\nabla + 2|e|\mathbf{A}(\mathbf{r})/c]^2 \Psi(\mathbf{r}) - b_2 |\Psi(\mathbf{r})| + b_3 |\Psi(\mathbf{r})|^2 \Psi(\mathbf{r}) = 0. \quad (22.36)$$

The most important parameter in (22.36) is the dimensionless ratio $\kappa^2(T)$ of the magnetic energy per Cooper pair $b_2 = \mu_0 H_c^2 V / N_c$ over the kinetic energy per Cooper pair, $\hbar^2 / 4m\lambda_L^2$. If $\kappa \ll 1$, the kinetic energy dominates over the magnetic one, and consequently, the uniform state is favored driving the system to type I superconductivity; if $\kappa \gg 1$, the magnetic energy dominates leading to type II superconductivity.

Problem 22.5t. Show that $\kappa(T)$ can be expressed in terms of the ratio of the critical magnetic flux $\Phi_c \equiv \mu_0 H_c(T) \lambda_L^2(T)$ over the flux quantum $\Phi_0 \equiv h/2e$ as follows

$$\kappa(T) = 2\pi\sqrt{2} \frac{\Phi_c}{\Phi_0}. \quad (22.37)$$

Problem 22.6t. Assume that the temperature dependence of $\lambda_L(T)$ is as follows:

$$\lambda_L(T) \simeq \frac{\lambda_L(0)}{[1 - t^4]^{1/2}}; \quad t \equiv \frac{T}{T_c}. \quad (22.38)$$

Show, then, that $\Phi_c(T)$ is weakly varying with temperature,

$$\Phi_c(T) \simeq \Phi_c(0) \frac{1}{1 + t^2}; \quad t \equiv \frac{T}{T_c}. \quad (22.39)$$

Problem 22.7t. Show that $\kappa(T)$ is weakly varying with $t \equiv T/T_c$ and that it satisfies the approximate relation

$$\kappa \simeq \frac{\lambda_L(0)}{\xi_0}. \quad (22.40)$$

Hint: Employ (23.39) or the relation $\mu_0 H_c^2(0) = \rho_F \Delta^2(0) / V$ to be shown in the next chapter.

Problem 22.8t. Show that the equation for the current follows simply by analogy to the well-known quantum mechanical relation $\mathbf{j} = \text{Re}(\Psi(\mathbf{r})(\hat{\mathbf{p}} - q\mathbf{A})\Psi(\mathbf{r}))$ and the assumption of a sufficiently stiff order parameter $\Psi(\mathbf{r})$. By decomposing $\Psi(\mathbf{r})$ as $\Psi(\mathbf{r}) = |\Psi(\mathbf{r})|\exp(i\Phi(\mathbf{r}))$ show the gauge invariance of the resulting expression for the current.

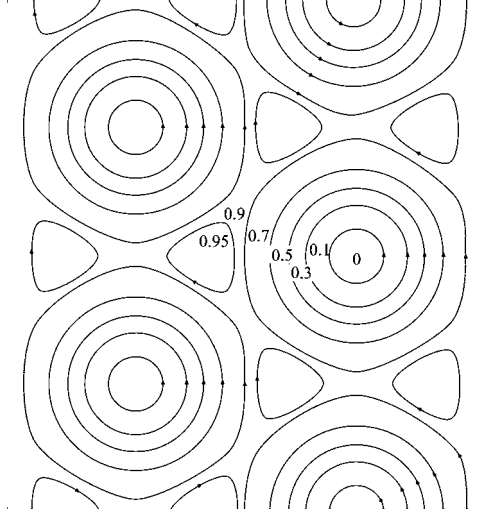


Fig. 22.13. Contours of equal value of $|\Psi(\mathbf{r})/\Psi_{\max}|^2$ in the x, y plane for the vortex state and $H \rightarrow H_{c2}$. The z -axis coincides with the external magnetic field and with the axis of the cylindrical type II superconductor (which corresponds to $\kappa \gg 1$). At the centers of the tiny cylinders $|\Psi|^2 = 0$ (which indicates normal state); as we move away from these centers the value of $|\Psi(\mathbf{r})|^2$ increases and it reaches its maximum value at the centers of the regions among the tiny touching cylinders which are arranged in a regular triangular lattice and they enclose one quantum of magnetic flux

These qualitative comments regarding the role of κ can be quantified by solving (22.36) in terms of the two parameters κ and H_c , as Abrikosov [22.12] did. In Fig. 22.13 we show results of such a calculation for the contours of equal value of $|\Delta(\mathbf{r})|^2$ or $|\Psi(\mathbf{r})|^2$. The H_{c2} is defined as the value of the external field at which the Gibbs free energy of the vortex state to be equal to that of the normal state; it turns out that H_{c2} is proportional to the product κH_c : $H_{c2} = \sqrt{2} \kappa H_c$. The lower critical field H_{c1} is determined by the equality of the free energy of the uniform superconducting state, $\Psi = \text{const.}$, with the free energy of the vortex state with only one vortex covering the cross-section of cylindrical superconductors. This requirement leads to the following relation

$$H_{c1} = \frac{1}{2\kappa} (\ln \kappa + 0.081) H_c, \quad \kappa \gg 1. \quad (22.41)$$

Combining (22.41) with the relation $H_{c2} = \sqrt{2} \kappa H_c$, we obtain

$$\sqrt{H_{c1} H_{c2}} = \left[\frac{1}{\sqrt{2}} (\ln \kappa + 0.081) \right]^{1/2} H_c \simeq H_c. \quad (22.42)$$

The transition from type I to type II superconductivity occurs when $H_{c1} = H_{c2} = H_c$, which in view of $H_{c2} = \sqrt{2} \kappa H_c$, means that the critical value of

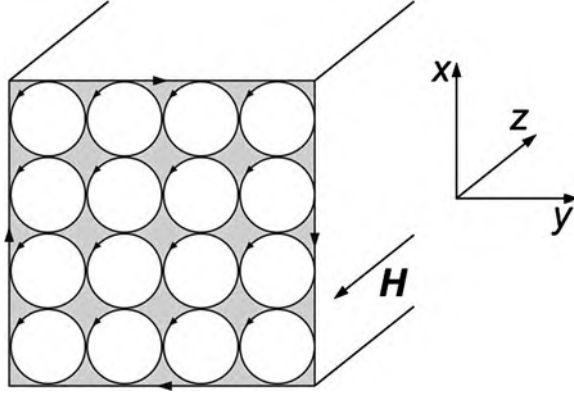


Fig. 22.14. Schematic representation of the vortex state for H just below H_{c2} . The tiny cylinders of cross-section $\pi R^2 = \Phi_0/\mu_0 H_{c2}$ are close-packed; at their center, $|\Psi(\mathbf{r})|^2 = 0$, while in the space among them, $|\Psi(\mathbf{r})|^2$ takes its maximum value

$\kappa = 1/\sqrt{2} \simeq 0.71$. Hence, $\kappa < 0.71$ implies type I superconductivity, while $\kappa > 0.71$ leads to type II superconductivity.

A simplified version of the detailed Abrikosov solution for $H \rightarrow H_{c2}$ is shown in Fig. 22.14, where the tiny cylinders are close-packed; in each one of them just one quantum of magnetic flux is enclosed, while the wave function is given by the following approximate form

$$\Psi(r, \theta) \sim r^a e^{in\theta}, \quad (22.43)$$

where, as we shall see in the next section, n must be integer (in order for Ψ to be single valued); furthermore, n gives the number of quanta of magnetic flux enclosed in each tiny cylinder. By substituting (22.43) in (22.34), we can calculate the difference $G_s - G_N$ as a function of a and n . This difference becomes negative or zero, if the following inequality is satisfied (see the book by Rickayzen [Su181], pp. 323–325):

$$\frac{H}{H_c} \leq \frac{\sqrt{2}n\kappa}{(a+1)[(a/2) + (n/a(a+1)(a+2))]} \quad (22.44)$$

The maximum value of the rhs of (22.44) is obtained when $n = 1^{16}$ and $a = 1/2$. Thus, the vortex state has a free energy lower than that of the normal state as long as

$$H < 1.2\kappa H_c \equiv H_{c2}. \quad (22.45)$$

This value of H_{c2} is close to the one obtained by the detailed Abrikosov solution: $H_{c2} = \sqrt{2}\kappa H_c$.

¹⁶ That the $n = 1$ will achieve the lowest Gibbs free energy for the vortex state among all the natural value of n is obvious because $n = 1$ minimizes the kinetic energy, while the other terms in (22.34) do not depend on n .

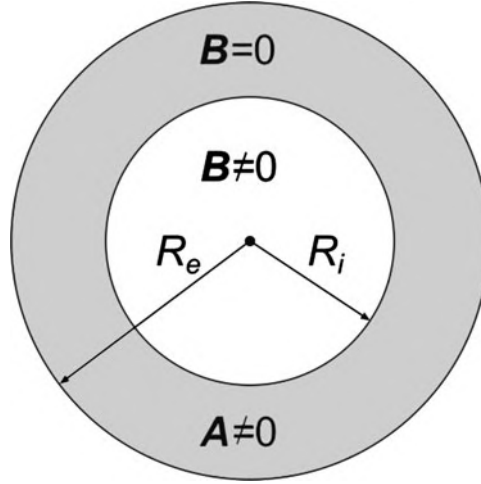


Fig. 22.15. The cross-section of a hollow superconducting cylinder, normal to its axis. The enclosed magnetic flux within the area πR_i^2 is $\pi R_i^2 B_0$

22.7 Quantization of the Magnetic Flux

Consider a hollow cylindrical superconductor and an external magnetic field $\mathbf{B}_0$ parallel to its axis. In the internal and the external surfaces, currents normal to $\mathbf{B}_0$, will circulate (over a thickness of the order of the penetration depth). The external surface current will induce a field $-\mathbf{B}_0$ for $r < R_e$ and zero otherwise (r is the radial distance within a cross-section normal to the axis (see Fig. 22.15)). The internal surface current will induce a field equal to $\mathbf{B}_0$ and $r < R_i$ and zero otherwise. Thus, ignoring the penetration depth as negligible the total field $\mathbf{B} = \mathbf{B}_0 + \mathbf{B}_{\text{ind}}$ is $\mathbf{B}_0$ for $r > R_e$, $\mathbf{B}_0$ and $r < R_i$, and zero for $R_i < r < R_e$. The enclosed in the superconducting tube magnetic flux Φ is equal to $\pi R_i^2 B_0$. The same flux will cross any surface S that will terminate on a closed line α lying entirely within the superconducting wall. If $\mathbf{B} = \nabla \times \mathbf{A}$ we have

$$\Phi = \int_s \mathbf{B} \cdot d\mathbf{S} = \oint_\alpha \mathbf{A} \cdot d\boldsymbol{\ell}. \quad (22.46)$$

Let us now write the superconducting “wave function” $\Psi(\mathbf{r})$ as

$$\Psi(\mathbf{r}) = \sqrt{n_c} e^{i\theta(\mathbf{r})}. \quad (22.47)$$

Then the superconducting current $\mathbf{j}$ can be calculated by combining $\mathbf{j} = -c\delta G_s/\delta \mathbf{A}$ and (22.34). The result is

$$\mathbf{j}(\mathbf{r}) = -\frac{|e| n_c \hbar}{m} \left[\nabla \theta + \frac{2|e|}{\hbar c} \mathbf{A} \right], \text{ G-CGS.} \quad (22.48)$$

(in SI delete c). In the interior of a superconductor no current can flow; hence, $\nabla\theta + (2|e|\hbar c)\mathbf{A} = 0$. If this relation is integrated along the closed line α , we obtain

$$\Phi = \oint_{\alpha} \mathbf{A} d\ell = -\frac{\hbar c}{2|e|} \oint_{\alpha} \nabla\theta d\ell = -\frac{\hbar c}{2|e|} (\theta_f - \theta_i); \quad \text{SI.} \quad (22.49)$$

Since the line α is closed, $\theta_f - \theta_i = 2\pi n$ where n is an integer. Thus, the flux Φ through a superconducting tube (or ring for that matter) is quantized [22.13].

$$\Phi = n\Phi_0; \quad \Phi_0 \equiv \frac{\hbar c}{2|e|}; \quad n \text{ integer, G-CGS.}^{17} \quad (22.50)$$

The field $B'_0 \approx B_0$ is slightly adjusted as to satisfy (22.50); this adjustment is achieved through the surface-current at the internal wall of the cylinder. The numerical value of Φ_0 is 2.0678×10^{-15} Tesla $\cdot$ m² or 2.0678×10^{-7} Gauss cm². The quantum of the magnetic flux is called *fluxoid*.

22.8 Key Points

- Besides zero DC resistivity and expulsion of the magnetic field, several other properties distinguish the superconducting state from the normal one. A gap, 2Δ , opens up at the Fermi level leading to exponentially vanishing electronic specific heat, easy transmission of EM waves of frequency $\omega < 2\Delta/\hbar$, reduced ultrasound attenuation, etc.; the electrons responsible for zero resistivity carry no heat.
- The superconducting state makes a transition to the normal one at the critical temperature T_c , which decreases as the magnetic field increases or the current density increases.
- An isotope effect occurs according to which $T_c \sim M^{-a}$ where, in many cases, $a = 1/2$, indicating a crucial role for the lattice vibrations.
- An external magnetic field surrounding the superconductor squeezes it and increases its Gibbs free energy; when this increase reaches a critical value, the superconducting state undergoes a transition to the normal state. This transition can be abrupt over the whole volume of the solid (type I superconductors) or gradual through a vortex state (type II superconductors). The ratio κ^2 of the critical magnetic energy over the kinetic energy determines the type of superconductivity, according to the Ginzburg–Landau theory: $\kappa^2 \lesssim 0.5$ implies type I superconductivity and $\kappa^2 \gtrsim 0.5$ type II.
- The physical mechanisms responsible for superconductivity are as follows: an indirect attraction occurs (usually due to phonon exchange) strong enough to overcome the screened Coulomb repulsion; this attraction with the help of the Fermi sea leads to bound pair formation (Cooper pairs) of zero total momentum and (almost in all cases) zero total spin; the

¹⁷ In SI, set $c = 1$ in (2.48)–(2.50).

pairs being bosons condense to a coherent quantum state exhibiting zero resistivity, expulsion of the magnetic field, etc.

- The binding energy of the Cooper pair 2Δ (at $T = 0$ K) and T_c are related according to the BCS theory:

$$\frac{2\Delta(0)}{k_B T} \simeq 3.53.$$

- The intrinsic coherence length is as follows: $\xi_0 = \hbar v_F / \pi \Delta(0)$.
- The basic superconducting properties are captured in London equations stating that

$$\mathbf{j} = -a \frac{en_s}{mc} \mathbf{A}, \nabla \cdot \mathbf{A} = 0,$$

where a , a correction factor, depends on the ratio ℓ/ξ_0 ; $a \rightarrow 1$ when $\ell \gg \xi_0$. Pippard generalized London equation to a non-local one.

- London equation leads to an exponential decay of the magnetic field inside a superconductor: $B(x) = B(0) \exp(-x/\lambda_L)$, where the penetration length (according to London) is

$$\lambda_L = \left(\frac{m}{\mu_0 n_s e^2} \right)^{1/2} = \left(\frac{\varepsilon_0 m c^2}{n_s e^2} \right)^{1/2} \simeq 42 \bar{r}_s^{3/2} \left[\frac{n_s(0)}{n_s(T)} \right]^{1/2} \quad \text{A, SI.}$$

(in G-CGS replace ε_0 by $1/4\pi$).

- The Ginzburg–Landau theory, in order to describe situations as in type II superconductors above H_{c1} , introduces a complex, position-dependent $\Delta(\mathbf{r}) \equiv (\Delta/\sqrt{n_c}) \Psi(\mathbf{r})$, on which the superconducting Gibbs free energy depends as follows:

$$G_s - G_N = -\frac{\hbar^2}{4m} \int d^3r \Psi^*(\mathbf{r}) \left[\nabla + \frac{2ie}{\hbar c} \mathbf{A}(\mathbf{r}) \right]^2 \Psi(\mathbf{r}) \\ - b_2 \int d^3r |\Psi(\mathbf{r})|^2 + \frac{1}{2} b_3 \int d^3r |\Psi(\mathbf{r})|^4, \quad \ell \gg \xi_0, \quad (\text{in SI delete } c).$$

where

$$b_2 = \frac{\mu_0 H_c^2}{n_c} = \frac{2\mu_0 H_c^2}{n_s}; \quad b_3 = \frac{\mu_0 H_c^2}{n_c^2} = \frac{4\mu_0 H_c^2}{n_s^2}, \quad \text{SI.}$$

(in G-CGS set $\mu_0 = 1/4\pi$). By minimizing G_s with respect to $\Psi^*(\mathbf{r})$ we obtain

$$\frac{1}{4m} [-i\hbar \nabla + 2|e| \mathbf{A}(\mathbf{r})/c]^2 \Psi(\mathbf{r}) - b_2 |\Psi(\mathbf{r})| + b_3 |\Psi(\mathbf{r})|^2 \Psi(\mathbf{r}) = 0,$$

which shows that for $\kappa \equiv 2\pi\sqrt{2}\Phi_c/\Phi_0 \approx \lambda_L(0)/\xi_0$ less than $1/\sqrt{2}$ we have type I superconductivity, while for $\kappa > 1/\sqrt{2}$ type II occurs. Moreover, $H_{c2} = \sqrt{2}\kappa H_c$ and $H_{c1}H_{c2} \simeq H_c^2$.

- The magnetic flux Φ through a superconducting ring is quantized:

$$\Phi = n \Phi_0,$$

where $\Phi_0 = hc/2|e| \simeq 2.07 \times 10^{-15}$ Tesla $\cdot$ m² = 2.07×10^{-7} Gauss $\cdot$ cm² is the quantum of the flux, called fluxoid and n is integer.

22.9 Problems

- 22.1 Consider a type I spherical superconductor placed in an external magnetic field H_0 . Show that, for $H_0 < 2H_c/3$, the magnetic field $\mathbf{B}$ is zero in the entire volume of the sphere, while, for $H_0 > H_c$, the field in the sphere is $\mu_0 H_0$; in the range $2H_c/3 < H_0 < H_c$, parts of the sphere are in the normal state and parts in the superconducting state.
- 22.2s Starting from (22.11), calculate the difference $C_s - C_N$ of the specific heats. For explicit results use (22.1) and $G_N - G_s = \frac{\rho_F \Delta^2}{2}$.
- 22.3 Starting from (22.11), prove the equality of the entropies, $S_s = S_N$, at $T = T_c$.
- 22.4 Show that the BCS result for $\Delta(T)$ as shown in the caption of Fig. 22.9 reduces to (22.3) as $T \rightarrow T_c^-$.
- 22.5s Show that (22.24) reduces to (22.17), if $\mathbf{A}(\mathbf{r}')$ is a constant independent of $\mathbf{r}'$ and $\xi_p = \xi_0$.
- 22.6 Prove (22.44).

Further Reading

- Most of the topics of this chapter are presented in Kittel's book [SS74], pp. 259–288, and in the book by Ashcroft & Mermin [SS75], pp. 726–749.

Superconductivity, II: Microscopic Theory

Abstract The physical mechanism by which a pair of electrons just above the Fermi energy forms a bound state is physically analyzed and explicit quantitative results for the binding energy and the critical superconducting temperature are obtained. The possibility of Cooper pair formation forces a reorganization of the Fermi sea along the line proposed by Bardeen–Cooper–Schrieffer. This leads to the self-consistent BCS theory, which is capable of obtaining the thermodynamic, transport, and other superconducting properties in terms of the dimensionless phonon attractions, λ , and the dimensionless screened Coulomb repulsion, μ^* . The generalization of the DFT to the superconducting state (aiming at material-specific ab initio calculations) is outlined. The DC and AC Josephson effects as well as the superconducting quantum interference phenomenon are presented.

As it was mentioned in Subsect.8.5.2 of Chap.8, the interpretation of superconductivity is based upon three main points: (a) The appearance of a dynamical (i.e., frequency dependent) indirect attractive el–el interaction strong enough to overcome the screened Coulomb repulsion at least at low frequencies. (b) The creation of bound pairs of electrons (Cooper pairs) as a result of the attraction and their 2D-like motion due to the Fermi sea (produced by all the other electrons). (c) The condensation of Cooper pairs into a coherent state exhibiting quantum effects at a macroscopic level and capable of producing the impressive phenomena presented in Chap. 22.

23.1 Electron–Electron Indirect Attraction

The only well-established indirect attractive interaction between electrons is the one mediated by phonons and given by the last term in the rhs of (8.50). This phonon mediated term is usually written as follows:

$$V_{\text{ee}}^{(\text{ph})}(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}) = - \sum_{s, \mathbf{G}} \frac{2\omega_{\mathbf{k}s} |F|^2}{\hbar(\omega_{\mathbf{k}s}^2 - \omega^2)}, \quad \hbar\omega = |\varepsilon_{n_1}(\mathbf{k}_1) - \varepsilon_{n_2}(\mathbf{k}_2)|, \quad (23.1)$$

where the energies $\varepsilon_{n_1}(\mathbf{k}_1)$, $\varepsilon_{n_2}(\mathbf{k}_2)$ and the crystal momenta (over $\hbar$) $\mathbf{k}_1, \mathbf{k}_2$ are those of the two interacting electrons (n_1 and n_2 are band indices); the superscript (ph) indicates that the interaction is through the exchange of a phonon of crystal momentum (over $\hbar$) $\mathbf{q} = \mathbf{k} + \mathbf{G}$, polarization index s , and eigenfrequency $\omega_{\mathbf{k}s}$; $\mathbf{k}$ is the momentum exchange (over $\hbar$) between the two electrons so that after the phonon exchange, their wavevectors are $\mathbf{k}'_1 = \mathbf{k}_1 + \mathbf{k}$ and $\mathbf{k}'_2 = \mathbf{k}_2 - \mathbf{k}$. In the simpler case of the jellium model (JM), $|F|^2$ is equal to $4\pi\hbar e^2(\omega_k^2 - \omega_t^2)/2\omega_k(ak^2 + k_{\text{TF}}^2)4\pi\varepsilon_0$ so that (23.1) reduces to the last term in (8.50); in realistic cases, $|F|^2$ is a complicated function of $\mathbf{k}_1, n_1, \mathbf{k}_2, n_2, \mathbf{k}$ and the vector $\mathbf{G}$ of the reciprocal lattice, entering in the relation $\mathbf{q} = \mathbf{k} + \mathbf{G}$.

We introduce also the dimensionless quantity λ , as in Sect. 5.4, which is essentially the product of the Fourier transform of the indirect el-el attraction times the density of states at E_F over the volume V , ρ_{FV} :

$$\lambda \equiv \rho_{FV} \sum \frac{2|F|^2}{\hbar\omega_{\mathbf{k}s}} = 2 \int d\omega \tilde{\phi}(\omega) \frac{\alpha^2(\omega)}{\omega}, \quad (23.2)$$

where the summation is over all variables; in the last relation the summation over the exchanged phonon has been singled out (as an integration over the phononic DOS $\tilde{\phi}(\omega)$) and all other summations of $|F|^2 \rho_{FV}$ have been incorporated in the quantity $\alpha^2(\omega)$. In the simple JM, the summation in (23.2) is reduced to an integration over the solid angle Ω , so that λ can be written as follows:

$$\lambda = \frac{\rho_{FV}}{4\pi} \int d\Omega \frac{2|F(\mathbf{k})|^2}{\hbar\omega_{\mathbf{k}}}, \quad (23.3)$$

where $d\Omega = \sin\theta d\theta d\phi$, θ and ϕ are the angles determining the direction of $\mathbf{k} \equiv \mathbf{k}'_1 - \mathbf{k}_1$. Keep in mind that both $|\mathbf{k}'_i|$ and $|\mathbf{k}_i|$ ($i = 1, 2$) are almost equal to k_F . Recall also that the phonon due resistivity of a metal at high temperatures is given in terms of λ_t by (5.55)

$$\rho_{\text{ph}} = \frac{8\pi^2\lambda_t}{4\pi\varepsilon_0\hbar\omega_{pf}^2} k_B T; \quad T \gtrsim \Theta_p, \quad \text{SI}, \quad (23.4)$$

where λ_t is similar to λ with an extra factor $(1 - \cos\theta)$ included in order to exclude the forward scattering (see Sect. 5.4). (In G-CGS delete $4\pi\varepsilon_0$).

Several other mechanisms, besides phonon exchange, have been proposed to account for the required indirect el-el attraction; none of them has been widely accepted, although many researchers believe that phonons alone cannot produce the strong el-el binding in the Cooper pairs observed in the high- T_c superconductors. Thus, it is possible that other processes (with or without the help of phonons) produce the strong el-el attraction in high- T_c superconductors.

23.2 Cooper Pairs

In problem 2.11, we have seen that a circular potential well of depth $-|\varepsilon|$ and radius a in 2D always sustains a bound state. The binding energy ε_b in the weak limit, $|\varepsilon| \ll E_0 \equiv \hbar^2/ma^2$, is given by

$$\varepsilon_b = (2E_0/e^{2\gamma}) \exp \left[-\frac{1}{\rho |\varepsilon|} \right], \quad (23.5)$$

where ρ is the free particle DOS per unit area in 2D, times πa^2 : $\rho = (m/2\pi\hbar^2)\pi a^2$. In Problem 18.13t, we have also examined the same problem of a bound state in a potential-well but within the framework of the LCAO. We found that the eigenenergy E_b of the bound eigenstates satisfies the relation

$$1 + |\varepsilon| \nu_0 g_0(E_b) = 0, \quad (23.6)$$

where

$$g_0(E) = \int_{E_{\min}}^{E_{\max}} \frac{dE' \rho_0(E')}{E - E'}, \quad \rho_0(E') = \frac{1}{N_a a^D} \sum_{\mathbf{k}} \delta(E' - E(\mathbf{k})). \quad (23.7)$$

$\rho_0(E')$ is the unperturbed DOS per unit “volume”, $\nu_0 = a^D$ is the “volume” of the potential well, and $E_{\min}$, $E_{\max}$ are the lower and upper edges of the unperturbed band. Notice that (23.6) and (23.7) are valid for any dimensionality, D . Furthermore, the behavior of $g_0(E)$ for E near $E_{\min}$ is determined by the dependence of $\rho_0(E')$ as $E' \rightarrow E_{\min}$: If $\rho_0(E') \rightarrow (E' - E_{\min})^{-a}$ as $E' \rightarrow E_{\min}^+$ with $0 < a < 1$, then $g_0(E) \rightarrow -|A| (E_{\min} - E)^{-a}$ as $E' \rightarrow E_{\min}^-$; for 1D systems the typical value of the exponent a is $1/2$. If $\rho_0(E')$ drops discontinuously to zero at $E' = E_{\min}$ with a discontinuity, ρ , then the leading term in $g_0(E)$ has the form

$$g_0(E) \rightarrow \rho \ln \frac{E_{\min} - E}{|C|}, \quad E \rightarrow E_{\min}^-. \quad (23.8)$$

For a square lattice $\rho = 1/4\pi |V_2| a^2$ and $C = 32 |V_2| = 4W$, where $W = 8 |V_2|$ is the band width. Combining (23.8) with (23.6), we find

$$\varepsilon_b \equiv E_{\min} - E_b = |C| \exp \left[-\frac{1}{\rho a^2 |\varepsilon|} \right] = |C| \exp \left[-\frac{4\pi |V_2|}{|\varepsilon|} \right], \quad (23.9)$$

which is of the same form as (23.5). Furthermore, (23.6) to (23.8) show that the characteristic exponential dependence of the binding energy on $-1/|\varepsilon|$ in (23.5) and (23.9) is a general consequence of the discontinuity of the unperturbed DOS at the lower band edge appearing naturally for a nonrelativistic massive particle moving in a 2D space. Such a discontinuity in the available unperturbed DOS will be created at any dimensionality in the presence of the Fermi sea (assuming $\rho_F \neq 0$) and will play a critical role for the formation

of Cooper pairs. To see how this happens, consider a pair of electrons each of which has an energy above the Fermi level E_F ; the latter is determined by the finite concentration of other electrons at $T = 0\text{ K}$. As we have mentioned in Problem 2.6s, the motion of the pair of particles is reduced to the free motion of their center of mass with momentum $\hbar\mathbf{K} = \hbar\mathbf{k}_1 + \hbar\mathbf{k}_2$, $M = m_1 + m_2$ and energy $\varepsilon(\mathbf{k}_1) + \varepsilon(\mathbf{k}_2)$, and the relative motion described by a Hamiltonian of the form $\mathbf{p}^2/2\mu + \mathcal{V}(\mathbf{r})$, where $\mu = m_1 m_2 / (m_1 + m_2) = m/2$ and $\mathcal{V}(\mathbf{r})$ is an attractive potential; ($\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ and $\mathbf{p} = \hbar\mathbf{k} = \mu d\mathbf{r}/dt$). To find out whether or not the potential $\mathcal{V}(\mathbf{r})$ is strong enough to create a bound pair, it is enough, according to (23.6) and (23.7), to calculate the unperturbed DOS, per unit volume, $\rho_0(E)$, for the relative motion of the pair:

$$\rho_0(E) = \int \frac{d^3k}{(2\pi)^3} \delta(E - \varepsilon(\mathbf{k}_1) - \varepsilon(\mathbf{k}_2)) \theta(k_1 - k_F) \theta(k_2 - k_F). \quad (23.10)$$

The θ functions guarantee that neither member of the pair occupies states already occupied by the electrons of the Fermi sea.

Problem 23.1ts. Show that the DOS $\rho_0(E)$ is equal to

$$\begin{aligned} \rho_0(E) &= \frac{t}{(2\pi)^2} \left(\frac{m}{\hbar^2} \right)^{3/2} \left[E - \frac{P^2}{4m} \right]^{1/2}, \quad E \geq \max \left[2E_F, \frac{P^2}{4m} \right], \\ &= 0, \quad \text{otherwise,} \end{aligned} \quad (23.11)$$

where

$$t = \min \left[1, \sqrt{m}(E - 2E_F) \left/ \left(E - \frac{P^2}{4m} \right)^{1/2} P \right. \right]. \quad (23.12)$$

The notation is that of problem 2.6s: $p_i = \hbar k_i$ ($i = 1, 2$), $P = \hbar K$, $p = \hbar k$, and $\varepsilon(k_i) = \hbar^2 k_i^2 / 2m$ ($i = 1, 2$). Show, then, that for $P = 0$

$$\rho_0(E) \rightarrow \frac{1}{(2\pi)^2} \left(\frac{m}{\hbar^2} \right)^{3/2} (2E_F)^{1/2} = \frac{\rho_{FV}}{2}, \quad \text{as } E \rightarrow 2E_F \quad (23.13)$$

while, for $0 < P^2 < 8mE_F$,

$$\rho_0(E) \rightarrow \frac{m^2}{(2\pi)^2 \hbar^3} \frac{E - 2E_F}{P}, \quad \text{as } E \rightarrow 2E_F. \quad (23.14)$$

Hints: $E = (P^2/4m) + (p^2/m)$ and $-t \leq \cos \theta \leq t$ where θ is the angle between $\mathbf{P}$ and $\mathbf{p}$.

Equation (23.11) shows that the unperturbed DOS per unit volume, ρ_0 , depends on both $E = \varepsilon_1 + \varepsilon_2$ and P ; when $P = 0$, the DOS drops to zero discontinuously at $E = 2E_F$ with a discontinuity $\rho = \rho_{FV}/2$, where ρ_{FV} is the single electron DOS at E_F (per spin and per unit volume). On the other

hand, when P is different from zero (and less than $(8mE_F)^{1/2}$), $\rho_0(E)$ goes linearly to zero as $E \rightarrow 2E_F$ with a slope that is inversely proportional to P .

Thus, according to (23.9), if the total momentum of the pair is zero, the two electrons will form a bound state, no matter how shallow or how small in extent the attractive potential is; their binding will be

$$\varepsilon_b = |C| \exp\left(-\frac{2}{|\varepsilon| \nu_0 \rho_{FV}}\right) = |C| \exp\left(-\frac{2}{\lambda}\right), \quad (23.15)$$

where $\lambda \equiv |\varepsilon| \nu_0 \rho_{FV}$; the attractive potential $\mathcal{V}(r)$ is assumed to be $-|\varepsilon|$ within the volume ν_0 , and zero otherwise. The prefactor $|C|$ is of the order of four times the bandwidth $E_{\max} - E_{\min}$ as in (23.8), where in the present case $E_{\max} - E_{\min}$ is of the order of $\hbar\omega_D$, since for $\hbar\omega > \hbar\omega_D$ there is no attraction according to (23.1). Thus, $C = c_1 4\hbar\omega_D$, where a more detailed study gives for the numerical constant the value $c_1 = 1$. By choosing a typical JM value for $\lambda \simeq 0.25$ and a typical value for $4\hbar\omega_D \simeq 100$ meV, we obtain for $\varepsilon_b \simeq 0.04$ meV, which is way too small. On the other hand, if instead of $-2/\lambda$ in the exponent we had $-1/\lambda$ the typical value of ε_b would be about 1.8 meV, which is in the range observed for phonon-induced superconductivity. We shall see that the $-1/\lambda$ in the exponent rather than $-2/\lambda$ is the correct starting point in estimating the size of the superconducting gap.

Problem 23.2ts. Show that, when $0 < P < \sqrt{8mE_F}$, a bound pair is formed, only if the following inequality holds

$$\nu_0 |\varepsilon| > \frac{(2\pi)^2 \hbar^3}{c_1 m^2 \hbar\omega_D} P. \quad (23.16)$$

Hint: Show first that $dg_0(E)/dE$ is negative, for $E < E_{\min} = 2E_F$; then calculate the value of $g_0(E)$ at $E = 2E_F$.

23.3 Comments

1. The lowest energy of a single additional pair of electrons attractively interacting with each other and in the presence of a Fermi sea of electrons is achieved when the total momentum of the pair is zero. This lowest energy corresponds to a bound pair (i.e., the Cooper pair) with binding energy below $2E_F$ given by (23.15) with $C \simeq 4\hbar\omega_D$.
2. If a pair of electrons each of which has an energy just above E_F forms a bound state of total energy, $2E_F - \varepsilon_b$, every other pair in the vicinity of the Fermi surface of total momentum $\mathbf{P} = 0$ must form a bound state. This implies a reorganization of the Fermi sea and demands a new self-consistent approach to the bound pair formation in the presence of all the other pairs (instead of the unperturbed Fermi sea).

3. If the attractive potential $\mathcal{V}$ is spherically symmetric, the ground state for the pair's relative motion $\psi(\mathbf{r})$ ought to be spherically symmetric, i.e., s-type, and hence, invariant under the transformation, $\mathbf{r} \rightarrow -\mathbf{r}$, which is equivalent to $\mathbf{r}_1 \rightarrow \mathbf{r}_2$ and $\mathbf{r}_2 \rightarrow \mathbf{r}_1$. Consequently, to preserve the antisymmetry under the transformation $1 \rightarrow 2$ and $2 \rightarrow 1$, the spin wave function must be antisymmetric, i.e., singlet, with total spin of the pair equal to zero. Almost all known superconductors are spin singlets,¹ which forces the spatial wave function to be invariant under the transformation $\mathbf{r} \rightarrow -\mathbf{r}$. Besides s-waves, any even ℓ spherical harmonic remains unchanged under the transformation $\mathbf{r} \rightarrow -\mathbf{r}$, and hence, it can be combined with spin singlet. Actually the high- T_c cuprates have been established as d-wave superconductors and the mechanism responsible for the formation of the Cooper pairs is still under debate.
4. The bound el-el pair (the Cooper pair) consists of a linear combination of states $|\mathbf{k} \rangle |-\mathbf{k} \rangle$ of the form $\sum_{\mathbf{k}} c_{\mathbf{k}} |\mathbf{k} \rangle |-\mathbf{k} \rangle$, where $c_{\mathbf{k}}$ is nonzero in a spherical shell around the Fermi surface of thickness $2\delta k$ such that $\varepsilon(k_F + \delta k) - \varepsilon(k_F - \delta k)$ is of the order of ε_b :

$$\varepsilon_b \simeq \varepsilon(k_F + \delta k) - \varepsilon(k_F - \delta k) = 2 \frac{\partial \varepsilon}{\partial k} \delta k = 2 \hbar v_F \delta k. \quad (23.17)$$

The linear extend ξ' of the Cooper pair must be of order of $1/2\delta k = \hbar v_F / \varepsilon_b$, i.e., of the order of the intrinsic coherence length ξ_0 defined in (22.26).

5. Equation (23.15) with $C \simeq 4\hbar\omega_D$ allows us to examine the role of the phonon spectrum in the phenomenon of superconductivity. Small values of the phonon eigenfrequencies (i.e., soft phonons) would increase the value of λ (if $|F|^2$ is independent of ω_{ks}) as it is clear from (23.2) or (23.3). On the other hand, soft phonons, which increase λ , and hence, the exponential factor, would reduce the preexponential factor $C \sim \hbar\omega_D$ in (23.15). Thus, it seems that there is an upper limit in the magnitude of ε_b obtained by phonon mediated superconductivity. Anyway, there is evidence that several superconductors with relatively high T_c (of the order of 5 – 20 K) and correspondingly large ε_b are soft materials (e.g., Pb with $\Theta_D \simeq 95$ K and $T_c = 7.2$ K) and some of them are in the verge of a structural phase transition. (Recall that a structural transition is accompanied by soft phonons, the eigenfrequency of which goes to zero at the critical point). Thus, materials with soft phonons or on the verge of structural instability may be good candidates for superconductivity with relatively high- T_c values. Actually, structural instabilities may unavoidably block the path to phonon-based superconductivity with very high values of T_c ; indeed, as the Cooper pair binding becomes very strong and its size shrinks, the lattice could possibly undergo a permanent deformation that will trap the Cooper pair in it and

¹ There is strong evidence for p-wave spin triplet superconductivity in Sr_2RuO_4 [23.1, 23.2] and in Bechgaard salts $((\text{TMTSF})_2\text{X})$ with $\text{X} = \text{PF}_6$ and ClO_4 [23.3–23.7] and possibly in UPt_3 .

thus, instead of a high- T_c superconductor, we will end up with an insulator. Solid molecular hydrogen may be viewed as the end stage of an instability of the metallic phase of hydrogen, where an extremely strongly bound “Cooper” pair mediates the formation of a proton pair and it is trapped permanently in it giving rise to the hydrogen molecule. It is expected that metallic hydrogen may be stable only under extremely high pressure (more than a few Mbars); such high *static* pressures cannot be obtained.

One can also correlate excellent metallic conductivity at high temperatures (i.e., very small resistance in the normal state) with weak superconductivity or no superconductivity at all, and vice versa: Poor *phonon-induced* conductivity in the normal state may imply strong superconductivity. The readers may check these statements by comparing Table 22.1 with Table H.15 (care must be exercised to exclude magnetic metals or semimetals). Theoretical support for this correlation stems from (23.4), which shows that the phonon-due resistivity in metals is proportional to λ_t ; the latter is almost equal to λ (see Table 5.2, p. 126), which determines the all-important exponential factor $\exp(-1/\lambda)$.

23.4 Corrected Binding Energy and the Critical Temperature

In arriving at (23.15) the Fermi sea played a passive role in simply making the single electron states with $E < E_F$ inaccessible. However, the Fermi sea can play an active role as well in providing two electrons at the final states $\mathbf{k}'_1$ and $\mathbf{k}'_2$, leaving behind two empty states, which will be occupied by the initial electrons at the states $\mathbf{k}_1$ and $\mathbf{k}_2$. This is an additional indirect channel that has the same initial and final state as the direct one, i.e., the one we considered in arriving at (23.15). To correctly calculate the binding of the Cooper pair, we have to add the contributions of both of these two channels. This is done by simply replacing $g_0(E)$ in (23.6) by $g_{0t} = g_0(E) + g_{0,\text{ind}}(E)$, where

$$g_{0,\text{ind}}(E) = - \int_{E'_{\text{min},i}}^{E'_{\text{max},i}} \frac{dE' \rho_{0,i}(E')}{E - E'}. \quad (23.18)$$

This minus sign in front of the integral in (23.18) is due to the antisymmetry of the two electron wave function $\Psi(1, 2)$ under the transformation $1 \rightarrow 2$ and $2 \rightarrow 1$. A more formal approach is needed² in order to justify this choice. The DOS $\rho_{0,i}(E')$ of the indirect channel for E' around $2E_F$ and $P = 0$ is $\rho_{FV}/2$ for $E' < 2E_F$ and zero for $E' > 2E_F$:

$$\rho_{0,i}(E') = \frac{1}{2} \rho_{FV} \theta(E_F - (E'/2)) \theta(E_F - (E'/2)). \quad (23.19)$$

² See the book by Kadanoff and Baym [MB44], pp 177–187 and pp 187–190.

The θ functions express the obvious restriction that each of the electrons of the Fermi sea has energy less than E_F . We have included two θ functions, although one would be sufficient, because we have in mind to generalize (23.19) to finite temperatures where each θ function will be replaced by the Fermi distribution. Thus,

$$\rho_{0,i}(E') = \frac{1}{2}\rho_{FV}f(E'/2)f(E'/2). \quad (23.20)$$

Similarly at finite temperatures the direct $\mathbf{P} = 0$ DOS will become

$$\rho_0(E') = \frac{1}{2}\rho_{FV} [1 - f(E'/2)] [1 - f(E'/2)], \quad (23.21)$$

and the total $g_{0,t}$ will be

$$g_{0,t}(E) = \int \frac{dE' \rho_{0,t}(E')}{E - E'} = \frac{1}{2}\rho_{FV} \int_{2E-2\hbar\omega_D}^{2E+2\hbar\omega_D} \frac{1 - 2f(E'/2)}{E - E'} dE'. \quad (23.22)$$

The integration limits were restricted to a range equal to $4\hbar\omega_D$ as before. From (23.22) we see that at $T = 0$ K the discontinuity at $E' = 2E_F$ is equal ρ_{FV} and not $\frac{1}{2}\rho_{FV}$ as before. Hence, by substituting $g_{0,t}(E)$ in (23.6) we obtain the following expression for the binding energy at $T = 0$ K:

$$\varepsilon_b = 4\hbar\omega_D e^{-1/\lambda}. \quad (23.23)$$

Furthermore, (23.22) allows us to determine the critical temperature T_c as the one at which the binding energy is just zero and hence, $E_b \equiv 2E_F - \varepsilon_b = 2E_F$:

$$-|\varepsilon|v_0g_{0,t}(2E_F;T_c) = 1. \quad (23.24)$$

Problem 23.3ts. Show that $g_{0,t}(2E_F;T)$ is equal to

$$-\rho_{FV} \ln \frac{2e^\gamma \hbar\omega_D}{\pi k_B T}, \quad (23.25)$$

in the limit $(\hbar\omega_D/k_B T) \gg 1$ ($\gamma = 0.57721\dots$ is Euler constant).

Hints: Change variables as follows: $E' = 2E_F + 2k_B T x$; then integrate by parts by setting $dx/x = d \ln |x|$; finally in the resulting integral set the upper limit $\hbar\omega_D/k_B T$ equal to ∞ . Combining (23.24) and (23.25) we obtain

$$T_c = \frac{2e^\gamma}{\pi} \Theta_D e^{-1/\lambda} \simeq 1.13 \Theta_D e^{-1/\lambda}. \quad (23.26)$$

This result for the T_c is identical to that obtained by the BCS self-consistent theory.

Problem 23.4ts. Assume that $\lambda = A/\Theta_D$, where the constant A is equal to the product of the typical value of λ ($\lambda \simeq 0.25$) by the typical value of Θ_D ($\Theta_D \simeq 320$ K). Calculate the maximum possible value of T_c according to (23.26)

Answer : $T_{c,\max} \simeq 33$ K obtained when $\Theta_D = A$. (23.27)

Calculations similar to those of problem 23.4t, together with the fact that the highest observed T_c up to 1986 was not higher than 23 K, have led to the widely accepted conjecture that about 35 K is the highest possible value for T_c . Experimental findings since 1986 have demolished this belief.

By identifying the binding energy ε_b with the experimentally observed gap $E_g(0) = 2\Delta(0)$, we obtain the following relation between $E_g(0)$ and $k_B T_c$ (see (23.23) and (23.26)):

$$\frac{\varepsilon_b}{k_B T_c} = \frac{E_g(0)}{k_B T_c} \equiv \frac{2\Delta(0)}{k_B T_c} = 3.5278. \quad (23.28)$$

Equation (23.28) is in impressive agreement with the experimental data shown in Table 22.2 (with the exceptions of Hg and Pb, where the observed values are equal to 4.6 and 4.38 instead of 3.53).

23.5 Further Corrections to the Formula for T_c

In arriving at (23.26) we have omitted the screened Coulomb el-el repulsion given by the first term in (8.50). The inclusion of this term will reduce λ , since in (23.3) the quantity $2|F(\mathbf{k})|^2/\hbar\omega_k$ must be replaced by $(2|F(\mathbf{k})|^2/\hbar\omega_k) - (4\pi e^2/4\pi\varepsilon_0(ak^2 + k_{TF}^2))$. Thus, instead of λ we shall have $\lambda - \mu^*$ where μ^* is given by

$$\mu^* \simeq \frac{\rho_{FV}}{4\pi} \int d\Omega \frac{4\pi e^2}{4\pi\varepsilon_0(ak^2 + k_{TF}^2)}. \quad (23.29)$$

The JM result for μ^* , is $\mu_0^* \simeq 0.25$ and a more realistic value³ of μ^* is 0.1 (unless ρ_{FV} is much larger than the JM value for this quantity).

Another source of error in the formula (23.26) for T_c is that we have implicitly assumed that the electron-phonon interaction V_{e-p} and the Coulomb repulsion V_c are so weak that they have no effect on the motion of the individual electrons that comprise the pairs. Actually, both V_{e-p} and V_c modify the properties of each electron; it is these modified electrons (which are called *dressed electrons*, or *quasi-electrons*) that combine to make up the pairs. One important difference between the bare and the dressed electrons is that the discontinuity at the Fermi level is reduced by a factor $w_F = (1 + \lambda)^{-1}$ for each electron of the pair. One way to understand this reduction is by taking into account that only a fraction w_F of each electron, propagates as a quasi electron, while the rest, $1 - w_F$, has no well-defined energy-momentum relation and thus does not produce any discontinuity at E_F . The net result is to multiply

³ If one takes into account that the integration limits in (23.29) do not terminate at $\hbar\omega_D$ but at E_F the expression for μ^* becomes $\mu^* = \mu_0^* [1 + \mu_0^* \ln(E_F/\hbar\omega_D)] \simeq 0.1$ (See the book by Rickayzen [Su181], pp. 143–145).

the DOS given by (23.20) and (23.21) by a factor w_F^2 . On the other hand, the el-ph interaction increases the DOS at E_F by a factor, $(1+\lambda)$. Thus, including these corrections, both λ and μ^* must be multiplied by $w_F^2(1+\lambda) = (1+\lambda)^{-1}$ and the formula for T_c will become

$$T_c = p \exp \left(-\frac{1+\lambda}{\lambda - \mu^*} \right), \quad (23.30)$$

where the prefactor p is not equal to that of (23.26) because of contributions due to the non-quasi-particle smooth background of each electron propagator.

A more rigorous analysis based on the Eliashberg⁴ gap equations ([23.8], see also [SS98], vol. 2) gives the following expression of T_c [23.9]:

$$T_c = p \exp \left(-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)} \right), \quad (23.31)$$

which is remarkably close to our simplified result. According to McMillan [23.9], the prefactor in (23.31) is

$$p = \frac{\hbar\omega_D}{1.45k_B}. \quad (23.32)$$

A more accurate value of p is given in [23.10].

Notice that when λ is small, (23.30) and (23.31) are reduced essentially to the BCS formula (23.26) with λ replaced by $\lambda - \mu^*$. On the other hand, when λ is large (i.e., $\lambda \gtrsim 1$) serious discrepancies from the BCS theory are expected. For such superconductors, which are called *strong-coupling superconductors*, more sophisticated approaches such as that by Eliashberg are needed for their realistic study. Lead (with $\lambda \simeq 1.55 \pm 0.02$) and mercury (with $\lambda \simeq 1.6 \pm 0.01$) are typical strong-coupling superconductors for which $E_g(0)/k_B T$ differs substantially from the 3.53 BCS result.

23.6 The Bardeen–Cooper–Schrieffer (BCS) Theory

The essence of the phenomenon of superconductivity is the formation of Cooper pairs; their eigenfunctions can be written as $\Sigma_{\mathbf{k}} c_{\mathbf{k}} |\mathbf{k} > | -\mathbf{k} >$, where $\Sigma_{\mathbf{k}} |c_{\mathbf{k}}|^2 = 1$. As it was mentioned in paragraph 23.3(2), a self-consistent ground state must incorporate the reorganization of the Fermi sea due to Cooper pair formation; hence, it must be based on the occupation of the various states $|\mathbf{k}, \bar{\mathbf{k}}\rangle \equiv |\mathbf{k}\rangle |-\mathbf{k}\rangle$ by pairs of electrons. If all states $|\mathbf{k}, \bar{\mathbf{k}}\rangle$ with $|\mathbf{k}| \leq \mathbf{k}_F$ are fully occupied by two electrons, we shall end up with the Fermi

⁴ In Eliashberg's approach, the process of the single electron dressing by V_{e-p} and V_c and the process of pairing of two electrons are treated on equal footing, without assuming that the first process takes place before the second.

sea and not with Cooper pairs. Thus, it is necessary that the states $|\mathbf{k}, \bar{\mathbf{k}}\rangle$ are partly occupied with probability amplitude $v_{\mathbf{k}}$ and partly empty with probability amplitude $u_{\mathbf{k}}$, where, of course, $|v_{\mathbf{k}}|^2 + |u_{\mathbf{k}}|^2 = 1$.⁵ Hence, the basic ingredient of the ground state is pair states of the form

$$\phi_2(k) \equiv u_{\mathbf{k}} O_{\mathbf{k}} + v_{\mathbf{k}} |\mathbf{k}, \bar{\mathbf{k}}\rangle, \quad (23.33)$$

where $O_{\mathbf{k}}$ denotes that the state $|\mathbf{k}, \bar{\mathbf{k}}\rangle$ is empty.⁶ This choice leaves space for the $c_{\mathbf{k}}$ of each Cooper pair to be nonzero even for k less k_F without violating the Pauli's principle. By omitting correlations among pair of electrons in different $\phi_2(\mathbf{k})$ states, we conclude that the total wave function must be a product of $\phi_2(\mathbf{k})$ states:

$$|G\rangle = \prod_{\mathbf{k}} \phi_2(k) \equiv \prod_{\mathbf{k}} (u_{\mathbf{k}} O_{\mathbf{k}} + v_{\mathbf{k}} |\mathbf{k}, \bar{\mathbf{k}}\rangle), \quad (23.34)$$

where k runs over all possible values (smaller or larger than k_F). Notice that $|G\rangle$ does not correspond to a fixed number of particles. This annoying feature is easily taken care of by working with the grand canonical ensemble, which means that, instead of minimizing the total energy U , we must minimize the grand thermodynamic potential $\Omega = U - TS - \mu N_e$, which at $T = 0$ K becomes⁷ $\Omega = U - N_e E_F$, where N_e is the average number of electrons (see App. C).

Having made a choice of the trial ground state, the next step is to find the ground state energy $U = \langle G | \hat{H} | G \rangle$ and then to subtract $N_e E_F$ in order to end up with Ω . The Hamiltonian $\hat{H}$ in our case will be taken to be the sum of the two terms: The unperturbed part $\hat{H}_0 = \sum_{\mathbf{q}} \varepsilon_{\mathbf{q}} \hat{n}_{\mathbf{q}}$, which consists of noninteracting dressed electrons and the part $\hat{H}_{e-e}$, which describes the attractive interaction of pairs of dressed electrons being initially at the state

⁵ For a uniform system, $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$ can be taken as real with no loss of generality; the validity of this statement is based on the fact that a constant phase in the wave function has no physical meaning and it can be omitted (In this respect see the book by Kaxiras [SS83] pp. 298–301). For a nonuniform system as in the Ginzburg–Landau theory $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$ are in general complex quantities and their phase does matter physically. In the present study, we shall keep the complex notation in expressions to be minimized because for any real function F of $z = x + iy$ and $z^* = x - iy$ we have that either $(\partial F / \partial z)_{z^*} = 0$ or $(\partial F / \partial z^*)_z = 0$ imply that both $(\partial F / \partial x)_y = 0$ and $(\partial F / \partial y)_x = 0$. Hence, to minimize any real function of z and z^* it is enough to set either $(\partial F / \partial z)_{z^*}$ or $(\partial F / \partial z^*)_z$ equal to zero.

⁶ The states $\phi_2(k)$ generated by (23.33) are sometimes called (pairs of opposite) Bogoliubov quasiparticles; each of these quasiparticles is of Fermionic character. Moreover, the present generalized mean-field theory used in the BCS formalism is sometimes called the Hartree–Fock–Bogoliubov approach.

⁷ Employing $\Omega = U - N_e E_F$ is equivalent to the use of $\hat{H} - \hat{N}_e E_F$ instead of the Hamiltonian $\hat{H}$.

$\phi_2(\mathbf{k})$ and being scattered to the state $\phi_2(\mathbf{k}')$ through the exchange of a phonon and a screened Coulomb potential as shown in Fig. 23.1. We have then, for $\langle G | \hat{H} | G \rangle = \langle G | \hat{H}_0 | G \rangle + \langle G | \hat{H}_{e-e} | G \rangle$, the following:

$$\langle G | \hat{H}_0 | G \rangle = \sum_q \varepsilon_q \langle G | \hat{n}_q | G \rangle = 2 \sum_{\mathbf{k}} \varepsilon_{\mathbf{k}} v_{\mathbf{k}} v_{\mathbf{k}}^*, \quad (23.35)$$

$$\begin{aligned} \langle G | \hat{H}_{e-e} | G \rangle &= \sum_{\mathbf{k}, \mathbf{k}'} \langle \varphi_2(\mathbf{k}) | \langle \varphi_2(\mathbf{k}') | \hat{H}_{e-e} | \varphi_2(\mathbf{k}') \rangle | \varphi_2(\mathbf{k}) \rangle \\ &= \sum_{\mathbf{k}, \mathbf{k}'} u_{\mathbf{k}}^* v_{\mathbf{k}'}^* \langle \mathbf{k}', \bar{\mathbf{k}}' | \hat{H}_{e-e} | \mathbf{k}, \bar{\mathbf{k}} \rangle u_{\mathbf{k}'} v_{\mathbf{k}} \\ &\equiv \frac{1}{V} \sum_{\mathbf{k}, \mathbf{k}'} u_{\mathbf{k}}^* v_{\mathbf{k}'}^*, u_{\mathbf{k}'} v_{\mathbf{k}} \mathcal{V}_{\mathbf{k}\mathbf{k}'}. \end{aligned} \quad (23.36)$$

To obtain the last expression in (23.35) we took into account that $\hat{n}_q \varphi_2(\mathbf{k}) = \hat{n}_q u_{\mathbf{k}} O_{\mathbf{k}} + \hat{n}_q v_{\mathbf{k}} | \mathbf{k}, \bar{\mathbf{k}} \rangle = O + v_{\mathbf{k}} \hat{n}_q | \mathbf{k}, \bar{\mathbf{k}} \rangle = v_{\mathbf{k}} \delta_{q, \mathbf{k}} | \mathbf{k}, \bar{\mathbf{k}} \rangle + v_{\mathbf{k}} \delta_{q, -\mathbf{k}} | \mathbf{k}, \bar{\mathbf{k}} \rangle$ and that $\langle \mathbf{k}', \bar{\mathbf{k}}' | \mathbf{k}, \bar{\mathbf{k}} \rangle = \delta_{\mathbf{k}, \mathbf{k}'}$. While deriving (23.35), we have singled out two pair states, $\phi_2(\mathbf{k})$ and $\phi_2(\mathbf{k}')$, out of all ϕ_2 's, because the process shown in Fig. 23.1, involves two and only two such states, and then we have summed over all possible choices of $\phi_2(\mathbf{k})$ and $\phi_2(\mathbf{k}')$. The rest of the factors $\varphi_2(q), q \neq \mathbf{k}, \mathbf{k}'$, entering in $|G\rangle$ give unity because of their normalization: $\langle \phi_2(q') | \phi_2(q) \rangle = \delta_{q'q}$; out of sixteen terms in $\langle \phi_2(\mathbf{k}) | \langle \phi_2(\mathbf{k}') | \hat{H}_{e-e} | \phi_2(\mathbf{k}') \rangle | \phi_2(\mathbf{k}) \rangle$, only the one shown in the second line of (23.36) corresponds to the process shown in Fig. 23.1⁸; finally we have defined the quantity $V_{\mathbf{k}\mathbf{k}'}$ as the matrix element in the second line

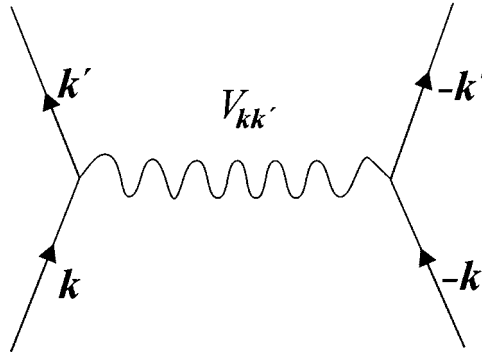


Fig. 23.1. A pair of dressed electrons of total momentum equal to zero and individual momenta (over $\hbar$) $\mathbf{k}$ and $-\mathbf{k}$ exchange momentum $\delta \mathbf{k} \equiv \mathbf{k} - \mathbf{k}'$ through interactions, which are phonon mediated and screened Coulomb. As a consequence, their individual momenta become $\mathbf{k} - \delta \mathbf{k} = \mathbf{k}'$ and $-\mathbf{k} + \delta \mathbf{k} = -\mathbf{k}'$

⁸ The matrix element shown in Fig. 23.1 corresponds to a transition from an initial state, where the pair state $|\mathbf{k}, \bar{\mathbf{k}}\rangle$ is occupied and the pair state $|\mathbf{k}', \bar{\mathbf{k}}'\rangle$ is empty,

of (23.36) times the volume V , $V_{\mathbf{k},\mathbf{k}'} \equiv V \langle \mathbf{k}', \bar{\mathbf{k}}' | \hat{H}_{e-e} | \mathbf{k}, \bar{\mathbf{k}} \rangle$. Notice that $V_{\mathbf{k},\mathbf{k}'} = V_{-\mathbf{k},-\mathbf{k}'}$ and that $V_{\mathbf{k},\mathbf{k}'}^* = V_{\mathbf{k}',\mathbf{k}}$.

To obtain $\Omega \equiv U - N_e E_F$ we replace N_e by $\sum_{\mathbf{q}} \langle \hat{n}_{\mathbf{q}} \rangle = 2 \sum_{\mathbf{k}} v_{\mathbf{k}} v_{\mathbf{k}}^*$ so that

$$\Omega = 2 \sum_{\mathbf{k}} \delta \varepsilon_{\mathbf{k}} v_{\mathbf{k}} v_{\mathbf{k}}^* + \langle G | \hat{H}_{e-e} | G \rangle, \quad (23.37)$$

where $\delta \varepsilon_{\mathbf{k}} \equiv \varepsilon_{\mathbf{k}} - E_F$. The final step is to minimize Ω with respect to each $v_{\mathbf{k}}^*$ taking into account that $\partial u_{\mathbf{k}}^* / \partial v_{\mathbf{k}}^* = -v_{\mathbf{k}} / u_{\mathbf{k}}$, because of $u_{\mathbf{k}} u_{\mathbf{k}}^* + v_{\mathbf{k}} v_{\mathbf{k}}^* = 1$. The result is

$$2 \delta \varepsilon_{\mathbf{k}} v_{\mathbf{k}} + \frac{1}{V} \sum_{\mathbf{k}'} V_{\mathbf{k}'\mathbf{k}} u_{\mathbf{k}'}^* u_{\mathbf{k}} v_{\mathbf{k}'} - \frac{1}{V} \frac{v_{\mathbf{k}}^2}{u_{\mathbf{k}}} \sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} v_{\mathbf{k}'}^* u_{\mathbf{k}'} = 0, \quad (23.38)$$

or taking into account the reality of $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$ we find

$$2 \delta \varepsilon_{\mathbf{k}} u_{\mathbf{k}} v_{\mathbf{k}} = \Delta_{\mathbf{k}} (v_{\mathbf{k}}^2 - u_{\mathbf{k}}^2), \quad (23.39)$$

where

$$\Delta_{\mathbf{k}} = \Delta_{\mathbf{k}}^* = \frac{1}{V} \sum_{\mathbf{k}'} V_{\mathbf{k}'\mathbf{k}} u_{\mathbf{k}'} u_{\mathbf{k}'} v_{\mathbf{k}'} = \frac{1}{V} \sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} u_{\mathbf{k}'} u_{\mathbf{k}'} v_{\mathbf{k}'}^*. \quad (23.40)$$

Taking into account (23.39) and the relation $u_{\mathbf{k}}^2 + v_{\mathbf{k}}^2 = 1$ we can express $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$ in terms of $\Delta_{\mathbf{k}}$ and $\delta \varepsilon_{\mathbf{k}}$ as follows

$$u_{\mathbf{k}}^2 = \frac{1}{2} \left(1 + \frac{\delta \varepsilon_{\mathbf{k}}}{E_{\mathbf{k}}} \right), \quad v_{\mathbf{k}}^2 = \frac{1}{2} \left(1 - \frac{\delta \varepsilon_{\mathbf{k}}}{E_{\mathbf{k}}} \right), \quad (23.41)$$

or

$$u_{\mathbf{k}}^2 = \frac{1}{2} \left(1 - \frac{\delta \varepsilon_{\mathbf{k}}}{E_{\mathbf{k}}} \right), \quad v_{\mathbf{k}}^2 = \frac{1}{2} \left(1 + \frac{\delta \varepsilon_{\mathbf{k}}}{E_{\mathbf{k}}} \right), \quad (23.42)$$

where

$$E_{\mathbf{k}} = \sqrt{\delta \varepsilon_{\mathbf{k}}^2 + \Delta_{\mathbf{k}}^2}, \quad E_{\mathbf{k}} \geq 0. \quad (23.43)$$

Problem 23.5ts. Prove that (23.41) or (23.42) together with (23.43) satisfy the condition $u_{\mathbf{k}}^2 + v_{\mathbf{k}}^2 = 1$ and the relation (23.39).

Hint: To see how we obtain (23.41) or (23.42), notice that the relation $u_{\mathbf{k}}^2 + v_{\mathbf{k}}^2 = 1$ is automatically satisfied if $u_{\mathbf{k}} = \cos \theta_{\mathbf{k}}$ and $v_{\mathbf{k}} = \sin \theta_{\mathbf{k}}$.

For the normal case, where $\Delta_{\mathbf{k}} = 0$, we have that $E_{\mathbf{k}} = |\delta \varepsilon_{\mathbf{k}}|$, and hence, $\delta \varepsilon_{\mathbf{k}} / E_{\mathbf{k}} = 1$, if $k > k_F$ and $\delta \varepsilon_{\mathbf{k}} / E_{\mathbf{k}} = -1$ if $k < k_F$. It follows that the solution (23.41) is the only one appropriate for the ground state $|G\rangle$, since this solution is the one that reduces to the unperturbed ground state.

to a final state, where the pair state $|\mathbf{k}, \bar{\mathbf{k}}\rangle$ is empty and the pair state $|\mathbf{k}', \bar{\mathbf{k}}'\rangle$ is occupied.

Problem 23.6ts. Show that, if for only one particular $\mathbf{k}$ the solution (23.41) would be replaced by (23.42), the $T = 0$ K ground thermodynamic potential will increase by $2E_{\mathbf{k}}$.

Hint: $\langle G | H_0 | G \rangle - N_e E_F$ will increase by $2\delta\varepsilon_{\mathbf{k}}^2/E_{\mathbf{k}}$ and $\langle G | H_{e-e} | G \rangle$ will increase by $2\Delta_{\mathbf{k}}^2/E_{\mathbf{k}}$.

Thus, $2E_{\mathbf{k}}$ is the electron-hole elementary excitation across the superconducting gap $E_g(0)$. Indeed the smallest value of $2E_{\mathbf{k}}$ is obtained when $\delta\varepsilon_{\mathbf{k}} = 0$; then we have than $\min 2E_{\mathbf{k}} = 2 \min \Delta_{\mathbf{k}} \equiv E_g(0)$.

To conclude the determination of the superconducting ground state, we have to obtain $\Delta_{\mathbf{k}}$. Combining the definition of $\Delta_{\mathbf{k}}$, (23.40) with (23.39) and (23.41), we have the following result:

$$\Delta_{\mathbf{k}} = -\frac{1}{V} \sum_{\mathbf{k}'} \frac{V_{\mathbf{k}\mathbf{k}'} \Delta_{\mathbf{k}'}}{2E_{\mathbf{k}'}} \quad (23.44)$$

The simplest possible form for $V_{\mathbf{k}\mathbf{k}'}$, is the following

$$V_{\mathbf{k}\mathbf{k}'} = -|\varepsilon| \nu_0 \theta(\hbar\omega_D - |\delta\varepsilon_{\mathbf{k}}|) \theta(\hbar\omega_D - |\delta\varepsilon_{\mathbf{k}'}|), \quad (23.45)$$

which corresponds to the attractive potential $\mathcal{V}(r_1 - r_2)$ being equal to $-|\varepsilon| \nu_0 \delta(r_1 - r_2)$; $|\varepsilon|$ is the effective depth of $\mathcal{V}(r_1 - r_2)$ and ν_0 is the effective volume outside of which $\mathcal{V}(r_1 - r_2)$ is zero. In the case of (23.45), we shall try a solution for $\Delta_{\mathbf{k}}$ of the form $\Delta \times \theta(\hbar\omega_D - |\delta\varepsilon_{\mathbf{k}}|)$, which substituted in (23.44) together with (23.45) yields:

$$\begin{aligned} 1 &= \frac{1}{V} (|\varepsilon| \nu_0) \sum_{\mathbf{k}} \frac{\theta(\hbar\omega_D - |\delta\varepsilon_{\mathbf{k}}|)}{2E_{\mathbf{k}}} \\ &= (\rho_{FV} |\varepsilon| \nu_0) \int_{-\hbar\omega_D}^{\hbar\omega_D} \frac{d(\delta\varepsilon)}{2\sqrt{\delta\varepsilon^2 + \Delta^2}} \\ &= \lambda \ln \frac{\hbar\omega_D + \sqrt{\hbar^2\omega_D^2 + \Delta^2}}{\Delta} \simeq \lambda \ln \frac{2\hbar\omega_D}{\Delta}. \end{aligned} \quad (23.46)$$

In the second line, we replaced the summation over $\mathbf{k}$ with an integration over the DOS: $\sum_{\mathbf{k}} \varphi(\delta\varepsilon) \rightarrow \int \rho_F \varphi(\delta\varepsilon) d(\delta\varepsilon)$, where $\varphi(\delta\varepsilon)$ is any smooth function of $\delta\varepsilon$ for $\delta\varepsilon$ around zero; in the third line we set $\lambda = \rho_F |\varepsilon| \nu_0 / V = \rho_{FV} |\varepsilon| \nu_0$ as before and we took into account that $\Delta \ll \hbar\omega_D$. Thus, we find again (23.23):

$$\Delta = 2\hbar\omega_D e^{-1/\lambda}. \quad (23.47)$$

(Recall that $\varepsilon_b \equiv E_g(0) = 2\Delta$).

A final check for the self-consistency of the BCS theory is to show that the superconducting zero temperature grand thermodynamic potential Ω_s is lower than the corresponding potential, Ω_N , of the normal state. We have

$$\Omega_N - \Omega_s = 2 \sum_{k < k_F} \delta\varepsilon_{\mathbf{k}} - 2 \sum_{k < k_F} \delta\varepsilon_{\mathbf{k}} v_{\mathbf{k}}^2 - 2 \sum_{k > k_F} \delta\varepsilon_{\mathbf{k}} v_{\mathbf{k}}^2 - \langle G | H_{e-e} | G \rangle. \quad (23.48)$$

The first term in the rhs of (23.48) is equal to $\Omega_N(0)$; the first three terms can be written as

$$-\sum_{\mathbf{k}} \left(1 - \frac{|\delta\varepsilon_{\mathbf{k}}|}{E_{\mathbf{k}}} \right) |\delta\varepsilon_{\mathbf{k}}|,$$

by taking into account that $\delta\varepsilon_{\mathbf{k}} = -|\delta\varepsilon_{\mathbf{k}}|$, if $k < k_F$, and $\delta\varepsilon_{\mathbf{k}} = |\delta\varepsilon_{\mathbf{k}}|$, if $k > k_F$. The term $\langle G | H_{e-e} | G \rangle$ can be written as $-\sum_{\mathbf{k}} \Delta_{\mathbf{k}}^2 / 2E_{\mathbf{k}}$ by employing (23.36), the definition of $\Delta_{\mathbf{k}}$, (23.40), and (23.39) and (23.41). Adding all the four terms of the rhs of (23.48), we obtain

$$\begin{aligned} \Omega_N - \Omega_s &= \sum_{\mathbf{k}} \left[\frac{\Delta_{\mathbf{k}}^2}{2E_{\mathbf{k}}} + \frac{|\delta\varepsilon_{\mathbf{k}}|^2}{E_{\mathbf{k}}} - |\delta\varepsilon_{\mathbf{k}}| \right] \\ &= \lim_{A \rightarrow \infty} \rho_F \int_{-A}^A \left(\frac{\Delta^2}{2E} + \frac{x^2}{E} - |x| \right) dx. \end{aligned} \quad (23.49)$$

Problem 23.7ts. Show that

$$\Omega_N - \Omega_s = \frac{1}{2} \rho_F \Delta^2. \quad (23.50)$$

Hint: Integrate each of the three terms in (23.49) from 0 to A , multiply by two and in the final expression take the limit $A \rightarrow \infty$.

We conclude this brief presentation of the zero temperature BCS theory by pointing out that in view of problem 23.6t, the superconducting DOS, $g(E)$, in the simple case (23.45), can be expressed in terms of the excitation energy $E_{\mathbf{k}} = \sqrt{\delta\varepsilon_{\mathbf{k}}^2 + \Delta^2}$. Since the number of states is conserved, we have that $g(E_k) dE_k = \rho(\delta\varepsilon_k) d(\delta\varepsilon_k)$ or

$$\begin{aligned} g(E) &= \rho(\delta\varepsilon) \frac{d(\delta\varepsilon)}{dE} = \rho_F \frac{\sqrt{\Delta^2 + \delta\varepsilon_{\mathbf{k}}^2}}{|\delta\varepsilon|} \\ &= \rho_F \frac{E}{\sqrt{E^2 - \Delta^2}}. \end{aligned} \quad (23.51)$$

In Fig. 23.2 we plot the DOS g vs E .

23.7 Thermodynamic Quantities

To study the thermodynamic quantities of a superconductor as a function of temperature ($0 \leq T \leq T_c$), we need, in the framework of the BCS theory, the grand thermodynamic potential, $\Omega_s(T)$. A hand-waving argument for obtaining $\Omega_s(T)$ is based on the observation that at any nonzero temperature

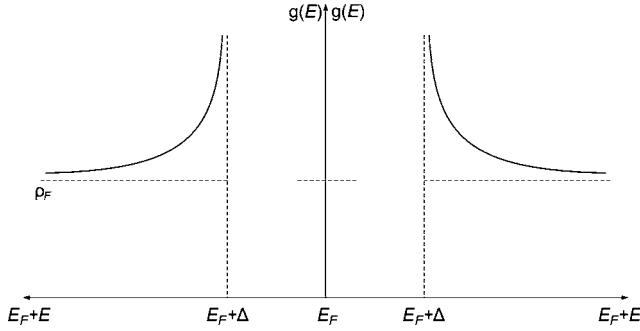


Fig. 23.2. DOS $g(E)$ for each of the two elementary excitations $E_{\mathbf{k}}$ involved in any physical process and the corresponding gap $E_g(0) = 2\Delta$. Notice that $g(E) = 0$ for $E < \Delta$, and that $g(E)$ blows up as $A(E - \Delta)^{-1/2}$ in the limit $E \rightarrow \Delta^+$, where $A = \rho_F \Delta / \sqrt{2\Delta}$

some of Cooper pairs will be broken into individual electrons. Let the average number of the individual electrons at the state $|\mathbf{k}\rangle$ and $|\bar{\mathbf{k}}\rangle$ be $n_{\mathbf{k}}$ and $n_{\bar{\mathbf{k}}} = n_{\mathbf{k}}$ respectively; $n_{\mathbf{k}}$ is to be determined. By conservation of the number of electrons the average number of pairs in the state $|\mathbf{k}, \bar{\mathbf{k}}\rangle$ will be equal to $1 - 2n_{\mathbf{k}}$. Hence, we can argue that the average value of $\hat{H} - \mu\hat{N}_e$ (where μ is the chemical potential, $\mu \rightarrow E_F$ as $T \rightarrow 0$ K) will be obtained by multiplying each term of the $T = 0$ K expression for $\langle \hat{H} - \mu\hat{N} \rangle$ by the remaining number of pairs $1 - 2n_{\mathbf{k}}$; in addition we must add the average energy of the individual electrons, which is equal to $\sum_{\mathbf{k}} n_{\mathbf{k}} \delta \varepsilon_{\mathbf{k}}$. We have then

$$\begin{aligned} \langle \hat{H} - \mu\hat{N}_e \rangle &= \sum_{\mathbf{k}} n_{\mathbf{k}} \delta \varepsilon_{\mathbf{k}} + 2 \sum_{\mathbf{k}} \delta \varepsilon_{\mathbf{k}} |v_{\mathbf{k}}|^2 (1 - 2n_{\mathbf{k}}) \\ &+ \frac{1}{V} \sum_{\mathbf{k}, \mathbf{k}'} V_{\mathbf{k}, \mathbf{k}'} u_{\mathbf{k}} v_{\mathbf{k}'} u_{\mathbf{k}'} v_{\mathbf{k}} (1 - 2n_{\mathbf{k}})(1 - 2n_{\mathbf{k}'}). \end{aligned} \quad (23.52)$$

To find Ω_s we must subtract from the rhs of (23.52) the product, $T S$, where the entropy S is due only to the individual electrons and is equal to⁹

$$S = -2k_B \sum_{\mathbf{k}} [n_{\mathbf{k}} \ln n_{\mathbf{k}} + (1 - n_{\mathbf{k}}) \ln(1 - n_{\mathbf{k}})]. \quad (23.53)$$

The independent variational variables are the $v_{\mathbf{k}}^*$ and $n_{\mathbf{k}}$. Since S does not involve $v_{\mathbf{k}}^*$, it is enough to set the partial derivatives of $\langle \hat{H} - \mu\hat{N}_e \rangle$ with respect to $v_{\mathbf{k}}^*$ equal to zero. The result would be as before, the only difference being the extra factor $(1 - 2n_{\mathbf{k}'})$ in the last term. Hence, we have

⁹ Eq (23.53) for the entropy can be obtained from $S = -\partial\Omega/\partial T$, where Ω is given by (C.44) and $n_{\mathbf{k}}$ is the Fermi distribution; it is also valid for any distribution $n_{\mathbf{k}}$ (see the book by Landau and Lifshitz, Stat. Physics [ST35], p. 161).

$$\Delta_{\mathbf{k}} = \frac{1}{V} \sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} u_{\mathbf{k}'} v_{\mathbf{k}'} (1 - 2n_{\mathbf{k}'}). \quad (23.54)$$

Equations (23.41), (23.42) and (23.43) are valid for any temperature with $\Delta_{\mathbf{k}}$ given by (23.54) and not by (23.40). Substituting (23.41) and (23.42) in (23.39) we have $u_{\mathbf{k}} v_{\mathbf{k}} = -\Delta_{\mathbf{k}}/2E_{\mathbf{k}}$. Combining this last relation with the definition of $\Delta_{\mathbf{k}}$ (23.54) we obtain an equation involving only $\Delta_{\mathbf{k}}$.

$$\Delta_{\mathbf{k}} = -\frac{1}{V} \sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} \frac{\Delta_{\mathbf{k}'}}{2E_{\mathbf{k}'}} (1 - 2n_{\mathbf{k}'}). \quad (23.55)$$

The variational condition $\partial\Omega_s/\partial n_{\mathbf{k}} = 0$ yields.

$$2\delta\varepsilon_{\mathbf{k}}(1 - 2v_{\mathbf{k}}^2) - 4\Delta_{\mathbf{k}}u_{\mathbf{k}}v_{\mathbf{k}} + 2k_{\text{B}}T \ln \frac{n_{\mathbf{k}}}{1 - n_{\mathbf{k}}} = 0. \quad (23.56)$$

Taking into account (23.39), (23.41) and (23.42) we obtain from (23.56) that

$$-\frac{E_{\mathbf{k}}}{k_{\text{B}}T} = \ln \frac{n_{\mathbf{k}}}{1 - n_{\mathbf{k}}} \Rightarrow n_{\mathbf{k}} = \frac{1}{e^{\beta E_{\mathbf{k}}} + 1}, \quad \beta = \frac{1}{k_{\text{B}}T} \quad (23.57)$$

Thus, $n_{\mathbf{k}}$ is the Fermi distribution in terms of the superconducting elementary excitation $E_{\mathbf{k}}$. Equation (23.55) allows us to determine the gap $\Delta_{\mathbf{k}}(T)$ at any temperature between zero and T_c .

Problem 23.8ts. Use the simple expression (23.45) for $V_{\mathbf{k},\mathbf{k}'}$ together with (23.55) to show that the gap equation (23.55) becomes

$$\int_0^{\hbar\omega_D} \frac{d\varepsilon}{(\varepsilon^2 + \Delta^2)^{1/2}} \tanh \left[\frac{(\varepsilon^2 + \Delta^2)^{1/2}}{2k_{\text{B}}T} \right] = \frac{1}{\lambda}. \quad (23.58)$$

Show that $\Delta(T)/\Delta(0)$ is a universal function of $\Delta(T)/k_{\text{B}}T \simeq 1.76 [\Delta(T)/\Delta(0)] [T_c/T]$. (See Fig. 22.9).

The critical temperature T_c can be determined by setting $\Delta = 0$ in (23.58). The resulting equation is equivalent to the combination of (23.22) and (23.24).

Problem 23.9ts. Use the general relation for the specific heat $C_V = T(\partial S/\partial T)_{N,V} \simeq T(\partial S/\partial T)_{\mu,V}$ together with (23.53) to show that

$$\begin{aligned} C_V &= -\frac{2}{T} \Sigma_{\mathbf{k}} \left(E_{\mathbf{k}}^2 + \frac{\beta}{2} \frac{\partial \Delta^2}{\partial \beta} \right) \frac{\partial n_{\mathbf{k}}}{\partial E_{\mathbf{k}}} \\ &= -\frac{2\rho_{\text{F}}}{T} \int_{-\infty}^{\infty} dE \left[E^2 + \frac{\beta}{2} \frac{\partial \Delta^2}{\partial \beta} \right] \frac{\partial n}{\partial E}. \end{aligned} \quad (23.59)$$

Show that the discontinuity of C_V at $T = T_c$ satisfies the relation

$$\frac{C_V(T_c^-) - C_V(T_c^+)}{C_V(T_c^+)} = 1.43. \quad (23.60)$$

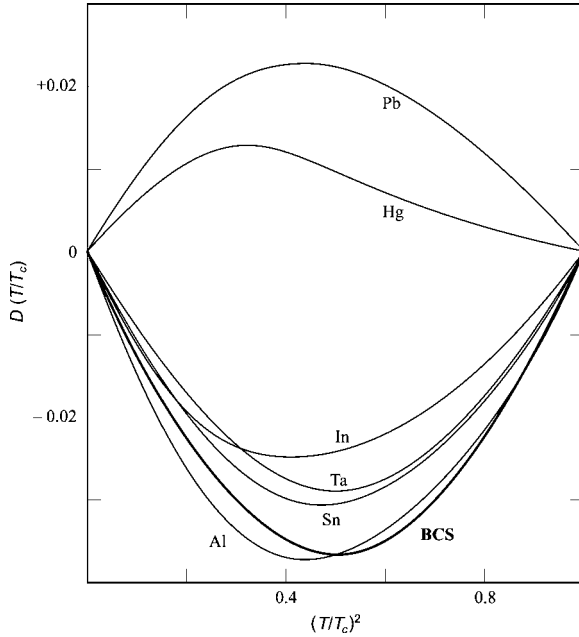


Fig. 23.3. The difference $D \equiv [H_c(T)/H_c(0)] - [1 - (T/T_c)^2]$ plotted as a function of $(T/T_c)^2$ according to the BCS theory (heavy line) and for various superconductors. Except for the strong coupling superconductors the other ones follow rather closely the BCS result. (Notice the scale of D)

Problem 23.10ts. Show that $\Omega_s = \langle \hat{H} - \mu \hat{N}_e \rangle - TS$ can be written as follows

$$\Omega_s = \sum_{\mathbf{k}} \left[2k_B T \ln(1 - n_{\mathbf{k}}) + (\delta\varepsilon_{\mathbf{k}} - E_{\mathbf{k}}) v_{\mathbf{k}}^2 - \frac{\Delta_{\mathbf{k}}^2}{E_{\mathbf{k}}} n_{\mathbf{k}} \right]. \quad (23.61)$$

Use (22.11) and the approximation $G_N - G_s \simeq \Omega_N - \Omega_s$ to calculate the critical field $H_c(T)$; in particular show that

$$H_c(0) = \sqrt{\rho_{FV}/\mu_0} \Delta(0). \quad (23.62)$$

Hint: See Fig. 23.3. (In G-CGS replace μ_0 by $1/4\pi$ in (23.62)).

23.8 Response to Electromagnetic Fields

Obtaining theoretically the current induced in a superconductor by the application of an external field¹⁰ $\mathbf{A}(\mathbf{r}, t)$ requires a lengthy and more advanced calculation. For this reason in this section we shall quote the main result and

¹⁰ $\mathbf{E}(\mathbf{r}, t) = -\partial \mathbf{A}/\partial t$ (G-CGS, in SI omit the c) and $\mathbf{B}(\mathbf{r}, t) = \nabla \times \mathbf{A}$.

we shall omit its derivation. (The interested readers may see all the details in the book by Richayen [Su181]). In what follows it is assumed that the field $\mathbf{A}$ is transverse, i.e., $\nabla \cdot \mathbf{A} = 0$.

We have already seen that the current-density $\mathbf{j}(\mathbf{r}, t)$ has two components: the diamagnetic one $\mathbf{j}_d(\mathbf{r}, t) = -(e^2 n/m)\mathbf{A}(\mathbf{r}, t)$ (in G-CGS m must be replaced by mc) and the paramagnetic one $\mathbf{j}_p(\mathbf{r}, t)$, the Fourier transform¹¹ of which, in a superconductor, is given by the following expression in the limits $\omega \rightarrow \infty$ (the static limit) and then $q \rightarrow 0$ (the uniform limit)

$$\begin{aligned} \lim_{\substack{\omega \rightarrow 0 \\ q \rightarrow 0}} \tilde{\mathbf{j}}_p(\mathbf{q}, \omega) &= -\tilde{\mathbf{A}}(0, 0) \frac{2e^2 \hbar^2}{3m^2 c} \int \frac{d^3 k}{(2\pi)^3} k^2 \frac{\partial f(E_k)}{\partial E_k} \\ &= -\tilde{\mathbf{A}}(0, 0) \frac{2e^2}{mc} \int d\varepsilon R_V(\varepsilon) \frac{\partial f(E)}{\partial E}, \quad \text{G - CGS (in SI delete } c), \end{aligned} \quad (23.63)$$

where $\tilde{\mathbf{A}}(\mathbf{q}, \omega)$ is the Fourier transform of $\mathbf{A}(\mathbf{r}, t)$, $R_V(\varepsilon)$ is the unperturbed number of states per unit volume and per spin with energy below ε , $E = \sqrt{\delta\varepsilon^2 + \Delta^2}$, $\delta\varepsilon = \varepsilon - \mu$ and $f(E) = [\exp(\beta E) + 1]^{-1}$. To obtain (23.63), we have assumed that $\varepsilon_k = \hbar^2 k^2 / 2m$ so that $R_V(\varepsilon) = \frac{2}{3} \rho_V(\varepsilon) \varepsilon$.

For the normal case $\Delta = 0$, $E = \varepsilon$ and the integral in (23.63) is equal to $-n/2$. Hence, $\tilde{\mathbf{j}}_p(0, 0) = (e^2 n/m)\tilde{\mathbf{A}}(0, 0)$, which cancels exactly the diamagnetic contribution in the limit $\omega \rightarrow 0$, $q \rightarrow 0$. This means that a constant $\mathbf{A}(\mathbf{r}, t)$ (in both $\mathbf{r}$ and t) does not induce any current when the material is in the normal state. In contrast, in the superconducting state (where Δ is positive) and for $T \rightarrow 0$, both $f(E)$ and $\partial f(E)/\partial E$ tend to zero, since the term $\exp(\beta E) > \exp(\beta \Delta)$ tends to infinity, as $T = 1/k_B \beta$ tends to zero. We conclude that for a superconductor in the London limit and as $T \rightarrow 0$ K the paramagnetic contribution is zero and the only surviving term is the diamagnetic one; thus starting from the microscopic BCS theory, we have recaptured (22.17) with $n_s = n$. One can trace the vanishing of $\tilde{\mathbf{j}}_p$ (in the limits $\omega \rightarrow 0$, $q \rightarrow 0$, $T \rightarrow 0$ K) to the fact that the ground state $|\Psi\rangle$ for a superconductor in the presence of $\mathbf{A}$ is the same as $|G\rangle$ (the ground state in the absence of $\mathbf{A}$). The formal reason for this is that in (22.22) the numerator contains a factor proportional to $u_{\mathbf{k}} v_{\mathbf{k}+\mathbf{q}} - u_{\mathbf{k}+\mathbf{q}} v_{\mathbf{k}}$ while in the denominator the difference $E_n - E_s = E_{\mathbf{k}} + E_{\mathbf{k}+\mathbf{q}} > 2\Delta$. Thus, as $q \rightarrow 0$, the numerator vanishes while the denominator remains larger than or equal to 2Δ . For finite temperatures the paramagnetic contribution does not vanish, but it does not cancel the diamagnetic contribution either. Adding together the two contributions, we have¹²

¹¹ The Fourier transform of a function $\psi(\mathbf{r}, t)$ is defined as $\tilde{\psi}(\mathbf{q}, \omega) \equiv \int d^3 r \, dt \exp[-i(\mathbf{q} \cdot \mathbf{r} - \omega t)] \psi(\mathbf{r}, t)$ and the inverse Fourier transform is then: $\psi(\mathbf{r}, t) \equiv \int \frac{d^3 q}{(2\pi)^3} \frac{d\omega}{2\pi} \exp[i(\mathbf{q} \cdot \mathbf{r} - \omega t)] \tilde{\psi}(\mathbf{q}, \omega)$.

¹² This relation is valid for clean specimen where the normal state mean free path ℓ is much larger than the coherence length $\xi_0 = \hbar v_F / \pi \Delta(0)$.

Table 23.1. The ratio n_s/n for various values of T/T_c , as calculated numerically according to (23.65) and the BCS theory; n_s is as in the London relation (22.17)

T/T_c	n_s/n	T/T_c	n_s/n
0	1	—	—
0.1	0.99999	0.7	0.5537
0.2	0.9989	0.8	0.3818
0.3	0.9818	0.9	0.1959
0.4	0.9279	0.92	0.1575
0.5	0.8340	0.94	0.1186
0.6	0.7067	0.96	0.0794

$$\lim_{\substack{\omega \rightarrow 0 \\ \mathbf{q} \rightarrow 0}} \tilde{\mathbf{j}}(\mathbf{q}, \omega) = -\tilde{\mathbf{A}}(0, 0) \frac{e^2 n_s}{mc}, \quad (23.64)$$

where n_s , the concentration of “superconducting” electrons, is given by

$$n_s = n - 2 \left| \int d\varepsilon R_V(\varepsilon) \frac{\partial f(E)}{\partial E} \right|. \quad (23.65)$$

In Table 23.1 we give the value of n_s/n as a function of T/T_c ; these values were obtained by employing the BCS $\Delta(T)$ and by numerical calculation of the integral in (23.65).

23.9 Towards Material-Specific Calculations of Superconducting Quantities

For the normal (i.e., nonsuperconducting) crystalline state we are in a position, generally speaking, to calculate *ab initio* the basic material-specific structural,¹³ thermodynamic, and transport quantities¹⁴ characterizing each elemental solid and most compounds. The introduction and development of the DFT¹⁵ played an important role in this achievement. For the phonon-induced superconducting state the BCS theory provides a valid qualitative physical explanation and provides quantitative determination of various universal numbers such as the ratio $2\Delta(0)/k_B T$, or the ratio $[C_V(T_c^-) - C_V(T_c^+)]/C_V(T_c^+)$, or the ratio $\Delta(0)\rho_{FV}^{1/2}/\mu_0^{1/2}H_c(0)$ (SI, in G-CGS set $\mu_0 = 1/4\pi$), etc. However,

¹³ The examined lattice structures are confined within a few common crystalline ones.

¹⁴ For transport properties dominated by defects or other departures from periodicity the *ab initio* approach fails in most cases.

¹⁵ We remind the readers that the DFT, by recognizing the unique role of the electronic density n , allows a realistic self-consistent determination of an effective single-electron potential $\mathcal{V}(\mathbf{r})$.

the BCS theory is not in a position to provide a material-specific ab initio calculation of quantities such as the T_c , since in this theory the dimensionless attractive interaction λ is essentially a phenomenological parameter. A decisive step to overcome this difficulty is the Eliashberg extension of the BCS theory. In Eliashberg's approach, the phonon degrees of freedom are treated explicitly and their role in dressing the electrons and in pairing them is studied on equal footing; nevertheless, the el-el interactions are still handled in a phenomenological way through the effective screened el-el repulsion parameter μ^* . Recently a scheme for an ab initio calculation of the superconducting parameters was proposed [23.11, 23.12] and implemented [23.13, 23.14], which is based on an extension of the DFT. Instead of the single pair of conjugate quantities $n(\mathbf{r})$ and $\mathcal{V}_e(\mathbf{r})$ (which are determined self-consistently) employed in normal state DFT, three pairs of conjugate quantities are introduced for the superconducting state: Besides the pair $n(\mathbf{r})$ together with $\mathcal{V}_e(\mathbf{r})$, the pair $\chi(\mathbf{r}, \mathbf{r}')$ together with $\Delta(\mathbf{r}, \mathbf{r}')$ and the pair $\Gamma(\mathbf{R}_1, \dots, \mathbf{R}_N)$ together with $\mathcal{V}_n(\mathbf{R}_1, \dots, \mathbf{R}_N)$ are introduced. The quantity $\chi(\mathbf{r}, \mathbf{r}')$ is the superconducting "density," which can be viewed as the superconducting order parameter, and $\Delta(\mathbf{r}, \mathbf{r}')$ is the superconducting gap, which in general is a function of both¹⁶ the center of mass coordinate $\frac{1}{2}(\mathbf{r} + \mathbf{r}')$ and the relative coordinate $\mathbf{r} - \mathbf{r}'$. The quantity $\Gamma(\mathbf{R}_i, \dots, \mathbf{R}_N)$ is the many-body density for the ions $\Gamma = |\Psi(\mathbf{R}_i, \dots, \mathbf{R}_N)|^2$ and $\mathcal{V}_n(\mathbf{R}_1, \dots, \mathbf{R}_N)$ is the interaction potential for all the N ions.

In principle, the quantities $\mathcal{V}_e(\mathbf{r})$, $\Delta(\mathbf{r}, \mathbf{r}')$ and $\mathcal{V}_n(\mathbf{R}_1, \dots, \mathbf{R}_N)$ are functionals of all the three densities: n , χ , and Γ , which in turn can be expressed in terms of two electronic functions $u_{n\mathbf{k}}(\mathbf{r})$, $v_{n\mathbf{k}}(\mathbf{r})$ and the ionic displacements $\mathbf{d}_j$ ($j = 1, \dots, N$); n is the band index and $\mathbf{k}$ is the Bloch wavevector. The cycle closes by writing down three coupled equations for $u_{n\mathbf{k}}$, $v_{n\mathbf{k}}$ and $\mathbf{d}_j$ in terms of $\mathcal{V}_e$, Δ , and $\mathcal{V}_n$.

The dependence of $\mathcal{V}_n$ on χ is negligible, and consequently, the phonon part is treated within the Born-Oppenheimer approximation with the spring constants obtained by the standard DFT as outlined in Sect. 8.3. The two coupled equations for the electronic wavefunctions u and v are as follows:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + \mathcal{V}_e(\mathbf{r}) - \mu \right] u_{n\mathbf{k}}(\mathbf{r}) + \int d^3r' \Delta(\mathbf{r}, \mathbf{r}') v_{n\mathbf{k}}(\mathbf{r}') = E_{n\mathbf{k}} u_{n\mathbf{k}}(\mathbf{r}), \quad (23.66)$$

$$- \left[-\frac{\hbar^2}{2m} \nabla^2 + \mathcal{V}_e(\mathbf{r}) - \mu \right] v_{n\mathbf{k}}(\mathbf{r}) + \int d^3r' \Delta(\mathbf{r}, \mathbf{r}') u_{n\mathbf{k}}(\mathbf{r}') = E_{n\mathbf{k}} v_{n\mathbf{k}}(\mathbf{r}). \quad (23.67)$$

¹⁶ For a uniform system, as in our presentation of the BCS theory, Δ is a function of only the relative coordinate $\mathbf{r} - \mathbf{r}'$. In the Ginzburg-Landau theory we have omitted the dependence on the relative coordinate and we have kept only the dependence on the center-of-mass coordinate $\frac{1}{2}(\mathbf{r} + \mathbf{r}')$.

To proceed with the solution to this system of equations, we neglect the very small contribution to $\mathcal{V}_e$ by $\chi(\mathbf{r}, \mathbf{r}')$ and we make the so-called decoupling approximation according to which

$$u_{n\mathbf{k}}(\mathbf{r}) \approx u_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r}), \quad (23.68)$$

$$v_{n\mathbf{k}}(\mathbf{r}) \approx v_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r}), \quad (23.69)$$

where $\psi_{n\mathbf{k}}$ are the normal-state eigenfunctions of band index n and Bloch wave vector $\mathbf{k}$ of the Hamiltonian $-(\hbar^2/2m)\nabla^2 + \mathcal{V}_e(\mathbf{r})$ with eigenvalues $\varepsilon_{n\mathbf{k}}$; both $\psi_{n\mathbf{k}}(\mathbf{r})$ and $\varepsilon_{n\mathbf{k}}$ can be calculated for each material by standard band structure techniques employing normal-state DFT. By substituting (23.68) and (23.69) in (23.66) and (23.67) and by defining $\Delta_{n\mathbf{k}}$ as follows

$$\Delta_{n\mathbf{k}} = \int d^3r \int d^3r' \psi_{n\mathbf{k}}^*(\mathbf{r}) \Delta(\mathbf{r}, \mathbf{r}') \psi_{n\mathbf{k}}(\mathbf{r}'), \quad (23.70)$$

we obtain

$$|u_{n\mathbf{k}}|^2 = \eta \left(1 + \frac{\delta\varepsilon_{n\mathbf{k}}}{E_{n\mathbf{k}}} \right), \quad (23.71)$$

$$|v_{n\mathbf{k}}|^2 = \eta \left(1 - \frac{\delta\varepsilon_{n\mathbf{k}}}{E_{n\mathbf{k}}} \right), \quad (23.72)$$

where

$$\delta\varepsilon_{n\mathbf{k}} = \varepsilon_{n\mathbf{k}} - \mu, \quad E_{n\mathbf{k}} = \sqrt{\delta\varepsilon_{n\mathbf{k}}^2 + |\Delta_{n\mathbf{k}}|^2} \geq 0, \quad (23.73)$$

and η is determined, from the normalization condition, to be equal to 1/2. The quantity $\Delta(\mathbf{r}, \mathbf{r}')$ depends on $\chi(\mathbf{r}, \mathbf{r}')$, which in turn depends on $\Delta_{n\mathbf{k}}$ and $\psi_{n\mathbf{k}}(\mathbf{r})\psi_{n\mathbf{k}}^*(\mathbf{r}')$. Thus, an integral equation for $\Delta_{n\mathbf{k}}$ results that has a structure similar to (23.55)

$$\Delta_{n\mathbf{k}} = - \sum_{n'\mathbf{k}'} F_{n\mathbf{k}, n'\mathbf{k}'} \frac{\Delta_{n'\mathbf{k}'}}{2E_{n'\mathbf{k}'}} \tanh \left(\frac{E_{n'\mathbf{k}'}}{2k_B T} \right), \quad (23.74)$$

where F has one contribution due to the exchange of phonons as in Fig. 23.1 (which is usually separated to a part, which is diagonal in $n\mathbf{k}$, $n'\mathbf{k}'$ part and to a purely off-diagonal part) and one due to el-el interactions:

$$F_{n\mathbf{k}n'\mathbf{k}'} = \delta_{nn'}\delta_{\mathbf{k}\mathbf{k}'} K_{n\mathbf{k}, n\mathbf{k}}^{\text{ph}, \text{d}} + K_{n\mathbf{k}, n'\mathbf{k}'}^{\text{ph}, \text{off-d}} + K_{n\mathbf{k}, n'\mathbf{k}'}^{\text{el}}. \quad (23.75)$$

Explicit expressions for the various K 's, involving the electronic eigenenergies $\delta\varepsilon_{n\mathbf{k}}$, the phononic eigenfrequencies $\omega_{s\mathbf{q}}$, and the electron-phonon coupling $g_{s\mathbf{q}}^{n\mathbf{k}, n'\mathbf{k}'}$ as well as the screened Coulomb interaction, are given in the paper by M.A.L. Marques et al. [23.13, pp. 3–4].

23.10 Josephson Effects and SQUID

Josephson effects [23.15] appear when two superconductors (from the same or from different materials) are in “close contact”, meaning structures as those shown in Fig. 23.4. In all cases of “close contact”, the separation of the two superconductors is such that the tunneling probability of a Cooper pair from one to the other is not negligible. Let us call V_2 the amplitude from transferring one Cooper pair from S_1 to S_2 and let Ψ_v ($v = 0, \pm 1, \pm 2, \dots$) be the state resulting from the transfer of v Cooper pairs from S_1 to S_2 . All states Ψ_v have the same energy and are connected by the matrix element $V_2 \equiv \langle \Psi_{v\pm 1} | \hat{H}_c | \Psi_v \rangle$ where H_c is the Cooper pair tunneling Hamiltonian. Mathematically the problem is exactly equivalent to the simple LCAO model examined in Sect. 6.3. Hence, the eigenfunctions and the eigenenergies of the Cooper pairs in the tunneling configuration are

$$\Psi_\phi = \sum_v e^{i\phi v} \Psi_v, \quad (23.76)$$

$$E(\phi) = \varepsilon_0 + 2V_2 \cos \phi, \quad (23.77)$$

where ϕ is the change in the phase of the Cooper pair due to its tunneling from S_1 and to S_2 as shown in Fig. 23.5

$$\phi = \theta_2 - \theta_1. \quad (23.78)$$

In the 1D LCAO problem, the position $x_v = va$ and the momentum $p = \hbar k$ are canonical variables satisfying as such Hamilton’s relation, $(\partial \langle x_\mu \rangle / \partial t) \equiv \langle v \rangle = \partial E(k) / \partial p$. Similarly, the variables v and $\hbar\phi$ are canonical variables, which satisfy Hamilton’s relation

$$\frac{\partial \langle v \rangle}{\partial t} = \frac{\partial E(\phi)}{\hbar \partial \phi} = -\frac{2}{\hbar} V_2 \sin \phi.$$

but the current I_{12} from S_1 to S_2 is equal to $-2e \partial \langle v \rangle / \partial t$:

$$I_{12} = \frac{4eV_2}{\hbar} \sin(\phi) = \frac{4eV_2}{\hbar} \sin(\theta_2 - \theta_1), \quad (23.79)$$

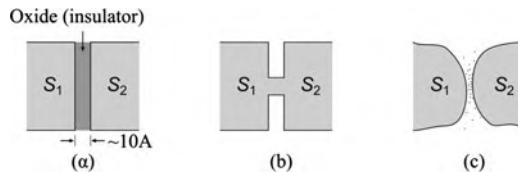


Fig. 23.4. Examples of “close contact” between two superconductors. (a) Josephson junction where the two superconductors are separated by a thin layer (of the order of 10Å) of insulating oxide. (b) A narrow bottleneck in the flow of electrons. (c) Proximity configuration

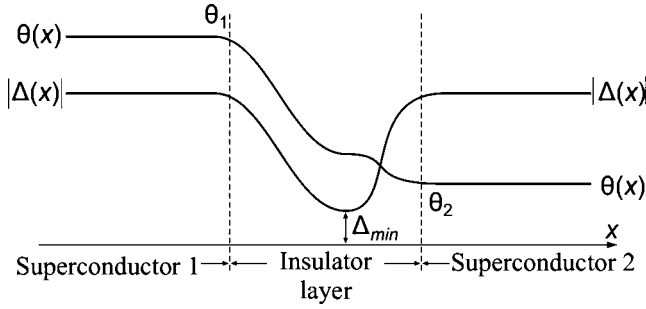


Fig. 23.5. Schematic presentation of the variation of the size $|\Delta(x)|$ and the phase $\theta(x)$ of the gap parameter $\Delta(x) = |\Delta(x)| \exp(i\theta(x))$, along the width of the insulating layer between the two superconductors; the angle ϕ appearing in (23.76) and (23.77) is the difference $\theta_2 - \theta_1$, since the gap Δ and the Cooper pair wave function $\psi(\mathbf{r})$ are connected $\Delta(\mathbf{r}) = (|\Delta| / \sqrt{n_c}) \psi(\mathbf{r})$

In the presence of an EM vector potential $\mathbf{A}(\mathbf{r})$, the phase difference $\phi \equiv \theta_2 - \theta_1$ must be replaced by the gauge invariant phase δ , where

$$\delta = \delta_0 - \frac{2|e|\hbar}{c} \int_1^2 \mathbf{A}(\mathbf{r}) d\ell, \quad \text{in SI set } c = 1. \quad (23.80)$$

Hence,

$$I_{12} = J_1 \sin \delta, \quad (23.81)$$

where the value of J_1 according to the BCS theory is

$$J_1 = \frac{\pi \Delta(T)}{2|e|R_n} \tanh \frac{\Delta(T)}{2k_B T}, \quad \text{if } |\Delta_1| = |\Delta_2| = \Delta, \quad (23.82)$$

and $R_n = (dV/dI)$ is the differential resistance of the close contact in the normal state. Equations (23.81) and (23.80) allow some important conclusions:

1. In the absence of external field ($\mathbf{A} = 0$), there is still superconducting current flowing through the close contact, as long as $\theta_1 \neq \theta_2$, in spite of the minute, but not zero, separation of the two superconductors. The maximum possible current J_1 is inversely proportional to the differential resistance R_n (and hence, it drops exponentially with the separation) and proportional to $\Delta(T)$. This is the so-called *DC Josephson effect*.
2. If a voltage $V_{12} = V_1 - V_2 = \int_1^2 \mathbf{E} \cdot d\ell$ is applied across the close contact, we have from (23.80) that

$$\frac{\partial \delta}{\partial t} = \frac{2|e|\hbar}{c} \int_1^2 \mathbf{E}(\mathbf{r}) d\ell = \frac{2|e|\hbar}{c} V_{12}, \quad (23.83)$$

which implies that $\delta = \omega t + \delta_0$, where

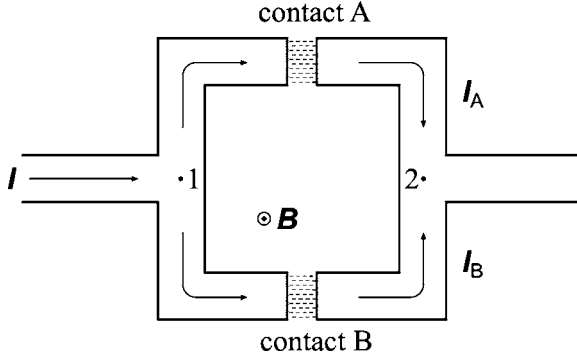


Fig. 23.6. Two Josephson contacts in parallel

$$\omega = \frac{2|e|\hbar}{\hbar} V_{12}. \quad (23.84)$$

Substituting δ in (23.81), we have

$$I_{12} = J_1 \sin(\omega t + \delta_0). \quad (23.85)$$

Equation (23.85) is called the *AC Josephson effect* according to which a DC voltage across the close contact produces an AC current of frequency, $\omega = (2|e|\hbar/\hbar)V_{12}$! This relation is served as the legal definition of the volt: 1 mV across a superconducting close contact produces an AC current of frequency $\omega/2\pi = 483.5979$ GHz.

3. Consider the setup shown in Fig. 23.6. The current I is branched off into two subcurrents I_A , passing through Josephson contact A, and subcurrent I_B , passing through Josephson contact B. In the absence of external electric and magnetic fields, the phases δ_A and δ_B along the paths 1A2 and 1B2 respectively are equal due to the assumed symmetry of the two paths. In the presence of a static magnetic field as shown in Fig. 23.6 the difference $\delta_A - \delta_B$ along the two paths is given by

$$\delta_A - \delta_B = \frac{2e}{\hbar} \oint_{1A2B1} \mathbf{A}(\mathbf{r}) \cdot d\mathbf{l} = \frac{2\pi\Phi}{ch/2e} = \frac{2\pi\Phi}{\Phi_0}, \quad (23.86)$$

where the magnetic flux Φ through the loop is given by $\Phi \equiv \int \mathbf{B} \cdot d\mathbf{S} = \oint \mathbf{A}(\mathbf{r}) \cdot d\mathbf{l}$ and $\Phi_0 \equiv ch/2e = 2\pi\hbar/2e = \pi\hbar/e$ is the quantum of the magnetic flux. In view of (23.86), we can write $\delta_{A,B} = \delta_0 \pm \pi\Phi/\Phi_0$, which allows us to write the total current as follows:

$$\begin{aligned} I = I_A + I_B &= J_1 [\sin \delta_A + \sin \delta_B] = 2J_1 \left[\sin \frac{\delta_A + \delta_B}{2} \cos \frac{\delta_A - \delta_B}{2} \right] = \\ &= 2J_1 \sin \delta_0 \cos \frac{\pi\Phi}{\Phi_0}. \end{aligned} \quad (23.87)$$

Equation (23.87) means that the total current I in the setup of Fig. 23.6 depends in a periodic way on the magnetic flux through the loop. Since Φ_0 is tiny ($\Phi_0 = 2.0678 \times 10^{-15} \text{ T m}^2$), the setup of Fig. 23.6 can serve as a very sensitive magnetometer known as DC superconducting quantum interference device (SQUID).

23.11 Key Points

- A phonon-mediated attraction between two electrons in the presence of the Fermi sea binds the two together, forming a so-called Cooper pair of zero total spin (exceptions exist; see [23.1–23.7]. The binding energy is maximum when the total momentum of the pair is zero and it is given by

$$\varepsilon_b = 4\hbar\omega_D \exp\left(-\frac{1}{\lambda}\right); \quad \lambda = |\varepsilon| v_0 \rho_{FV}.$$

- A Cooper pair is described by a linear combination of states $|\mathbf{k}\rangle$ and $|\mathbf{-k}\rangle$, $\sum_{\mathbf{k}} c_{\mathbf{k}} |\mathbf{k}\rangle |\mathbf{-k}\rangle$, where $c_{\mathbf{k}}$ is nonzero in a spherical shell around the Fermi surface of width $2\delta k \simeq \varepsilon_b/\hbar v_F$; its linear extent is $\xi_0 \sim 1/2\delta k \sim \hbar v_F/\varepsilon_b$.
- Cooper pair formation forces a reorganization of the Fermi sea so that each pair state $|\mathbf{k}\rangle |\mathbf{-k}\rangle$ is occupied with probability amplitude $v_{\mathbf{k}}$ (The BCS basic assumption). By minimizing the quantity $\langle \hat{H} - \mu \hat{N}_e \rangle$, we find that

$$u_{\mathbf{k}}^2 = \frac{1}{2} \left(1 + \frac{\delta\varepsilon_{\mathbf{k}}}{E_{\mathbf{k}}} \right), \quad v_{\mathbf{k}}^2 = \frac{1}{2} \left(1 - \frac{\delta\varepsilon_{\mathbf{k}}}{E_{\mathbf{k}}} \right); \quad u_{\mathbf{k}}^2 + v_{\mathbf{k}}^2 = 1,$$

where

$$\delta\varepsilon_{\mathbf{k}} = \varepsilon_{\mathbf{k}} - \mu, \quad E_{\mathbf{k}} = \sqrt{\delta\varepsilon_{\mathbf{k}}^2 + \Delta_{\mathbf{k}}^2}, \quad \Delta_{\mathbf{k}} = E_g/2 = \varepsilon_b/2.$$

- The quantity $\Delta_{\mathbf{k}}$, which is half the binding energy, is obtained for any temperature less than, or equal to, T_c as solution to the equation

$$\Delta_{\mathbf{k}} = -\frac{1}{V} \sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} \frac{\Delta_{\mathbf{k}'}}{2E_{\mathbf{k}'}} (1 - 2n_{\mathbf{k}'}),$$

where $n_{\mathbf{k}} = [\exp(\beta E_{\mathbf{k}}) + 1]^{-1}$ is the Fermi distribution. For $T \equiv 1/k_B\beta = 0 \text{ K}$ the resulting value of 2Δ coincides with the value of ε_b given earlier. As T approaches the critical temperature T_c , $\Delta(T) \rightarrow 0$. Hence, T_c is obtained by setting $\Delta = 0$ in the equation determining Δ vs T . We find

$$T_c = \frac{2e^\gamma}{\pi} \Theta_D e^{-1/\lambda} \simeq 1.13 \Theta_D e^{-1/\lambda}.$$

By taking into account the screened Coulomb repulsion and the effect of el-ph interaction on the individual electrons making up the pairs, T_c becomes

$$T_c = p \exp \left(-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)} \right)$$

$$p \simeq \frac{\hbar\omega_D}{1.45k_B}.$$

- The superconducting ground state energy is lower than that of the normal state by $\frac{1}{2}\rho_F\Delta^2$ and the DOS of the superconducting state for $E \approx E_F$ is

$$g(E) = \rho_F \frac{E}{\sqrt{E^2 - \Delta^2}}, \quad |E| > \Delta,$$

$$= 0, \quad |E| < \Delta.$$

- The critical magnetic field at $T = 0$ K is determined by equating the magnetic field energy density to $\frac{1}{2}\rho_{FV}\Delta^2$
 $\frac{1}{2}\mu_0 H_c^2 = \frac{1}{2}\rho_{FV}\Delta^2$, SI (in G – CGS set $\mu_0 = 1/4\pi$).
- The Fourier transform of the current-density in the presence of a transverse field $\tilde{\mathbf{A}}(\mathbf{q}, \omega)$ is given by

$$\lim_{\substack{\omega \rightarrow 0 \\ \mathbf{q} \rightarrow 0}} \tilde{\mathbf{j}}(\mathbf{q}, \omega) = -\tilde{\mathbf{A}}(0, 0) \frac{e^2 n_s}{mc}, \quad \text{in SI set } c = 1.$$

$$n_s = n - 2 \left| \int d\varepsilon R_V(\varepsilon) \frac{\partial f(E)}{\partial E} \right|.$$

- The DFT has been generalized for the superconducting state aiming at ab initio calculation of superconducting properties for each specific material.
- The current I_{12} between two superconductors in close contact is given by

$$I_{12} = J_1 \sin \delta,$$

$$\delta \equiv \theta_2 - \theta_1 = \delta_0 - \frac{2|e|\hbar}{hc} \int_1^2 \mathbf{A}(\mathbf{r}) d\ell, \quad \text{in SI set } c = 1.$$

Thus in the absence of external field, I_{12} is in general different from zero (DC Josephson effect). In the presence of a DC voltage $V_{12} = V_1 - V_2$ between the two superconductors, an AC current flows, since then $\delta = \delta_0 + \omega t$ where

$$\omega = \frac{2|e|\hbar}{h} V_{12}.$$

This is the AC Josephson effect.

- The current I through two parallel paths involving Josephson contacts (Fig. 23.6) varies with the magnetic flux Φ enclosed by the loop as follows:

$$2J_1 \sin \delta_0 \cos \frac{\pi \Phi}{\Phi_0}.$$

This is technologically used in the so-called SQUIDS for accurate measurements of magnetic field strengths.

23.12 Problems

- 23.1s Calculate the binding energy of the Cooper pair, the wave function of which in the relative coordinate $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ is

$$\psi(\mathbf{r}) = \frac{1}{\sqrt{V}} \sum_{\mathbf{k}} c_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{r}}.$$

Work in $\mathbf{k}$ -space; take into account that the states below E_F are inaccessible. The attractive potential is $\mathcal{V}(\mathbf{r}) = \sum_{\mathbf{k}'} \mathcal{V}_{\mathbf{k}} \exp(i\mathbf{k}' \cdot \mathbf{r})/V$, where

$$\mathcal{V}_{\mathbf{k}-\mathbf{k}'} = -|\varepsilon| \nu_0 \theta(\hbar\omega_D - |\delta\varepsilon_{\mathbf{k}}|) \theta(\hbar\omega_D - |\delta\varepsilon_{\mathbf{k}'}|), \quad \delta\varepsilon_{\mathbf{k}} = (\hbar^2 k^2 / 2m) - E_F.$$

Hint: Transform the summation over $\mathbf{k}$ to integration over $\varepsilon = \varepsilon_{\mathbf{k}} = \hbar^2 k^2 / 2m$ times the DOS ρ_F to end up with

$$(2\varepsilon - E) a(\varepsilon) = \lambda \int_{E_F}^{\varepsilon + \hbar\omega_D} d\varepsilon' a(\varepsilon'),$$

where we set $c_{\mathbf{k}} = a(\varepsilon) \theta(\hbar\omega_D - |\delta\varepsilon_{\mathbf{k}}|)$.

- 23.2 Calculate the integral

$$-I \equiv \int_{2E_F - 2\hbar\omega_D}^{2E_F + 2\hbar\omega_D} dE' \frac{\tilde{\rho}_V(E')}{E' - 2E_F},$$

where

$$\tilde{\rho}_V(E') = \frac{1}{2} \rho_{FV} \left[1 - \frac{2}{\exp[\beta(\frac{1}{2}E' - E_F)] + 1} \right].$$

Hint: Change variable from E' to x where $E' = 2E_F + (2x/\beta)$ and then integrate by parts.

- 23.3 Show that μ_0^* within the JM is approximately equal to 0.25.
 23.4 Show how (23.1) is reduced to the attractive part of (8.50).

Further Reading

- See the Kaxiras book [SS83], pp. 297–310 as well as the Marder book [SS82], pp. 802–824.
- For more advanced and comprehensive treatments the readers may consult the books [Su179]–[Su182].
- Some recent ideas for obtaining higher T_c are presented in [23.16] and in references therein.

Part VII

Appendices

A

Elements of Electrodynamics of Continuous Media

A.1 Field Vectors, Potentials, and Maxwell's Equations

Let $\mathbf{e}$ and $\mathbf{b}$ be the microscopic vectors of the electric and the magnetic fields respectively, which are defined through the equation of the Lorentz force $\mathbf{F}$:

$$\begin{aligned}\mathbf{F} &= q(\mathbf{e} + \mathbf{v} \times \mathbf{b}), \quad \text{SI,} \\ &= q\left(\mathbf{e} + \frac{1}{c}\mathbf{v} \times \mathbf{b}\right), \quad \text{G-CGS,}\end{aligned}\tag{A.1}$$

$\mathbf{F}$ is the force exercised on a test charge q moving with velocity $\mathbf{v}$. For the connection of the Gauss(G)-CGS system of units with the SI one see the last two pages of this appendix.

We define the macroscopic fields $\mathbf{E}(\mathbf{r})$ and $\mathbf{B}(\mathbf{r})$ by averaging over a volume ΔV centered at the point $\mathbf{r}$ and such that $a^3 \ll \Delta V \ll \lambda^3$, where the length a is of atomic scale and λ is the length characterizing the variation of $\mathbf{E}(\mathbf{r})$ and $\mathbf{B}(\mathbf{r})$:

$$\mathbf{E}(\mathbf{r}) \equiv \frac{1}{\Delta V} \int_{\Delta V} \mathbf{e}(\mathbf{r}') d^3r', \tag{A.2}$$

$$\mathbf{B}(\mathbf{r}) \equiv \frac{1}{\Delta V} \int_{\Delta V} \mathbf{b}(\mathbf{r}') d^3r'. \tag{A.3}$$

Similarly, we define the macroscopic charge density $\bar{\rho}_e$ and the macroscopic current density, $\mathbf{j}_t$, the macroscopic polarization, $\mathbf{P}$, and the macroscopic magnetization, $\mathbf{M}$, of the medium under consideration:

$$\bar{\rho}(\mathbf{r}) = \frac{1}{\Delta V} \int_{\Delta V} \rho(\mathbf{r}') d^3r', \tag{A.4}$$

$$\mathbf{j}_t(\mathbf{r}) = \frac{1}{\Delta V} \int_{\Delta V} \rho(\mathbf{r}') \mathbf{v}(\mathbf{r}') d^3r', \tag{A.5}$$

$$\mathbf{P}(\mathbf{r}) \equiv \frac{\Delta \mathbf{p}}{\Delta V}, \quad \text{where} \quad \Delta \mathbf{p}(\mathbf{r}) \equiv \int_{\Delta V} \mathbf{r}' \rho(\mathbf{r}') d^3r', \tag{A.6}$$

$$\mathbf{M}(\mathbf{r}) \equiv \frac{\Delta \mathbf{m}}{\Delta V}, \quad \text{where} \quad \Delta \mathbf{m}(\mathbf{r}) \equiv \frac{1}{2c} \int_{\Delta V} \mathbf{r}' \times \rho(\mathbf{r}') \mathbf{v}(\mathbf{r}') d^3 r', \quad \text{G-CGS},^1 \quad (\text{A.7})$$

where $\Delta \mathbf{p}$ and $\Delta \mathbf{m}$ are the local macroscopic electric and magnetic moments respectively. Obviously, outside the material all quantities $\bar{\rho}$, $\mathbf{j}_t$, $\mathbf{P}$, $\mathbf{M}$ are zero. Furthermore, one can show that

$$\nabla \cdot \mathbf{P} = -\bar{\rho}, \quad (\text{A.8})$$

$$\mathbf{P} \cdot \mathbf{n} = \bar{\sigma}, \quad (\text{A.9})$$

$$\frac{\partial \mathbf{P}}{\partial t} + c \nabla \times \mathbf{M} = \mathbf{j}_t, \quad \text{G-CGS}^2, \quad (\text{A.10})$$

$$\mathbf{M} \times \mathbf{n} = \frac{1}{c} \mathbf{g}, \quad \text{G-CGS},^1 \quad (\text{A.11})$$

where $\mathbf{n}$ is the outward unit vector normal to the surface of the material body, and $\bar{\sigma}$ and $\mathbf{g}$ are the macroscopic surface density of electric charge and electric current respectively. Equation (A.10) shows that the total macroscopic current density (given by (A.5)) can be separated in two components, one “magnetic” ($\mathbf{j}_M \equiv c \nabla \times \mathbf{M}$) and one “electric” ($\mathbf{j} \equiv \partial \mathbf{P} / \partial t$). It is worthwhile to point out that usually the total charge density $\rho(\mathbf{r})$ is separated also in two components: $\rho(\mathbf{r}) = \rho_f(\mathbf{r}) + \rho_b(\mathbf{r})$, where $\rho_f(\mathbf{r})$ is associated with free-to-move charge carriers, and $\rho_b(\mathbf{r})$ is due to bound charge particles (electrons or ions), or more generally, to charges that do not contribute to the electric current in the presence of a time-independent electric field. Then it follows from (A.6) that $\mathbf{P} = \mathbf{P}_f + \mathbf{P}_b$, and consequently, that $\mathbf{j} = \mathbf{j}_f + \mathbf{j}_b$. Notice that in most books of electrodynamics the term polarization and the symbol $\mathbf{P}$ are used only for the bound part, $\mathbf{P}_b$. The free part is described exclusively through the current, $\mathbf{j}_f$. With these definitions the total current $\mathbf{j}_t$ consists of three contributions

$$\mathbf{j}_t = \mathbf{j}_M + \mathbf{j}_f + \mathbf{j}_b, \quad (\text{A.12})$$

where $\mathbf{j}_b = \partial \mathbf{P} / \partial t$ and $\mathbf{P}$ is our $\mathbf{P}_b$. However, this separation to free and bound charges becomes less significant for AC fields, since then all charges (free and bound) undergo forced oscillations. In this Appendix and in the rest of this book, the quantities, $\bar{\rho}$, $\bar{\sigma}$, and $\mathbf{j}$ are associated with all charges of the material body both free and bound. As a result, $\mathbf{P}$ in our notation includes both $\mathbf{P}_b$ and $\mathbf{P}_f$, and hence, instead of the relation, $\mathbf{j} = \mathbf{j}_f + (\partial \mathbf{P}_b / \partial t)$, we have

$$\mathbf{j} = \frac{\partial \mathbf{P}}{\partial t}. \quad (\text{A.13})$$

¹ In SI set $c = 1$. To change formulae from SI to G-CGS (and vice versa), see the table at the end of App. A. The relation $\mu_0 = 1/e_0 c^2$ may help in transforming formulas from SI to G-CGS.

² In SI, set $c = 1$.

From (A.13), (A.10), and (A.8) the charge conservation follows. Indeed

$$\nabla \cdot \mathbf{j}_t = \nabla \cdot \mathbf{j} = \frac{\partial}{\partial t} \nabla \cdot \mathbf{P} = -\frac{\partial \bar{\rho}}{\partial t}. \quad (\text{A.14})$$

Usually we combine $\mathbf{E}$ and $\mathbf{P}$ to define the so-called *electric induction* $\mathbf{D}$, and $\mathbf{B}$ and $\mathbf{M}$ to define the so-called “auxiliary” magnetic field $\mathbf{H}$:

$$\begin{aligned} \mathbf{D} &\equiv \varepsilon_0 \mathbf{E} + \mathbf{P}, & \text{SI,} \\ &\equiv \mathbf{E} + 4\pi \mathbf{P}, & \text{G-CGS,} \end{aligned} \quad (\text{A.15})$$

$$\begin{aligned} \mathbf{H} &\equiv \frac{1}{\mu_0} \mathbf{B} - \mathbf{M}, & \text{SI,} \\ &\equiv \mathbf{B} - 4\pi \mathbf{M}, & \text{G-CGS,} \end{aligned} \quad (\text{A.16})$$

where ε_0 (the permittivity of vacuum) and μ_0 (the magnetic permeability of the vacuum) are universal constants (see Table H.1) the product of which equals to the inverse of the square of the velocity of light in vacuum.

In terms of the vectors $\mathbf{E}$, $\mathbf{D}$, $\mathbf{B}$ and $\mathbf{H}$, Maxwell's equations are:

$$\begin{aligned} \nabla \cdot \mathbf{D} &= \rho_e, & \text{SI,} \\ &= 4\pi \rho_e, & \text{G-CGS,} \end{aligned} \quad (\text{A.17})$$

$$\begin{aligned} \nabla \times \mathbf{E} &= -\frac{\partial \mathbf{B}}{\partial t}, & \text{SI,} \\ &= -\frac{1}{c} \frac{\partial \mathbf{B}}{\partial t}, & \text{G-CGS,} \end{aligned} \quad (\text{A.18})$$

$$\nabla \cdot \mathbf{B} = 0, \quad (\text{A.19})$$

$$\begin{aligned} \nabla \times \mathbf{H} &= \mathbf{j}_e + \frac{\partial \mathbf{D}}{\partial t}, & \text{SI,} \\ &= \frac{4\pi}{c} \mathbf{j}_e + \frac{1}{c} \frac{\partial \mathbf{D}}{\partial t}, & \text{G-CGS,} \end{aligned} \quad (\text{A.20})$$

where ρ_e and $\mathbf{j}_e$ are external charges and currents not belonging to the material body. The advantage of employing $\mathbf{D}$ and $\mathbf{H}$ is due to the fact that their sources are only the external ones, which are usually assumed known.

Quite often we introduce vector and scalar potentials, $\mathbf{A}$ and ϕ respectively, which are related with the fields $\mathbf{E}$ and $\mathbf{B}$ as follows:

$$\mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} - \nabla \phi, \quad \text{G-CGS}^3, \quad (\text{A.21})$$

$$\mathbf{B} = \nabla \times \mathbf{A}. \quad (\text{A.22})$$

³ In SI the c in (A.21) must be replaced by 1.

The potentials are not uniquely defined: The transformations

$$\mathbf{A} \rightarrow \mathbf{A}' = \mathbf{A} + \nabla\psi \quad (\text{A.23})$$

$$\phi \rightarrow \phi' = \phi - \frac{1}{c} \frac{\partial\psi}{\partial t}, \quad \text{G-CGS}^4, \quad (\text{A.24})$$

leave the fields $\mathbf{E}$ and $\mathbf{B}$ invariant. This feature is called *gauge invariance*. We can take advantage of the freedom in choosing $\mathbf{A}$ and ϕ to simplify our formalism. For example, we can always make the scalar potential zero. Another possibility, called the *Coulomb gauge*, is to choose $\nabla \cdot \mathbf{A} = 0$. A third one, appropriate for the case where $\mathbf{D} = \varepsilon\mathbf{E}$ and $\mathbf{B} = \mu\mathbf{H}$, is to set $\nabla \cdot \mathbf{A} + \mu\varepsilon(\partial\phi/\partial t) = 0$; this is called the *Lorenz gauge*.

A.2 Relations Among the Fields

To solve Maxwell's equations, we have to express two of the four vectors $\mathbf{E}$, $\mathbf{B}$, $\mathbf{D}$, $\mathbf{H}$ in terms of the other two, e.g.,

$$\mathbf{D} = f_1(\mathbf{E}, \mathbf{H}; x_i), \quad (\text{A.25})$$

$$\mathbf{B} = f_2(\mathbf{E}, \mathbf{H}; x_i), \quad (\text{A.26})$$

where x_i stand for other variables that influence how $\mathbf{D}$ and $\mathbf{B}$ depend on $\mathbf{E}$ and $\mathbf{H}$. For example, x_i may represent mechanical stresses (which lead to the phenomenon of piezoelectricity) or temperature gradient (which lead to thermoelectric effects) or chemical potential gradients, or rotations (which leads to gyromagnetic phenomena), etc. In general, the dependence of $\mathbf{D}$ and $\mathbf{B}$ on $\mathbf{E}$ and $\mathbf{H}$ is complicated and nonlinear especially in the presence of powerful lasers where several very interesting phenomena with technological applications are due exactly to this nonlinearity. Nonlinear effects appear also in the presence of strong static magnetic fields (e.g., in the phenomena of magnetoresistance and the Hall effect) or strong electric field (e.g., dielectric breakdown in insulators). Some of these nonlinear effects are examined in this book.

For weak fields the rhs of (A.25) and (A.26) can be expanded in powers of $\mathbf{E}$ and $\mathbf{H}$. Keeping up to the first power, we have⁵

⁴ In SI the c in (A.24) must be replaced by 1.

⁵ Since $\mathbf{D}$ and $\mathbf{E}$ are polar vectors, while $\mathbf{B}$ and $\mathbf{H}$ are axial vectors, no linear relation between $\mathbf{D}$ and $\mathbf{H}$ or between $\mathbf{B}$ and $\mathbf{E}$ is possible, unless, e. g., there is another polar vector $\mathbf{g}$ to form the cross product $\mathbf{g} \times \mathbf{H}$ or the cross product $\mathbf{g} \times \mathbf{E}$ (for use in (A.27) or in (A.28) respectively). In materials having no center of inversion symmetry and exhibiting natural optical activity, $\mathbf{g}$ is effectively proportional to the wave vector $\mathbf{k}$. (See [E15], p. 359 and 362–365). In this case, additional terms $\xi\mathbf{H}$ and $\xi^*\mathbf{E}$ may appear in the rhs of (A.27) and (A.28) respectively. If ξ is purely imaginary the material is called **chiral**. (See the last two references at the end of this Appendix)

$$\mathbf{D} = \mathbf{D}_0 + \hat{\varepsilon}\mathbf{E}, \quad (\text{A.27})$$

$$\mathbf{B} = \mathbf{B}_0 + \hat{\mu}\mathbf{H}, \quad (\text{A.28})$$

where $\hat{\varepsilon}$ and $\hat{\mu}$ are in general *linear tensor operators*. The quantity $\hat{\varepsilon}$ is called *permittivity* or *electrical permeability* or *dielectric constant* (or function)⁶. The quantity $\hat{\mu}$ is called *magnetic permeability* or simply *permeability*. If $\mathbf{D}_0 \neq 0$, the material is called *pyroelectric*. In the particular case, where the change from $\mathbf{D}_0 \neq 0$ to $\mathbf{D}_0 = 0$ takes place through a second-order phase transition, the material is called *ferroelectric*. For most materials, $\mathbf{D}_0 = 0$; even in the cases where $\mathbf{D}_0 \neq 0$, its value is very small. Materials for which $\mathbf{B}_0$ is different from zero are called *ferromagnets*. They are studied together with other ordered magnetic phases in the present book.

Employing the definitions (A.15) and (A.16), we can express $\mathbf{P}$ and $\mathbf{M}$ in terms of $\mathbf{E}$ and $\mathbf{H}$, respectively:

$$\begin{aligned} \mathbf{P} &= \mathbf{P}_0 + (\hat{\varepsilon} - \varepsilon_0 I) \mathbf{E}, & \mathbf{P}_0 &= \mathbf{D}_0, & \text{SI}, \\ &= \mathbf{P}_0 + \frac{\hat{\varepsilon} - I}{4\pi} \mathbf{E}, & \mathbf{P}_0 &= \frac{\mathbf{D}_0}{4\pi}, & \text{G-CGS}, \end{aligned} \quad (\text{A.29})$$

$$\begin{aligned} \mathbf{M} &= \mathbf{M}_0 + \frac{\hat{\mu} - \mu_0 I}{\mu_0} \mathbf{H}, & \mathbf{M}_0 &= \frac{\mathbf{B}_0}{\mu_0}, & \text{SI}, \\ &= \mathbf{M}_0 + \frac{\hat{\mu} - I}{4\pi} \mathbf{H}, & \mathbf{M}_0 &= \frac{\mathbf{B}_0}{4\pi}, & \text{G-CGS}, \end{aligned} \quad (\text{A.30})$$

where I is the unit tensor. The dimensionless quantity

$$\begin{aligned} \hat{\chi}_e &\equiv \frac{\hat{\varepsilon} - \varepsilon_0 I}{\varepsilon_0}, & \text{SI}, \\ &\equiv \frac{\hat{\varepsilon} - I}{4\pi}, & \text{G-CGS}, \end{aligned} \quad (\text{A.31})$$

is called *electric susceptibility*, while the corresponding dimensionless quantity

$$\begin{aligned} \hat{\chi}_m &\equiv \frac{\hat{\mu} - \mu_0 I}{\mu_0}, & \text{SI}, \\ &\equiv \frac{\hat{\mu} - I}{4\pi}, & \text{G-CGS}, \end{aligned} \quad (\text{A.32})$$

is called *magnetic susceptibility*⁷. It should be pointed out that the values of χ_e in SI and G-CGS are not the same. Actually

$$\hat{\chi}_{e,\text{SI}} = 4\pi \hat{\chi}_{e,\text{G-CGS}}. \quad (\text{A.33})$$

⁶ In the SI system it is customary to call $\hat{\varepsilon}$ permittivity and the ratio $\hat{\varepsilon}/\varepsilon_0$ dielectric constant, where ε_0 is the value of ε in vacuum. We shall adopt this convention in this book.

⁷ The magnetic susceptibility as defined here is equal to $\hat{\chi}_m \equiv (\partial \mathbf{M} / \partial \mathbf{H})_T$ in the limit $H \rightarrow 0$. This last condition can be removed; then, $\hat{\chi}_m$ may become a function of $\mathbf{H}$, or $\mathbf{B}$.

Similarly

$$\hat{\chi}_{\text{m,SI}} = 4\pi\hat{\chi}_{\text{m,G-CGS}}. \quad (\text{A.34})$$

From (A.31) and (A.32) we can express $\hat{\varepsilon}$ and $\hat{\mu}$ in terms of $\hat{\chi}_{\text{e}}$ and $\hat{\chi}_{\text{m}}$ respectively

$$\begin{aligned} \hat{\varepsilon} &= \varepsilon_0 (I + \hat{\chi}_{\text{e}}), & \hat{\mu} &= \mu_0 (I + \hat{\chi}_{\text{m}}), & \text{SI,} \\ \hat{\varepsilon} &= I + 4\pi\hat{\chi}_{\text{e}}, & \hat{\mu} &= I + 4\pi\hat{\chi}_{\text{m}}, & \text{G-CGS.} \end{aligned} \quad (\text{A.35})$$

In terms of $\hat{\chi}_{\text{e}}$ and $\hat{\chi}_{\text{m}}$ (A.29) and (A.30) become

$$\begin{aligned} \mathbf{P} - \mathbf{P}_0 &= \varepsilon_0 \hat{\chi}_{\text{e}} \mathbf{E}, & \text{SI,} \\ &= \hat{\chi}_{\text{e}} \mathbf{E}, & \text{G-CGS,} \end{aligned} \quad (\text{A.36})$$

$$\mathbf{M} - \mathbf{M}_0 = \hat{\chi}_{\text{m}} \mathbf{H}. \quad (\text{A.37})$$

Let us assume now that the time dependence of the various fields is of the form $\exp(-i\omega t)$ (with the exceptions of $\mathbf{P}_0$ and $\mathbf{M}_0$, which are time-independent). Then (A.13) becomes

$$\begin{aligned} \mathbf{j} &= -i\omega (\mathbf{P} - \mathbf{P}_0) = -i\omega (\hat{\varepsilon} - \varepsilon_0 I) \mathbf{E}, & \text{SI,} \\ &= -i\omega \frac{\hat{\varepsilon} - I}{4\pi} \mathbf{E}, & \text{G-CGS.} \end{aligned} \quad (\text{A.38})$$

The coefficient in front of $\mathbf{E}$ in the rhs of (A.38) is by definition the AC electrical conductivity $\hat{\sigma}(\omega)$ (which, according to our definition includes the contributions of both the free and the bound charges). Hence, $\hat{\sigma}(\omega)$ is directly related to the permittivity and the electrical susceptibility:

$$\begin{aligned} \hat{\sigma}(\omega) &= -i\omega (\hat{\varepsilon} - \varepsilon_0 I) = -i\omega \varepsilon_0 \hat{\chi}_{\text{e}}, & \text{SI,} \\ &= -i\omega \frac{\hat{\varepsilon} - I}{4\pi} = -i\omega \hat{\chi}_{\text{e}}, & \text{G-CGS.} \end{aligned} \quad (\text{A.39})$$

Inverting (A.39), we can express $\hat{\varepsilon}(\omega)$ in terms of $\hat{\sigma}(\omega)$

$$\begin{aligned} \hat{\varepsilon}(\omega) &= \varepsilon_0 I + \frac{i\hat{\sigma}(\omega)}{\omega}, & \text{SI,} \\ &= I + \frac{4\pi i\hat{\sigma}(\omega)}{\omega}, & \text{G-CGS.} \end{aligned} \quad (\text{A.40})$$

Relations (A.35), (A.39), and (A.40) allow us to obtain immediately two of the three quantities, $\hat{\varepsilon}$, $\hat{\chi}_{\text{e}}$, $\hat{\sigma}$, if we know the third. Usually – especially for conductors – it is easier to calculate first the AC conductivity, $\hat{\sigma}(\omega)$, and then, using (A.40) and (A.39), to obtain $\hat{\varepsilon}(\omega)$ and $\hat{\chi}_{\text{e}}(\omega)$ respectively. In the case of atomic or molecular insulators, we calculate first each atomic (or molecular) dipole moment $\mathbf{p}_{\alpha}$, which is assumed to be proportional to the *local* electric field,

$$\mathbf{p}_{\alpha} = \hat{\alpha}_{\text{e}} \mathbf{E}_{\text{loc}}, \quad (\text{A.41})$$

and then, taking into account that $\Delta \mathbf{p} = \sum_a \mathbf{p}_a$ (where summation is over the particles within the volume ΔV), we obtain $\mathbf{P}$ from (A.6). We need to express E_{loc} in terms of the average field $\mathbf{E}$ to end up with $\hat{\chi}_e(\omega)$. (Under the assumption of cubic symmetry, we have that $\mathbf{E}_{\text{loc}} = \mathbf{E} + (\mathbf{P}/3\epsilon_0) = [1 - (\sum a_e/3\epsilon_0\Delta V)]^{-1} \mathbf{E}$). The quantity $\hat{\alpha}_e$ is called atomic (or molecular or ionic) *electric polarizability*.

Note that the more general form of $\hat{\varepsilon}$ becomes clear if we express (A.27) explicitly (for $\mathbf{D}_0 = 0$):

$$D_i(\mathbf{r}, t) = \sum_j \int dt' \int d^3r' \varepsilon_{ij}(\mathbf{r}, \mathbf{r}'; t - t') E_j(\mathbf{r}', t'), \quad (\text{A.42})$$

where the indices i, j denote Cartesian components of the vectors $\mathbf{D}$ and $\mathbf{E}$ and of the tensor $\hat{\varepsilon}$. It is clear from (A.42) that in general the relation between $\mathbf{D}(\mathbf{r}, t)$ and $\mathbf{E}(\mathbf{r}', t')$ is neither local nor instantaneous. In other words, the value of $\mathbf{D}(\mathbf{r}, t)$ at the point $\mathbf{r}$ depends not only on $\mathbf{E}(\mathbf{r})$ but also on the values of $\mathbf{E}$ in the neighborhood of $\mathbf{r}$ (the linear extent of this neighborhood is in conductors of the order of the mean free path, ℓ). Furthermore, the value of $\mathbf{D}$ at t depends not only on the value $\mathbf{E}$ at time t , but also on the values of $\mathbf{E}$ at previous times, $t' \leq t$. If we have spatial homogeneity, ε_{ij} depends on the difference, $\mathbf{r} - \mathbf{r}'$, and not separately on $\mathbf{r}$ and $\mathbf{r}'$. Then (A.42) takes a simpler and more familiar form in terms of the Fourier transforms of $\mathbf{D}$, $\mathbf{E}$, and ε :

$$D_i(\mathbf{r}, t) = \frac{1}{(2\pi)^4} \int \tilde{D}_i(\mathbf{k}, \omega) e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} d^3k d\omega, \quad (\text{A.43})$$

$$E_j(\mathbf{r}', t') = \frac{1}{(2\pi)^4} \int \tilde{E}_j(\mathbf{k}', \omega') e^{i(\mathbf{k}' \cdot \mathbf{r}' - \omega' t')} d^3k' d\omega', \quad (\text{A.44})$$

$$\varepsilon_{ij}(\mathbf{r} - \mathbf{r}', t - t') = \frac{1}{(2\pi)^4} \int \tilde{\varepsilon}_{ij}(\mathbf{q}, \omega'') e^{i[\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}') - \omega''(t - t')]} d^3q d\omega'', \quad (\text{A.45})$$

$$\tilde{D}_i(\mathbf{k}, \omega) = \sum_{j=1}^3 \tilde{\varepsilon}_{ij}(\mathbf{k}, \omega) \tilde{E}_j(\mathbf{k}, \omega). \quad (\text{A.46})$$

For isotropic systems (and under some additional conditions) the tensor $\tilde{\varepsilon}_{ij}$ is proportional to $\tilde{\varepsilon}(\mathbf{k}, \omega) \delta_{ij}$ and hence

$$\tilde{\mathbf{D}}(\mathbf{k}, \omega) = \tilde{\varepsilon}(\mathbf{k}, \omega) \tilde{\mathbf{E}}(\mathbf{k}, \omega). \quad (\text{A.47})$$

Strictly speaking, $\tilde{\varepsilon}(\mathbf{k}, \omega)$ is independent of $\mathbf{k}$, ω , i.e., a constant ε , if and only if, $\varepsilon(\mathbf{r} - \mathbf{r}'; t - t') = \varepsilon \delta(\mathbf{r} - \mathbf{r}') \delta(t - t')$. However, if $kL \ll 1$, we can write approximately $\tilde{\varepsilon}(\mathbf{k}, \omega) \simeq \tilde{\varepsilon}(0, \omega)$ and similarly, if $\omega\tau \ll 1$, $\tilde{\varepsilon}(\mathbf{k}, \omega) \simeq \tilde{\varepsilon}(\mathbf{k}, 0)$; L is the characteristic length, over which the integration over $\mathbf{r}'$ in (A.42) is extended and τ is the characteristic time, over which the integration over t' in (A.42) is extended.

If k is so large that $1/k$ is comparable to or smaller than interatomic distances, we can still define $\tilde{\varepsilon}(\mathbf{k}, \omega)$; however, in this case it is not allowed to use averages as in (A.2) and (A.3), because the double inequality $a^3 \ll \Delta V \ll \lambda^3$ cannot be satisfied. We have, then, to employ microscopic quantities to define the microscopic permittivity:

$$\tilde{\varepsilon}(\mathbf{k}, \omega) \equiv \frac{\rho_{\text{ext}}(\mathbf{k}, \omega)}{\rho_{\text{tot}}(\mathbf{k}, \omega)}, \quad (\text{A.48})$$

where $\rho_{\text{ext}}(\mathbf{k}, \omega)$ is the Fourier transform of an external charge distribution and $\rho_{\text{tot}}(\mathbf{k}, \omega) = \rho_{\text{ext}}(\mathbf{k}, \omega) + \rho_i(\mathbf{k}, \omega)$ is the Fourier transform of the total charge distribution consisting of the external charge and the induced charge distribution, $\rho_i(\mathbf{k}, \omega)$.

The relation $\tilde{\varepsilon}(0, \omega) \simeq \tilde{\varepsilon}(0, 0)$ when $\omega\tau \ll 1$ is not valid in the case of conducting materials, because according to (A.40), we have in the limit, $\omega \rightarrow 0$:

$$\begin{aligned} \tilde{\varepsilon}(0, \omega) &\rightarrow \frac{i\sigma_0}{\omega}, & \text{SI,} \\ &\rightarrow \frac{4\pi i\sigma_0}{\omega}, & \text{G-CGS,} \end{aligned} \quad (\text{A.49})$$

where $\sigma_0 = \sigma(0, 0)$ is the static (DC) electrical conductivity of the material.

It is important to stress that as a result of causality, $\varepsilon(\mathbf{r}, \mathbf{r}', t - t') = 0$, when $t' > t$. It follows then that $\tilde{\varepsilon}(\omega)$ is an *analytic function* for ω in the upper half plane ($\text{Im } \omega > 0$). This follows immediately from the Fourier inverse of (A.45) and the fact that $\varepsilon(t) = 0$ for $t < 0$:

$$\tilde{\varepsilon}(\omega) = \int_{-\infty}^{+\infty} \varepsilon(t) e^{i\omega t} dt = \int_0^{\infty} \varepsilon(t) e^{i\omega t} dt. \quad (\text{A.50})$$

The last expression converges absolutely for $\text{Im } \omega > 0$ and consequently can be differentiated with respect to ω under the integration. From (A.50) it follows also that $\tilde{\varepsilon}^*(\omega) = \tilde{\varepsilon}(-\omega^*)$, or more explicitly:

$$\tilde{\varepsilon}_1(\omega) = \tilde{\varepsilon}_1(-\omega^*), \quad (\text{A.51})$$

$$\tilde{\varepsilon}_2(\omega) = -\tilde{\varepsilon}_2(-\omega^*), \quad (\text{A.52})$$

where $\tilde{\varepsilon}(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$. For real ω , (A.51) and (A.52) mean that the real part of $\tilde{\varepsilon}(\omega)$ is an even function of ω , while the imaginary part is an odd function of ω (See [E15], p. 360).

By integrating the analytic function $\tilde{\varepsilon}(\omega')/(\omega' - \omega)$ (for $\text{Im } \omega' > 0$ and $\text{Im } \omega = 0$) over a closed contour in the upper half plane ω' (passing just above the real axis (from $-\infty$ to $+\infty$) and being closed by an infinite semicircle in the upper half-plane), using the analyticity to conclude that this integral is zero, and taking into account that $\tilde{\varepsilon}(\omega) \rightarrow \varepsilon_{\text{inf}} + \mathcal{O}(\omega^{-2})$ for $\omega \rightarrow \infty$ (see (A.40)), while $\varepsilon(\omega) \rightarrow A i \sigma_0 / \omega$, for $\omega \rightarrow 0$ (see (A.49)), we obtain the *Kramers–Kronig relations*, which allow the determination of $\tilde{\varepsilon}_1(\omega)$ from $\tilde{\varepsilon}_2(\omega)$ and vice versa:

$$\tilde{\varepsilon}_1(\omega) = \varepsilon_{\text{inf}} + \frac{2}{\pi} P \int_0^{\infty} \frac{\omega' \tilde{\varepsilon}_2(\omega') d\omega'}{\omega'^2 - \omega^2}, \quad (\text{A.53})$$

$$\tilde{\varepsilon}_2(\omega) = A \frac{\sigma_0}{\omega} - \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\varepsilon_1(\omega') - \varepsilon_{\text{inf}}}{\omega' - \omega} d\omega', \quad (\text{A.54})$$

where $\varepsilon_{\text{inf}} = \varepsilon_0$ or 1 and $A = 1$ or 4π for SI or G-CGS respectively. The P in front of the integration symbol denotes the principal value of the integral.

We shall conclude this appendix by giving formulae for the energy of a material body in the presence of electric or magnetic fields.

- (a) Let U be the energy of the combined system consisting of a dielectric body and the actual electric field $\mathbf{E}(\mathbf{r})$ inside and outside it. The elementary change, δU , of U due to a change $\delta\rho_e$ in the external charge density (assuming that the other natural independent thermodynamic variables, S (the entropy), V , N_i (number of various types of particles) are kept constant) is given by

$$\begin{aligned} \delta U &= \int_V \phi \delta\rho_e dV = \int_V \mathbf{E} \cdot \delta\mathbf{D} dV, & \text{SI,} \\ \delta U &= \int_V \phi \delta\rho_e dV = \frac{1}{4\pi} \int_V \mathbf{E} \cdot \delta\mathbf{D} dV, & \text{G-CGS.} \end{aligned} \quad (\text{A.55})$$

Let $\mathbf{E}_0$ be the electric field generated by the same charge distribution, $\rho_e(\mathbf{r})$, but in the absence of the dielectric body. Then the interaction energy, U_{int} , of the field $\mathbf{E}_0$ with the dielectric body is given by

$$\begin{aligned} U_{\text{int}} &\equiv U - U_0 - \frac{1}{2} \varepsilon_0 \int \mathbf{E}_0^2 dV, & \text{SI,} \\ &\equiv U - U_0 - \frac{1}{8\pi} \int \mathbf{E}_0^2 dV, & \text{G-CGS,} \end{aligned} \quad (\text{A.56})$$

where U_0 is the energy of the dielectric body in the absence of the external field $\mathbf{E}_0$ and the last term is the energy of the electric field alone. The change, δU_{int} , due to a change, $\delta\mathbf{E}_0$ (under S , V , $N_i = \text{constant}$) is given by

$$\delta U_{\text{int}} = - \int \mathbf{P} \cdot \delta\mathbf{E}_0 dV. \quad (\text{A.57})$$

Equation (A.57) allows us to obtain $\mathbf{P}$ as the functional derivative of either U_{int} or $U' \equiv U_{\text{int}} + U_0 = U - \frac{1}{2} \varepsilon_0 \int \mathbf{E}_0^2 dV$ (since U_0 does not depend on $\mathbf{E}_0$) with respect to $\mathbf{E}_0$. If $\mathbf{E}_0$ is uniform, we have

$$\begin{aligned} \mathbf{P} &= -\frac{1}{V} \left(\frac{\partial U'}{\partial \mathbf{E}_0} \right)_{S, V, N_i} = -\frac{1}{V} \left(\frac{\partial F'}{\partial \mathbf{E}_0} \right)_{T, V, N_i} = -\frac{1}{V} \left(\frac{\partial G'}{\partial \mathbf{E}_0} \right)_{T, P, N_i} \\ &= -\frac{1}{V} \left\langle \frac{\partial \hat{H}_{\text{int}}}{\partial \mathbf{E}_0} \right\rangle, \end{aligned} \quad (\text{A.58})$$

where $F' = U' - TS$, $G' = F' + PV$ (and P is the pressure).

- (b) Consider next a system consisting of a body and a magnetic field, $\mathbf{B}(\mathbf{r})$, the external current density sources, $\mathbf{j}_e(\mathbf{r})$, of which would generate a magnetic field, $\mathbf{B}_0$, in the absence of the body. The total energy, U_t , of the system can be written as the sum of three terms: the energy, U_0 , of the body in the absence of external current sources; the work, U_c , done by external forces to bring the elementary contributions to the current sources from infinity to their final places in the presence of the body (this work is negative, since parallel currents attract each other); and the energy supplied by external “batteries”, U_b , to keep each elementary current loop constant as it moves from infinity to their final position. U_b is given by

$$\begin{aligned} U_b &= \int \mathbf{B} \cdot \mathbf{H} dV, \quad \text{SI,} \\ &= \frac{1}{4\pi} \int \mathbf{B} \cdot \mathbf{H} dV, \quad \text{G-CGS.} \end{aligned} \quad (\text{A.59})$$

The elementary change, $\delta\tilde{U}$, of $\tilde{U} \equiv U_0 + U_c$ due to an elementary change, $\delta\mathbf{j}_e$ (while S , V , N_i are kept constant), is equal to

$$\begin{aligned} \delta\tilde{U} &= - \int \mathbf{A} \cdot \delta\mathbf{j}_e dV = - \int \mathbf{B} \cdot \delta\mathbf{H} dV, \quad \text{SI} \\ &= - \frac{1}{c} \int \mathbf{A} \cdot \delta\mathbf{j}_e dV = - \frac{1}{4\pi} \int \mathbf{B} \cdot \delta\mathbf{H} dV, \quad \text{G-CGS,} \end{aligned} \quad (\text{A.60})$$

where $\mathbf{B} = \nabla \times \mathbf{A}$. We see that $\delta\tilde{U}$ in (A.60) is the analog of the (A.55), apart from the minus sign. As a result, the interaction energy, $\tilde{U}_{\text{int}}$, of the body with the preexisting field, $\mathbf{B}_0$, is given by

$$\begin{aligned} U_{\text{int}} &\equiv \tilde{U} - U_0 - U_c(\mathbf{B}_0) = \tilde{U} - U_0 - \left(-\frac{1}{2} \int \mathbf{B}_0 \cdot \mathbf{H}_0 dV \right), \quad \text{SI} \\ &\equiv \tilde{U} - U_0 - \left(-\frac{1}{8\pi} \int \mathbf{B}_0^2 dV \right), \quad \text{G-CGS.} \end{aligned} \quad (\text{A.61})$$

The elementary change, $\delta\tilde{U}_{\text{int}} = \delta U'$, where $U' = \tilde{U}_{\text{int}} + U_0 = \tilde{U} - U_c(\mathbf{B}_0)$, due to a change in $\delta\mathbf{B}_0$ is given by

$$\delta U' = - \int \mathbf{M} \cdot \delta\mathbf{B}_0 dV. \quad (\text{A.62})$$

Thus, for uniform $\mathbf{B}_0$

$$\begin{aligned} \mathbf{M} &= -\frac{1}{V} \left(\frac{\partial \tilde{U}'}{\partial \mathbf{B}_0} \right)_{S,V,N_i} = -\frac{1}{V} \left(\frac{\partial \tilde{F}'}{\partial \mathbf{B}_0} \right)_{T,V,N_i} = -\frac{1}{V} \left(\frac{\partial \tilde{G}'}{\partial \mathbf{B}_0} \right)_{T,P,N_i} \\ &= -\frac{1}{V} \left\langle \frac{\partial \hat{H}_{\text{int}}}{\partial \mathbf{B}_0} \right\rangle, \end{aligned} \quad (\text{A.63})$$

where $\tilde{F}' = \tilde{U}' - TS$, $\tilde{G}' = F' + PV$ (P is the pressure). The symbol $\langle \rangle$ denotes full average value both quantum mechanical and statistical.

In the following two columns we summarize some of the main formulae of electromagnetism both in SI and in G-CGS. We remind the readers that $\tilde{\varepsilon}$, $\hat{\chi}_e$, $\hat{a}_e$, $\hat{\sigma}$, $\hat{\mu}$, $\hat{\chi}_m$, $\hat{a}_m$ are in general linear, integral, tensor operators (see (A.42)).

SI	G-CGS
$\mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B})$	$\mathbf{F} = q\left(\mathbf{E} + \frac{1}{c}\mathbf{v} \times \mathbf{B}\right)$
$\nabla \cdot \mathbf{P} = -\bar{\rho}$	$\nabla \cdot \mathbf{P} = -\bar{\rho}$
$\nabla \times \mathbf{M} = \mathbf{j}_M$	$\nabla \times \mathbf{M} = \frac{1}{c}\mathbf{j}_M$
$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P}$	$\mathbf{D} = \mathbf{E} + 4\pi \mathbf{P}$
$\mathbf{H} = \frac{1}{\mu_0} \mathbf{B} - \mathbf{M}$	$\mathbf{H} = \mathbf{B} - 4\pi \mathbf{M}$
$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$	$\nabla \times \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{B}}{\partial t}$
$\nabla \cdot \mathbf{D} = \rho_e$	$\nabla \cdot \mathbf{D} = 4\pi \rho_e$
$\nabla \times \mathbf{H} = \mathbf{j}_e + \frac{\partial \mathbf{D}}{\partial t}$	$\nabla \times \mathbf{H} = \frac{4\pi}{c} \mathbf{j}_e + \frac{1}{c} \frac{\partial \mathbf{D}}{\partial t}$
$\nabla \cdot \mathbf{B} = 0$	$\nabla \cdot \mathbf{B} = 0$
$\mathbf{D} = \hat{\varepsilon} \mathbf{E} = \varepsilon_0 \mathbf{E} + \mathbf{P}$	$\mathbf{D} = \hat{\varepsilon} \mathbf{E} = \mathbf{E} + 4\pi \mathbf{P}$
$\mathbf{B} = \hat{\mu} \mathbf{H} = \mu_0 \mathbf{H} + \mu_0 \mathbf{M}$	$\mathbf{B} = \hat{\mu} \mathbf{H} = \mathbf{H} + 4\pi \mathbf{M}$
$\mathbf{P} = \varepsilon_0 \hat{\chi}_e \mathbf{E}$	$\mathbf{P} = \hat{\chi}_e \mathbf{E}$
$\mathbf{P} = \frac{1}{V} \sum_i \mathbf{p}_i$	$\mathbf{P} = \frac{1}{V} \sum_i \mathbf{p}_i$
$\mathbf{p} = \hat{\alpha}_e \mathbf{E}_{\text{loc}}$	$\mathbf{p} = \hat{a}_e \mathbf{E}_{\text{loc}}$
$\hat{\varepsilon} = \varepsilon_0 I + \varepsilon_0 \hat{\chi}_e$	$\hat{\varepsilon} = I + 4\pi \hat{\chi}_e$
$\mathbf{M} = \hat{\chi}_m \mathbf{H}$	$\mathbf{M} = \hat{\chi}_m \mathbf{H}$
$\mathbf{M} = \frac{1}{V} \sum_i \mathbf{m}_i$	$\mathbf{M} = \frac{1}{V} \sum_i \mathbf{m}_i$
$\mathbf{m} = \hat{a}_m \mathbf{H}$	$\mathbf{m} = \hat{a}_m \mathbf{H}$
$\hat{\mu} = \mu_0 I + \mu_0 \hat{\chi}_m$	$\hat{\mu} = I + 4\pi \hat{\chi}_m$
$\hat{\varepsilon} = \varepsilon_0 I + \frac{i\hat{\sigma}}{\omega}$	$\hat{\varepsilon} = I + \frac{4\pi i\hat{\sigma}}{\omega}$
$\hat{\sigma} = -i\omega(\hat{\varepsilon} - \varepsilon_0 I)$	$\hat{\sigma} = -\frac{i\omega}{4\pi}(\hat{\varepsilon} - I)$
$\delta U = \int \mathbf{E} \cdot \delta \mathbf{D} dV$	$\delta U = \frac{1}{4\pi} \int \mathbf{E} \cdot \delta \mathbf{D} dV$
$\delta U' = -\int \mathbf{P} \cdot \delta \mathbf{E}_0 dV$	$\delta U' = -\int \mathbf{P} \cdot \delta \mathbf{E}_0 dV$
$\delta U_t = \int \mathbf{H} \cdot \delta \mathbf{B} dV$	$\delta U_t = \frac{1}{4\pi} \int \mathbf{H} \cdot \delta \mathbf{B} dV$
$\delta \tilde{U}' = -\int \mathbf{M} \cdot \delta \mathbf{B}_0 dV$	$\delta \tilde{U}' = -\int \mathbf{M} \cdot \delta \mathbf{B}_0 dV$
$\mathbf{P} = -\frac{1}{V} \left(\frac{\partial F'}{\partial \mathbf{E}_0} \right)_T$	$\mathbf{P} = -\frac{1}{V} \left(\frac{\partial F'}{\partial \mathbf{E}_0} \right)_T$
$\mathbf{M} = -\frac{1}{V} \left(\frac{\partial F'}{\partial \mathbf{E}_0} \right)_T$	$\mathbf{M} = -\frac{1}{V} \left(\frac{\partial F'}{\partial \mathbf{E}_0} \right)_T$

To change formulae from SI to G-CGS (and vice versa), do the following replacements. In some cases the transition from the SI to the G-CGS is facilitated by expressing μ_0 in terms of ε_0 and c (the velocity of light in vacuum):

$$\mu_0 = \frac{1}{\varepsilon_0 c^2}$$

SI	G-CGS
B	B/c
ε_0	$1/4\pi$
μ_0	$4\pi/c^2$
M	cM
D	$D/4\pi$
H	$cH/4\pi$
A	A/c
χ_e	$4\pi\chi_e$
χ_m	$4\pi\chi_m$

Further Reading

- D. J. Griffiths, *Introduction to Electrodynamics*, 2nd ed. Prentice Hall 1996 [E14].
- L. D. Landau & E. M. Lifshitz, *Electrodynamics of continuous media*, 2nd ed., Pergamon Press, Oxford (1984) [E15].
- I. V. Lindell et al., *Electromagnetic Waves in Chiral and Bi-Isotropic Media*, (Artech House, Boston, London, (1994)).
- A. Serdyukov et al., *Electromagnetics of Bi-Anisotropic Materials: Theory and Applications*, (Gordon and Breach Science Publishers, Amsterdam, (2001)).

B

Elements of Quantum Mechanics

B.1 General Formalism

Consider a non-relativistic spinless particle of mass m moving under the influence of a potential energy $\mathcal{V}(\mathbf{r}, t)$. Its state at any time t is fully determined by a complex wavefunction $\phi(\mathbf{r}, t)$; the quantity $|\phi(\mathbf{r}, t)|^2 d^3r$ gives the probability of finding the particle at time t in the infinitesimal volume d^3r around the point $\mathbf{r}$, provided that $\phi(\mathbf{r}, t)$ has been normalized so that $\int_V |\phi(\mathbf{r}, t)|^2 d^3r = 1$.

Quantities of physical interest can be obtained once $\phi(\mathbf{r}, t)$ is known. For example, the average value, of momentum $\mathbf{p}$, and the position $\mathbf{r}$ are given by integrals of the form

$$\langle \mathbf{p} \rangle = \int \phi^*(\mathbf{r}, t) [\hat{\mathbf{p}}\phi(\mathbf{r}, t)] d^3r, \quad (\text{B.1})$$

$$\langle \mathbf{r} \rangle = \int \phi^*(\mathbf{r}, t) [\hat{\mathbf{r}}\phi(\mathbf{r}, t)] d^3r, \quad (\text{B.2})$$

where $\hat{\mathbf{p}}$, the operator acting on ϕ and corresponding to the momentum $\mathbf{p}$ is given by

$$\hat{\mathbf{p}} = -i\hbar \nabla_{\mathbf{r}} = -i\hbar \left[\mathbf{i} \frac{\partial}{\partial x} + \mathbf{j} \frac{\partial}{\partial y} + \mathbf{k} \frac{\partial}{\partial z} \right], \quad (\text{B.3})$$

while the operator corresponding to $\mathbf{r}$ implies simply multiplication by $\mathbf{r}$ itself, i.e. $\hat{\mathbf{r}}\phi(\mathbf{r}, t) = \mathbf{r}\phi(\mathbf{r}, t)$. The quantity $\hbar$ is Planck's constant (divided by 2π), probably the most important physical constant of nature.

For any quantity $A(\mathbf{p}, \mathbf{r})$, which is a function of momentum $\mathbf{p}$ and position $\mathbf{r}$, we obtain the corresponding operator by the replacement $\mathbf{p} \rightarrow \hat{\mathbf{p}}$ and $\mathbf{r} \rightarrow \hat{\mathbf{r}} = \mathbf{r}$

$$\hat{A} = A(\hat{\mathbf{p}}, \hat{\mathbf{r}}). \quad (\text{B.4})$$

In analogy with (B.1, B.2), the average value, $\langle A \rangle$, is given by

$$\langle A \rangle = \int \phi^*(\mathbf{r}, t) [\hat{A} \phi(\mathbf{r}, t)] d^3r. \quad (\text{B.5})$$

Using formulae similar to (B.1), (B.2), and (B.5), one can obtain not only the average value of any physical quantity $A(\mathbf{p}, \mathbf{r})$ but also standard deviations and central moments of any degree; the latter determine the full probability distribution of $A(\mathbf{p}, \mathbf{r})$. For example, the central moment, μ_n , (of n degree, $n = 2, 3, \dots$) of the quantity $A(\mathbf{p}, \mathbf{r})$ is given by the integral

$$\mu_n = \int \phi^*(\mathbf{r}, t) \left\{ [\hat{A} - \langle A \rangle]^n \phi(\mathbf{r}, t) \right\} d^3r, \quad (\text{B.6})$$

where $\hat{A}$ is as in (B.4) and $\langle A \rangle$ as in (B.5). $[\hat{A} - \langle A \rangle]^n \equiv [\hat{A} - \langle A \rangle]^{n-1} (\hat{A} - \langle A \rangle)$.

Thus, the average value of the total energy, $E_t = E_K + E_P$, where $E_K = p^2/2m$ is the kinetic energy and $E_P = \mathcal{V}$ is the potential energy, is given by the integral

$$\langle E_t \rangle = \int \phi^*(\mathbf{r}, t) [\hat{H} \phi(\mathbf{r}, t)] d^3r. \quad (\text{B.7})$$

The operator $\hat{H}$ corresponding to the total energy and acting on ϕ is given according to (B.4) by

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + \mathcal{V}(\mathbf{r}, t) = -\frac{\hbar^2}{2m} \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] + \mathcal{V}(\mathbf{r}, t). \quad (\text{B.8})$$

The operator, $\hat{H}$, which is called the Hamiltonian operator or simply the Hamiltonian, is of central importance, because it determines the time evolution of the system according to the so-called time-dependent Schrödinger equation

$$i\hbar \frac{\partial \phi}{\partial t} = \hat{H} \phi \equiv -\frac{\hbar^2}{2m} \left[\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} + \frac{\partial^2 \phi}{\partial z^2} \right] + \mathcal{V} \phi. \quad (\text{B.9})$$

If $\mathcal{V}$ does not depend on t , i.e., if $\mathcal{V}$ is a function of $\mathbf{r}$ only, we can proceed one step in the solution of (B.9) by writing

$$\phi(\mathbf{r}, t) = \psi(\mathbf{r}) e^{-iEt/\hbar}, \quad (\text{B.10})$$

and substituting (B.10) in (B.9).¹ We obtain then the so-called time-independent Schrödinger equation for $\psi(\mathbf{r})$:

$$E\psi = \hat{H}\psi \equiv -\frac{\hbar^2}{2m} \left[\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right] + \mathcal{V}\psi. \quad (\text{B.11})$$

¹ For $\phi(\mathbf{r}, t)$ and $\psi(\mathbf{r})$ to be solutions they must satisfy boundary conditions at infinity as well: $\phi(\mathbf{r}, t) \rightarrow f(t)$, $\psi(\mathbf{r}) \rightarrow c_1$ as $\mathbf{r} \rightarrow \infty$ where both $f(t)$ and c_1 must be either finite or zero.

Then, using (B.8), (B.10), and (B.11), we find that $\langle E_t \rangle = E$; furthermore the central moment μ_n of degree n ($n = 2, 3, \dots$) of the total energy is according to its definition (see (B.6)) and (B.10) equal to zero

$$\begin{aligned}\mu_n &= \int \phi^*(\mathbf{r}, t) \left\{ [\hat{H} - E]^n \phi(\mathbf{r}, t) \right\} d^3r \\ &= \int \psi^*(\mathbf{r}) \left\{ [\hat{H} - E]^n \psi(\mathbf{r}) \right\} d^3r \\ &= \int \psi^*(\mathbf{r}) \{ [E - E]^n \psi(\mathbf{r}) \} d^3r = 0.\end{aligned}\quad (\text{B.12})$$

The last equation follows from (B.11). The physical meaning of (B.12) is as follows. For the wavefunction satisfying (B.10) and (B.11), the total energy has no quantum fluctuations around its average value; in other words, the total energy of the state described by ψ satisfying (B.11) has the value E with probability one. We say then that ψ is an eigenfunction of the Hamiltonian and E is an eigenvalue of the total energy. This feature is generalized to any operator: an eigenfunction of a physical operator $\hat{A}$ is the solution, ψ_A , to the equation

$$\hat{A}\psi_A = A\psi_A, \quad (\text{B.13})$$

where A , called an eigenvalue of the physical quantity $A(\mathbf{p}, \mathbf{r})$, is any real value for which (B.13) has solutions satisfying the boundary conditions; ψ_A describes a state for which the physical quantity corresponding to the operator $\hat{A}$ has the value A with probability one. The eigenfunctions of any physical operator form a complete orthogonal set which can be normalized to one. This means that

$$\int \psi_A^* \psi_{A'} d^3r = \delta_{AA'}, \quad (\text{B.14})$$

$$\psi(\mathbf{r}) = \sum_A c_A \psi_A(\mathbf{r}), \quad (\text{B.15})$$

where $\psi(\mathbf{r})$ is any wave function describing a state of the particle. Because of the orthonormality of the ψ_A s, $c_A = \int \psi_A^*(\mathbf{r}) \psi(\mathbf{r}) d^3r$; $|c_A|^2$ is the probability that the quantity $A(\mathbf{p}, \mathbf{r})$ has the value A when the state of the particle ψ is given by² (B.15).

The eigenfunctions of the momentum operator are plane waves

$$\hat{\mathbf{p}} \left(\frac{1}{\sqrt{V}} e^{i\mathbf{k} \cdot \mathbf{r}} \right) = \hbar \mathbf{k} \left(\frac{1}{\sqrt{V}} e^{i\mathbf{k} \cdot \mathbf{r}} \right), \quad (\text{B.16})$$

as one can verify immediately using (B.3). The volume V within which the particle is moving is assumed to approach infinity, while periodic boundary conditions are imposed. By choosing $\hat{A}$ to be the momentum, (B.15) becomes

² This follows from the relations $\sum_A |c_A|^2 = 1$ and $\langle (A(\mathbf{p}, \mathbf{r}) - \langle A \rangle)^n \rangle = \sum_A |c_A|^2 (A - \langle A \rangle)^n$ which can be obtained by using (B.5), (B.6), (B.14), and (B.15).

$$\psi(\mathbf{r}) = \frac{1}{\sqrt{V}} \sum_k c_k e^{i\mathbf{k} \cdot \mathbf{r}}, \quad (\text{B.17})$$

$$c_k = \frac{1}{\sqrt{V}} \int d^3r' e^{-i\mathbf{k} \cdot \mathbf{r}'} \psi(\mathbf{r}') d^3r'. \quad (\text{B.18})$$

In the limit $V \rightarrow \infty$ the summation over $\mathbf{k}$ becomes an integral of the form³

$$\sum_k \rightarrow \frac{V}{(2\pi)^3} \int d^3k. \quad (\text{B.19})$$

Hence, (B.17) and (B.18) are nothing but the Fourier integral expansions.

B.2 Bra and Ket Notation

Equations (B.15) and (B.17) show that the state of the quantum system can be represented equally well by either $\psi(\mathbf{r})$ or by the set $\{c_A\}$ (a particular case of which is the set $\{c_{\mathbf{k}}\}$). If we do not want to specify which representation we are going to use for the state of the system, we can introduce an abstract symbol for this state denoted (following Dirac's notation) by $|\psi\rangle$ and called ket. The conjugate state is denoted by $\langle\psi|$ and is called bra. We introduce also the bracket notation $\langle\psi_i|\psi_j\rangle$, which is equal to

$$\langle\psi_i|\psi_j\rangle = \int \psi_i^*(\mathbf{r}) \psi_j(\mathbf{r}) d^3r. \quad (\text{B.20})$$

If we denote by $|\mathbf{r}\rangle$, $|\mathbf{k}\rangle$, $|A\rangle$ the kets, which correspond to the eigenfunctions of the position operator with eigenvalue $\mathbf{r}$, $[\hat{\mathbf{r}}|\mathbf{r}\rangle = \mathbf{r}|\mathbf{r}\rangle]$ of the momentum operator with eigenvalue $\hbar\mathbf{k}$, $[\hat{\mathbf{p}}|\mathbf{k}\rangle = \hbar\mathbf{k}|\mathbf{k}\rangle]$ and of the operator $\hat{A}$ with eigenvalue A , $[\hat{A}|A\rangle = A|A\rangle]$ respectively, we obtain particular representations of $|\psi\rangle$ by

$$\langle\mathbf{r}|\psi\rangle = \psi(\mathbf{r}), \quad (\text{B.21})$$

$$\langle\mathbf{k}|\psi\rangle = c_{\mathbf{k}}, \quad (\text{B.22})$$

$$\langle A|\psi\rangle = c_A. \quad (\text{B.23})$$

Taking into account that $\psi_A(\mathbf{r}) = \langle\mathbf{r}|A\rangle$, (B.21), and (B.23), we can write (B.15) as follows

³ The proof of (B.19) is obtained by imposing periodic boundary conditions on the surface of a cube of volume V as $V \rightarrow \infty$. The physical meaning of (B.19) is that the number of states is equal to the volume of phase space, i.e., equal to the volume, V , in real space times the volume $\int d^3p$ in momentum space divided by $h^3 = (2\pi\hbar)^3$, which is the elementary quantum of volume in phase space, according to Heisenberg's principle. Recalling that $\mathbf{p} = \hbar\mathbf{k}$, we end up with (B.19).

$$\langle \mathbf{r} | \psi \rangle = \sum_A \langle \mathbf{r} | A \rangle \langle A | \psi \rangle, \quad (\text{B.24})$$

or

$$|\psi\rangle = \sum_A |A\rangle \langle A | \psi \rangle. \quad (\text{B.25})$$

Hence, since $|\psi\rangle$ is an arbitrary state, we have

$$\sum_A |A\rangle \langle A| = 1. \quad (\text{B.26})$$

In particular

$$\int d^3r |\mathbf{r}\rangle \langle \mathbf{r}| = 1, \quad (\text{B.27})$$

and

$$\sum_{\mathbf{k}} |\mathbf{k}\rangle \langle \mathbf{k}| = 1. \quad (\text{B.28})$$

Taking into account that $\langle \psi_i | \psi_j \rangle^* = \langle \psi_j | \psi_i \rangle$ and (B.27), we can prove (B.20). Because of (B.20), orthonormality is denoted in the Dirac notation by

$$\langle \psi_i | \psi_j \rangle = \delta_{ij}, \quad (\text{B.29})$$

and in particular

$$\langle \mathbf{r} | \mathbf{r}' \rangle = \delta(\mathbf{r} - \mathbf{r}'), \quad (\text{B.30})$$

$$\langle \mathbf{k} | \mathbf{k}' \rangle = \delta_{\mathbf{k}\mathbf{k}'}. \quad (\text{B.31})$$

Using a complete orthonormal set of kets $\{|n\rangle\}$, we can transform Schrödinger's equation (B.11) to a matrix equation:

$$|\psi\rangle = \sum_n c_n |n\rangle, \quad (\text{B.32})$$

$$\hat{H} |\psi\rangle = E |\psi\rangle \Rightarrow \sum_n c_n \hat{H} |n\rangle = E \sum_n c_n |n\rangle, \quad (\text{B.33})$$

$$\langle m | \hat{H} |\psi\rangle = \sum_n c_n \langle m | \hat{H} |n\rangle = E c_m, \quad (\text{B.34})$$

$$\sum_n H_{mn} c_n = E c_m, \quad (\text{B.35})$$

where $H_{mn} = \langle m | \hat{H} |n\rangle$.

B.3 Spherically Symmetric Potentials

This is the case where the potential energy $\mathcal{V}$ depends only on the distance, r , from a center and not on the angles, θ and ϕ , which determine the orientation of the position vector $\mathbf{r}$. The importance of spherically symmetric potentials stems from the fact that this type of potential is experienced by electron(s) in the hydrogen atom and in other atoms (on the average). Since $\mathcal{V}$ depends on r only, it is convenient to use spherical coordinates and express the solution to (B.11) as a product

$$\psi_{n\ell m}(\mathbf{r}) = R_{n\ell}(r) Y_{\ell m}(\theta, \phi). \quad (\text{B.36})$$

The functions $\psi_{n\ell m}$ for obvious reasons, are referred to as atomic orbitals. By substituting (B.36) in (B.11), we obtain after some manipulations (see Problem 2.3)

$$-\frac{\hbar^2}{2m} \frac{d^2 u_{n\ell}}{dr^2} + \frac{\hbar^2 \ell(\ell+1)}{2mr^2} u_{n\ell} + \mathcal{V} u_{n\ell} = E_{n\ell} u_{n\ell}, \quad (\text{B.37})$$

where

$$u_{n\ell}(r) \equiv r R_{n\ell}(r), \quad (\text{B.38})$$

and

$$\hat{\ell}^2 Y_{\ell m}(\theta, \phi) = \hbar^2 \ell(\ell+1) Y_{\ell m}(\theta, \phi), \quad (\text{B.39})$$

$$\hat{\ell}_z Y_{\ell m}(\theta, \phi) = \hbar m Y_{\ell m}(\theta, \phi), \quad (\text{B.40})$$

where

$$\hat{\ell}^2 = - \left[\frac{\hbar^2}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} + \frac{\hbar^2}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) \right], \quad (\text{B.41})$$

$$\hat{\ell}_z = -i\hbar \frac{\partial}{\partial \phi}. \quad (\text{B.42})$$

In (B.41) $\hat{\ell}^2$ is the square of the angular momentum operator, $\hat{\ell} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}$; $\hbar^2 \ell(\ell+1)$ with $\ell = 0, 1, 2, 3, \dots$ are the eigenvalues of $\hat{\ell}^2$; $\hat{\ell}_z$ is the operator of the z-component of the angular momentum, and $\hbar m$ with $m = -\ell, -\ell+1, \dots, \ell-1, \ell$ are the eigenvalues of $\hat{\ell}_z$. The eigenvalues, $E_{n\ell}$, of the Hamiltonian depend on ℓ and on the so-called principal quantum number n . For *hydrogenic potential*, $\mathcal{V}(r) = -Ze^2/4\pi\epsilon_0 r$, $E_{n\ell}$ depends only on n as follows

$$E_n = -\frac{Z^2 e^2}{4\pi\epsilon_0 a_B} \frac{1}{2n^2}, \quad n = l+1, l+2, \dots \quad (\text{B.43})$$

Notice that the radial equation (B.37) expressed in terms of $u_{n\ell}(r) = r R_{n\ell}(r)$ looks like a one-dimensional Schrödinger equation where the effective potential energy includes besides $\mathcal{V}(\mathbf{r})$ the centrifugal term $\langle \hat{\ell}^2 \rangle / 2I =$

$\hbar^2 \ell(\ell+1)/2mr^2$ (the “moment of inertia” $I \equiv mr^2$). The functions $Y_{\ell m}(\theta, \phi)$ called spherical harmonics, are given by the following formula

$$Y_{\ell m}(\theta, \phi) = i^\ell (-1)^{(|m|+m)/2} \left[\frac{(2\ell+1)}{4\pi} \frac{(\ell-|m|)!}{(\ell+|m|)!} \right]^{1/2} P_\ell^{|m|}(\cos\theta) e^{im\phi}, \quad (\text{B.44})$$

where $P_\ell^m(\cos\theta)$ are the so-called associated Legendre polynomials. Usually, the factor i^ℓ is not included in the definition of $Y_{\ell m}(\theta, \phi)$ (see [Q25], pp.90, 91).

It is worthwhile to point out that the equations (B.39)–(B.42), which determine $Y_{\ell m}$, do not involve the potential energy, $\mathcal{V}(r)$; as a result, $Y_{\ell m}$ do not depend on the form or the values of $\mathcal{V}(r)$. This observation allows us to determine $Y_{\ell m}$ without any reference to the rather complicated formula (B.44) by choosing conveniently the form of $\mathcal{V}(r)$. Indeed, if we choose $\mathcal{V}(r) = E$, (B.11) reduces to Laplace equation

$$\nabla^2 \psi = 0. \quad (\text{B.45})$$

Then we find polynomial solutions⁴ to (B.45) from which we extract their angular dependence. The latter would coincide (apart from a constant factor) with $Y_{\ell m}$ as shown in Table B.1. A polynomial of zero degree, i.e., a constant, satisfies (B.45). This corresponds to $\ell = m = 0$ and $Y_{00} = (4\pi)^{-1/2}$. There are three independent polynomials of first degree, $\psi_1 \sim x$, $\psi_2 \sim y$, $\psi_3 \sim z$, which satisfy (B.45) and have angular dependence $p_x = x/r = \sin\theta \cos\phi$, $p_y = y/r = \sin\theta \sin\phi$, and $p_z = z/r = \cos\theta$. These solutions correspond to $\ell = 1$ with $p_x - ip_y$ corresponding to $Y_{1,-1}$, p_z to $Y_{1,0}$, and $p_x + ip_y$ to $-Y_{1,1}$. Similarly, there are five independent polynomials of second degree that satisfy (B.45) and the angular dependence of which corresponds to the five $Y_{\ell m}$ for $\ell = 2$ and $m = -2, -1, 0, 1, 2$, as shown in Table B.1 (see p. 704.). In general, there are $2\ell + 1$ independent polynomial solutions of (B.45) consisting of a sum of terms all of which are of ℓ degree. Such polynomial can be written as $r^\ell Y_{\ell m}(\theta, \phi)$. Notice that the $\ell = 0$ solutions are referred to as *s* solutions, the $\ell = 1$ as *p* solutions, the $\ell = 2$ as *d* solutions, the $\ell = 3$ as *f* solutions, and so on. The next step is to prove (B.39) and (B.37). Taking into account that $-\hbar^2 \nabla^2 = \hat{\mathbf{p}}^2 = \hat{\mathbf{p}}_r^2 + (\hat{\ell}^2/r^2)$, where

$$\hat{\mathbf{p}}_r^2 = -\frac{\hbar^2}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right), \quad (\text{B.46})$$

and that the polynomial solutions of (B.45) are of the form $\psi = r^\ell Y_{\ell m}$, we can rewrite $\nabla^2 \psi = 0$ as follows (by multiplying by $-\hbar^2$)

$$\left(\hat{\mathbf{p}}_r^2 + \frac{\hat{\ell}^2}{r^2} \right) r^\ell Y_{\ell m} = 0, \quad (\text{B.47})$$

⁴ Each term in these polynomial solutions is of the same degree.

Table B.1. Tabulation of the polynomial solutions of Laplace equation and determination of the spherical harmonics

Degree of polynomial	Solution, $\psi(r)$	Angular dependence	Value and symbol of ℓ	Relation with $Y_{\ell m}$
0	$\psi = \text{const.}$	$Y = \text{const.}$	0 s	$Y_{00} \sim \text{const}$
1	$\psi \sim x$ $\psi \sim y$ $\psi \sim z$	$Y \sim x/r = \sin \theta \cos \phi \equiv p_x$ $Y \sim y/r = \sin \theta \sin \phi \equiv p_y$ $Y \sim z/r = \cos \theta \equiv p_z$	1 p	$Y_{1,-1} \sim p_x - ip_y = \sin \theta e^{-i\phi}$ $Y_{1,0} \sim p_z = \cos \theta$ $Y_{1,1} \sim p_x + ip_y = \sin \theta e^{i\phi}$
2	$\psi \sim xy$ $\psi \sim yz$ $\psi \sim zx$ $\psi \sim x^2 - y^2$ $\psi \sim 2z^2 - x^2 - y^2$	$Y \sim xy/r^2 = \sin^2 \theta \cos \phi \sin \phi \equiv d_{xy}$ $Y \sim yz/r^2 = \sin \theta \cos \theta \sin \phi \equiv d_{yz}$ $Y \sim zx/r^2 = \cos \theta \sin \theta \cos \phi \equiv d_{zx}$ $Y \sim (x^2 - y^2)/r^2 = \sin^2 \theta (\cos^2 \phi - \sin^2 \phi) \equiv d_{x^2-y^2}$ $Y \sim (3z^2 - r^2)/r^2 = 3 \cos^2 \theta - 1 \equiv d_{3z^2-r^2}$	2 d	$Y_{2,\pm 2} \sim d_{x^2-y^2} \pm 2id_{xy}$ $Y_{2,\pm 1} \sim d_{zx} \pm id_{yz}$ $Y_{2,0} \sim d_{3z^2-r^2}$
3	$\psi \sim xyz$ $\psi \sim z(x^2 - y^2)$ $\psi \sim x(y^2 - z^2)$ $\psi \sim y(z^2 - x^2)$ $\psi \sim y[x^2 - (y^2/3)]$ $\psi \sim z[y^2 - (z^2/3)]$ $\psi \sim x[z^2 - (x^2/3)]$	$Y \sim xyz/r^3 = \sin^2 \theta \cos \theta \cos \phi \sin \phi \equiv f_{xyz}$ $Y \sim z(x^2 - y^2)/r^3 = f_{z(x^2-y^2)}$ $Y \sim x(y^2 - z^2)/r^3 = f_{x(y^2-z^2)}$ $Y \sim y(z^2 - x^2)/r^3 = f_{y(z^2-x^2)}$ $Y \sim y[x^2 - (y^2/3)]/r^3$ $Y \sim z[y^2 - (z^2/3)]/r^3$ $Y \sim x[z^2 - (x^2/3)]/r^3$	3 f	Landau and Lifshitz Quantum Mechanics, 3rd ed., Pergamon Press App. c., p. 655

The symbol $\sim$ is used instead of $=$, because the normalization factor has been omitted.

or (using (B.46))

$$-\hbar^2 \ell(\ell+1) \frac{r^\ell}{r^2} Y_{\ell m} + \frac{r^\ell}{r^2} \hat{\ell}^2 Y_{\ell m} = 0, \quad (\text{B.48})$$

which is equivalent to (B.39). To prove (B.37), we write Schrödinger's equation, $\hat{H}\psi = E\psi$, as follows

$$\left[\frac{\hat{\mathbf{p}}_r^2}{2m} + \frac{\hat{\ell}^2}{2mr^2} + \mathcal{V}(r) \right] \psi_{n\ell m} = E_{n\ell} \psi_{n\ell m}. \quad (\text{B.49})$$

Looking for a solution of the form, $(u_{n\ell}/r) Y_{\ell m}$, and taking into account (B.46) and (B.39), we end up with (B.37).⁵

Let us return now to the eigenvalues of the Hamiltonian, $E_{\ell m}$, which for non-hydrogenic potentials depend on both n and ℓ . The following inequality in non-hydrogenic atoms or ions is valid

$$E_{n\ell'} > E_{n\ell}, \quad \text{for } \ell' > \ell. \quad (\text{B.50})$$

This is so because electrons of higher angular momentum (but for the same principal quantum number, n) are on average further away from nucleus;

⁵ For hydrogenic potentials, $\mathcal{V}(r) = -Ze^2/4\pi\epsilon_0 r$, we choose units such as $Ze^2/4\pi\epsilon_0 = 1$, $m = 1$, $\hbar = 1$ and we try a solution of (B.37) of the form $\pi_n(r) \exp(-ar)$, where $\pi_n(r)$ is a polynomial of n degree

$$\pi_n(r) = b_\nu r^\nu + b_{\nu+1}^{\nu+1} + \dots + b_n r^n, \quad \nu \leq n,$$

Substituting this trial solution in (B.37) and taking the limits $r \rightarrow 0$ and $r \rightarrow \infty$, we find respectively

$$\begin{aligned} -\nu(\nu-1)b_\nu r^{\nu-2} + \ell(\ell+1)b_\nu r^{\nu-2} + \mathcal{O}(r^{\nu-1}) &= 0, \\ nab_n r^{n-1} - \frac{1}{2}a^2 b_n r^n - \frac{1}{2}a^2 b_{n-1} r^{n-1} - b_n r^{n-1} &= E_n b_n r^n \\ &+ E_n b_{n-1} r^{n-1} + \mathcal{O}(r^{n-2}). \end{aligned}$$

From the first equation we obtain

$$\nu = \ell + 1 \Rightarrow n \geq \ell + 1, \quad \ell = 0, 1, 2, \dots$$

while the second gives

$$E_n = -\frac{1}{2}a^2,$$

and

$$na = 1.$$

Thus

$$E_n = -\frac{1}{2n^2}, \quad n = 1, 2, 3,$$

which reduces to (B.43) after reinstating the ordinary units.

Table B.2. Electronic levels in non-hydrogenic atoms. The ordering of these levels and Pauli's principle determines the structure of the periodic table of the elements (PTE)

ENERGY ↑	Number of electrons in the fully occupied shell				Total number of electrons up to this shell	
	<i>7s</i>	<i>7p</i>	<i>6d</i>	<i>5f</i>		
					32	32+86=118 7 th shell 7 th line
	<i>6s</i>	<i>6p</i>	<i>5d</i>	<i>4f</i>	32	32+54=86 6 th shell 6 th line
	<i>5s</i>	<i>5p</i>	<i>4d</i>		18	18+36=54 5 th shell 5 th line
	<i>4s</i>	<i>4p</i>	<i>3d</i>		18	18+18=36 4 th shell 4 th line
	<i>3s</i>	<i>3p</i>			8	8+10=18 3 rd shell 3 rd line
	<i>2s</i>	<i>2p</i>			8	8+2=10 2 nd shell 2 nd line
	<i>1s</i>				2	2 1 st shell 1 st line in P.T.E
	<i>s</i> ⇔ <i>l</i> = 0	<i>p</i> ⇔ <i>l</i> = 1	<i>d</i> ⇔ <i>l</i> = 2	<i>f</i> ⇔ <i>l</i> = 3		
	2	6	10	14	Maximum number of electrons for each value of <i>l</i>	

hence, the nuclear charge is screened more effectively by other electrons and the average potential is shallower, pushing the energy eigenvalues higher. More specifically, we have the following relations

$$E_{ns} < E_{np} < E_{nd} < E_{nf}, \tag{B.51}$$

$$E_{n+2,s} \simeq E_{n+1,d} \simeq E_{nf} < E_{n+2,p}. \tag{B.52}$$

It must be stressed that the ordering of the energy levels is very important because – by employing Pauli's exclusion principle – it determines which atomic orbitals in the ground state of the atom are occupied and which are empty; this in turn determines the chemical behavior of the atoms and what kind of solids they form. In Table B.2 the ordering of the energy levels is shown; this ordering leads to the electron configuration of each atom and the structure of the periodic table of the elements. Notice that the energy ordering of the $(n+2, s)$, $(n+1, d)$ and (n, f) levels changes in a non-monotonic way as

the occupation of the d and f increases (see transition elements, lanthanides, and actinides in the periodic table of elements). In Table B.3 the theoretical values (according to the Hartree–Fock approximation) for the levels $E_{n's}$, $E_{n'p}$, and $E_{n'-1,d}$ are shown; n' is the highest partially or fully occupied subshell (be it s , and/or p) of each atom in its ground state. These quantities are very important in determining the chemical properties of the elements. Notice that the ordering of these energy levels is very important in determining the chemical properties of the elements and the electronic and structural behavior of the solids.

We conclude this section with an important observation regarding the size of the orbitals $(n+2, s)$, $(n+1, d)$, and (n, f) ; these are orbitals of comparable energy. Since this size is determined mainly by the principal quantum number n , it follows that $(n+1, d)$ is mostly in the interior of $(n+2, s)$ and (n, f) is mostly in the interior of $(n+1, d)$ (see Fig. B.1). Thus, f orbitals among neighboring atoms in molecules and solids have very small overlap and consequently play a minor role in the chemical bonding and other properties. (That is why all the lanthanides and actinides are usually represented collectively in the periodic table of the elements.) For the transition elements the partially occupied $(n+1, d)$ orbitals are not as important as the $(n+2, s)$ orbitals but by no means insignificant.

B.4 Perturbation Results

In most cases, the Hamiltonian $\hat{H}$ can be separated in two parts: $\hat{H} = \hat{H}_0 + \hat{H}_1$. The eigenfunctions and eigenenergies of $\hat{H}_0$ are assumed known: $\hat{H}_0 |\chi_n\rangle = E_{0n} |\chi_n\rangle$; we wish to find how $|\chi_n\rangle$ and E_{0n} are modified because of the presence of $\hat{H}_1$. If the latter is a small perturbation to $\hat{H}_0$, the problem can be solved by essentially expanding these modifications in powers of $\hat{H}_1$. We shall present first some results and then we shall offer a kind of justification for them.

If $\hat{H}_0$ and $\hat{H}_1$ are time independent and the spectrum of $\hat{H}_0$ is discrete and not degenerate,⁶ we have for the eigenfunction $|\psi_n\rangle$ and the eigenvalue E_n of $\hat{H}$ the following result:

$$|\psi_n\rangle = |\chi_n\rangle + \sum_{m \neq n} \frac{\langle \chi_m | \hat{H}_1 | \chi_n \rangle}{E_{0n} - E_{0m}} |\chi_m\rangle + \cdots, \quad (\text{B.53})$$

$$E_n = E_{0n} + \langle \chi_n | \hat{H}_1 | \chi_n \rangle + \sum_{m \neq n} \frac{|\langle \chi_m | \hat{H}_1 | \chi_n \rangle|^2}{E_{0n} - E_{0m}} + \cdots. \quad (\text{B.54})$$

⁶ A discrete eigenenergy, E_n , is called non-degenerate if there is only one eigenfunction associated with it. If two or more eigenfunctions correspond to the same eigenvalue, then this eigenvalue is called degenerate.

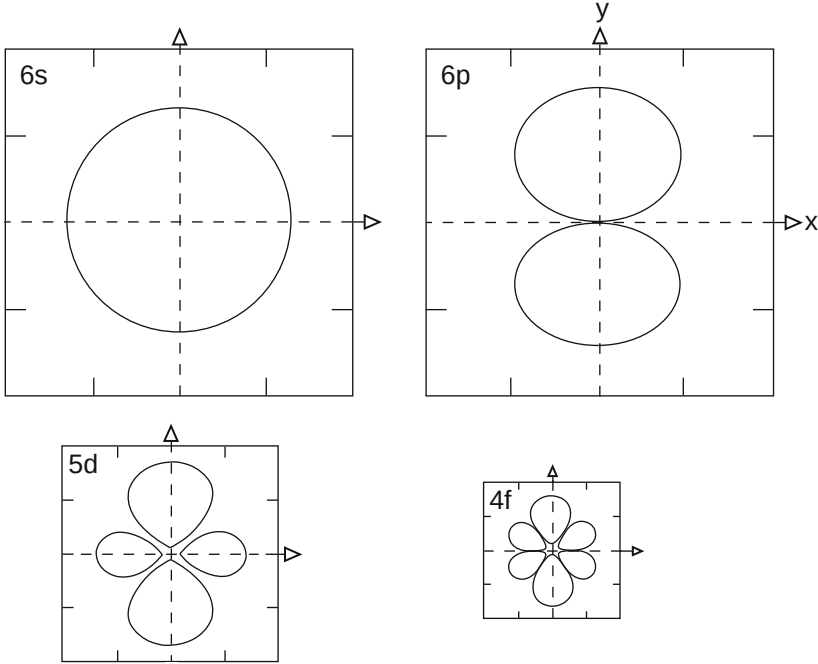


Fig. B.1. Relative size of the orbitals 6s, 6p, 5d, and 4f, which have comparable energy

If the unperturbed level, E_{0n} , is degenerate, (B.53) and (B.54) fail because some denominators $E_{0n} - E_{0m}$ vanish. The only way out is to make the corresponding numerators equal to zero; this can be achieved by diagonalizing the matrix $A_{mn} \equiv \langle \chi_m | \hat{H}_1 | \chi_n \rangle$, where m and n runs over all the unperturbed states belonging to the degenerate level E_{0n} . The diagonal matrix elements (after diagonalization) give the first order corrections to E_{0n} . For example, if the level E_{0n} is twofold degenerate, we have to diagonalize a 2×2 matrix, which is achieved by setting to zero the corresponding determinant

$$\det \begin{vmatrix} A_{11} - \delta E_n & A_{12} \\ A_{21} & A_{22} - \delta E_n \end{vmatrix} = 0, \quad (\text{B.55})$$

which implies that the first-order corrections to E_{0n} are

$$\delta E_n = A \pm \sqrt{\delta A^2 + A_{12}A_{21}}, \quad (\text{B.56})$$

where $A = (A_{11} + A_{22})/2$, $\delta A = (A_{11} - A_{22})/2$, and $A_{ij} \equiv \langle \chi_{ni} | \hat{H}_1 | \chi_{nj} \rangle$ ($i, j = 1, 2$). We see that the perturbation $\hat{H}_1$ removes the degeneracy by pushing the energy $E_{0n} + A$ of one state down and the other up by the amount $(\delta A^2 + A_{12}A_{21})^{1/2}$. This is called level repulsion.

Now we turn to the case where both $\hat{H}_0$ and $\hat{H}$ possess continuous spectrum. Let E be an eigenenergy belonging to the continuous spectrum of both $\hat{H}_0$ and $\hat{H}$. We would like to see how the corresponding eigenstates $|\psi\rangle$ and $|\chi\rangle$ of $\hat{H}$ and $\hat{H}_0$ respectively are connected. The equation $\hat{H}|\psi\rangle = E|\psi\rangle$ can be written as follows

$$(E - \hat{H})|\psi\rangle = (E - \hat{H}_0 - \hat{H}_1)|\psi\rangle = 0,$$

or

$$(E - \hat{H}_0)|\psi\rangle = \hat{H}_1|\psi\rangle. \quad (\text{B.57})$$

Pretending that the rhs is known, (B.57) has the form of an inhomogeneous differential equation the general solution to which is the solution to the homogeneous (which is $|\chi\rangle$) plus a special solution to the inhomogeneous (which can be obtained by applying to (B.57) the inverse operator⁷ $(E - \hat{H}_0)^{-1}$; the latter is usually denoted by $\hat{G}_0(E)$). Thus we have:

$$|\psi\rangle = |\chi\rangle + \hat{G}_0(E) \hat{H}_1|\psi\rangle. \quad (\text{B.58})$$

By replacing $|\psi\rangle$ on the rhs by $|\chi\rangle$, we obtain the first-order correction, which has a similar form as (B.53); to see this enter $1 = \sum_m |\chi_m\rangle \langle \chi_m|$ between $\hat{G}_0$ and $\hat{H}_1$ and take into account that $\hat{G}_0(E)|\chi_m\rangle = (E - E_m)^{-1}|\chi_m\rangle$. Equation (B.58) allows a complete formal “solution” by repeatedly replacing $|\psi\rangle$ on the rhs by (B.58). We have then

$$\begin{aligned} |\psi\rangle &= |\chi\rangle + \hat{G}_0 \hat{H}_1 |\chi\rangle + \hat{G}_0 \hat{H}_1 \hat{G}_0 \hat{H}_1 |\chi\rangle + \cdots + (\hat{G}_0 \hat{H}_1)^n |\chi\rangle + \cdots \\ &= |\chi\rangle + \left[1 + \hat{G}_0 \hat{H}_1 + (\hat{G}_0 \hat{H}_1)^2 + \cdots \right] \hat{G}_0 \hat{H}_1 |\chi\rangle \\ &= |\chi\rangle + \left[1 - \hat{G}_0 \hat{H}_1 \right]^{-1} (E - \hat{H}_0)^{-1} \hat{H}_1 |\chi\rangle \\ &= |\chi\rangle + \left[(E - \hat{H}_0) (1 - \hat{G}_0 \hat{H}_1) \right]^{-1} \hat{H}_1 |\chi\rangle \\ &= |\chi\rangle + \hat{G}(E) \hat{H}_1 |\chi\rangle, \end{aligned} \quad (\text{B.59})$$

where, $\hat{G}(E)$, the so-called *resolvent* or *Green's function*, is defined as

$$\hat{G}(E) \equiv \lim_{s \rightarrow 0^+} \frac{1}{E + is - \hat{H}}. \quad (\text{B.60})$$

Notice that the poles of $\hat{G}(E)$ or the poles of $[1 - \hat{G}_0 \hat{H}_1]^{-1}$ give the discrete eigenenergies of $\hat{H}$, since, $|\psi\rangle$ can be nonzero in the absence of $|\chi\rangle$ ($|\chi\rangle = 0$).

⁷ Because this operator is singular we add to E a small positive imaginary part and then we take the limit as this small part tends to zero.

Related with $\hat{G}(E)$ is the so-called t-matrix operator, $\hat{T}(E)$, which is defined as follows

$$\hat{T}(E) = \hat{H}_1 + H_1 \hat{G}(E) \hat{H}_1, \quad (\text{B.61})$$

and which gives the exact result of the differential elastic scattering cross-section⁸ $d\sigma/d\Omega$ of a plane wave $|\mathbf{k}\rangle$ by a time-independent perturbation $\hat{H}_1$:

$$\frac{d\sigma}{d\Omega}(\theta, \varphi) = \frac{V^2 m^2}{4\pi^2 \hbar^4} \left| \langle \mathbf{k}_f | \hat{T}(E) | \mathbf{k} \rangle \right|^2 \simeq \frac{m^2}{4\pi^2 \hbar^4} \left| \tilde{\mathcal{V}}(\mathbf{k}_f - \mathbf{k}) \right|^2, \quad (\text{B.62})$$

where $E = \hbar^2 \mathbf{k}^2 / 2m = \hbar^2 \mathbf{k}_f^2 / 2m$, $\mathbf{k}_f$ is in the direction θ, ϕ ,

$$\tilde{\mathcal{V}}(\mathbf{q}) \equiv \int d^3r \mathcal{V}(\mathbf{r}) e^{-i\mathbf{q} \cdot \mathbf{r}}, \quad (\text{B.63})$$

and

$$\langle \mathbf{r}' | \hat{H}_1 | \mathbf{r} \rangle = \delta(\mathbf{r} - \mathbf{r}') \mathcal{V}(\mathbf{r}). \quad (\text{B.64})$$

The last term in the rhs of (B.62) is the lowest order approximation to the differential cross-section usually referred to as the *Born approximation*.

We conclude by stating the formula for the probability per unit time, $dw_{i \rightarrow f}$, for a transition from an initial state $|i\rangle$ to a bunch of $d\nu_f$ final states $|f\rangle$, all of energy E_f in the continuum under the influence of a time-dependent perturbation

$$\hat{H}_1(t) = \mathcal{V}(\mathbf{r}, \mathbf{p}) e^{i\omega t} + \mathcal{V}^*(\mathbf{r}, \mathbf{p}) e^{-i\omega t}, \quad (\text{B.65})$$

$$dw_{i \rightarrow f} \simeq \frac{2\pi}{\hbar} \left| \langle f | \mathcal{V}^\dagger(\mathbf{r}, \mathbf{p}) | i \rangle \right|^2 \delta(E_f - E_i - \hbar\omega) d\nu_f, \quad (\text{B.66})$$

$$dw_{i \rightarrow f} \simeq \frac{2\pi}{\hbar} \left| \langle f | \mathcal{V}(\mathbf{r}, \mathbf{p}) | i \rangle \right|^2 \delta(E_f - E_i + \hbar\omega) d\nu_f. \quad (\text{B.67})$$

Equations (B.66) (absorption of $\hbar\omega$) and (B.67) (emission of $\hbar\omega$) are the lowest order results for $dw_{i \rightarrow f}$ and they are known as *Fermi's golden rule*. Note also that $\langle f | \mathcal{V} | i \rangle^* = \langle i | \mathcal{V}^\dagger | f \rangle$.

B.5 Interaction of Matter with an External Electromagnetic Field

We consider an external electromagnetic (EM) field described by a vector potential $\mathbf{A}$ and a scalar potential ϕ . In the presence of such field, the unperturbed Hamiltonian is modified as follows. (a) Terms are added to the Hamiltonian of the form

⁸ The differential scattering cross-section, $d\sigma/d\Omega$, is defined as the number of particles per unit time scattered by the action of a potential $\mathcal{V}(\mathbf{r})$ into an elementary solid angle $d\Omega$ around the direction θ, ϕ divided by $d\Omega$ and by the flux of the incoming particles each of fixed velocity.

$$\sum_i q_i \phi(r_i) - \sum_j \mathbf{m}_j \cdot \mathbf{B}(\mathbf{r}_j), \quad (\text{B.68})$$

where q_i are the charges of the ions and the electrons and $\mathbf{m}_j$ are the intrinsic magnetic moments of electrons and nuclei ($\mathbf{m}_j = -g_e \mu_B \mathbf{s}$ for electrons and $\mathbf{m}_j = g_N \mu_N \mathbf{J}$ for nuclei). (b) Each momentum, $\mathbf{p}_i$, is replaced by $\mathbf{p}_i - (q_i/c) \mathbf{A}(\mathbf{r}_i)$ (in G-CGS) or $\mathbf{p}_i - q_i \mathbf{A}(\mathbf{r}_i)$ (in SI). Thus, the kinetic energy of a particle of charge q_i and mass m_i is replaced by (in G-CGS)

$$\frac{1}{2m_i} \mathbf{p}_i^2 \rightarrow \frac{1}{2m_i} \left(\mathbf{p}_i - \frac{q_i}{c} \mathbf{A}_i \right)^2 = \frac{1}{2m_i} \mathbf{p}_i^2 + \frac{q_i^2 A_i^2}{2m_i c^2} - \frac{q_i}{m_i c} (\mathbf{p}_i \cdot \mathbf{A}_i + \mathbf{A}_i \cdot \mathbf{p}_i). \quad (\text{B.69})$$

For the Coulomb gauge, $\nabla \cdot \mathbf{A} = 0$, $\mathbf{p}_i, \mathbf{A}_i$ commute and consequently the last term in (B.69) is reduced to $-(q_i/m_i c) \mathbf{A}_i \cdot \mathbf{p}_i$.

The current density $\mathbf{j}_i$ of a particle of charge q_i and mass m_i in the presence of the vector potential $\mathbf{A}$ acquires an extra term proportional to $\mathbf{A}$ to read:

$$\mathbf{j}_i = \frac{iq_i \hbar}{2m_i} [(\nabla \Psi^*) \Psi - \Psi^* (\nabla \Psi)] + c \nabla \times \mathbf{M}_{si} - \frac{q_i^2}{m_i c} \mathbf{A} \Psi^* \Psi, \text{ G-CGS, } (\text{B.70})$$

where $\mathbf{M}_{si} = -g_s \mu_B \Psi^* \mathbf{s}_i \Psi$ is the spin magnetization (see (A.10); in SI set $c = 1$). The first term in the rhs of (B.70) is called the paramagnetic contribution to the current density and the last one is called the diamagnetic contribution (see LL, QM[Q25], § 115).

Further Reading

- R. Eisberg, R. Resnick, *Quantum Physics of Atoms, Molecules, Solids, Nuclei and Particles*, J. Wiley, New York, 1974 [Q23].
- J.J. Sakurai, *Modern Quantum Mechanics*, Addison-Wesley, Reading, MA, 1994 [Q24].
- L.D. Landau, E.M. Lifshitz, *Quantum Mechanics*, Pergamon Press, 3rd ed., Oxford, 1977 [Q25].

Elements of Thermodynamics and Statistical Mechanics

C.1 Thermodynamic Relations

The thermodynamic quantities of interest are – among others – the various thermodynamic potentials, such as

- The *Internal Energy of simply Energy* U or E . (C.1)

- The *Helmholtz Free Energy* $F \equiv U - TS$. (C.2)

- The *Gibbs Free Energy* $G \equiv F + PV$. (C.3)

- The *Enthalpy* $H \equiv U + PV$. (C.4)

- The *Grand Thermodynamic Potential* $\Omega = F - \mu N = -PV$. (C.5)

In these expressions T is the absolute temperature, S is the entropy, and μ is the so-called *chemical potential*, a quantity of special interest. The expression of the Gibbs free energy is based on the assumption that the work done by the system on the environment is given exclusively by PdV ; if there are other contributions to the work, e.g., the electrostatic contribution, $\int \mathbf{P} \cdot \delta \mathbf{E}_0 dV$, then corresponding terms such as $-\int \mathbf{P} \cdot \delta \mathbf{E}_0 dV$ should be included to the definition of the differential dF (see (C.17) below). The expression of Ω is based on the assumption that the system consists of one type of particles; if there are several types of particles, the term μN is replaced by $\sum_{\alpha} \mu_{\alpha} N_{\alpha}$.

Various derivatives of the thermodynamic potentials are also of interest. Among them are the specific heats

$$C_V \equiv T \left(\frac{\partial S}{\partial T} \right)_{V,N} = \left(\frac{\partial U}{\partial T} \right)_{V,N}, \quad (C.6)$$

$$C_P \equiv T \left(\frac{\partial S}{\partial T} \right)_{P,N} = \left(\frac{\partial H}{\partial T} \right)_{P,N}, \quad (C.7)$$

the chemical potential

$$\mu \equiv \left(\frac{\partial U}{\partial N} \right)_{S,V} = \left(\frac{\partial F}{\partial N} \right)_{T,V} = \frac{G}{N}, \quad (\text{C.8})$$

the bulk¹ thermal expansion coefficient

$$\alpha_b \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{P,N}, \quad (\text{C.9})$$

and the bulk modulus

$$B_T \equiv -V \left(\frac{\partial P}{\partial V} \right)_{T,N}, \quad (\text{C.10})$$

$$B_S \equiv -V \left(\frac{\partial P}{\partial V} \right)_{S,N}. \quad (\text{C.11})$$

The *First Law of Thermodynamics* expresses the basic law of energy conservation distinguishing though between the quantity of heat,² $\bar{d}Q$, received by the system and the quantity of work, $\bar{d}W$, done by the system on the environment; if there is exchange of matter, there is an additional term, $\mu \bar{d}N$, (or $\sum_a \mu_a \bar{d}N_a$, if there are several kinds of particles in the system) in determining the change of the internal energy, U :

$$\bar{d}U = \bar{d}Q - \bar{d}W + \mu \bar{d}N. \quad (\text{C.12})$$

The quantity of work is usually given by $\bar{d}W = PdV$; other contributions due to electric and/or magnetic fields, surface tension, etc., could also be present in $\bar{d}W$ (see some relevant formulae in Appendix A).

The *Second Law of Thermodynamics*, one of the most general of Physics, connects the exchange of heat with the entropy change: For a system that does not exchange matter with the environment, there are two contributions to the change of entropy

$$\bar{d}S = \bar{d}S_e + \bar{d}S_i, \quad (\text{C.13})$$

where the first,

$$\bar{d}S_e \equiv \frac{\bar{d}Q}{T}, \quad (\text{C.14})$$

is due to the exchange of heat, and the second,

$$\bar{d}S_i \geq 0, \quad (\text{C.15})$$

¹ Quite often the linear thermal expansion coefficient is given defined by the relation $a_L \equiv (\partial L / \partial T)_{P,N} / L$ and connected to a_b by $a_b = 3a_L$.

² The symbol $\bar{d}$ (d bar) in front of $\bar{d}Q$ or $\bar{d}W$, etc, denotes an elementary quantity which is a differential form and not a perfect differential, i.e., $\bar{d}Q$ or $\bar{d}W$, etc is *not* the infinitesimal change of a function Q or a function W , etc. Such functions do not exist, since Q , or W , etc *cannot* be defined as functions of the state of the system.

is due to irreversible processes taking place within the system. *This second part is always positive* (in extreme limiting cases can be considered as zero). Equation (C.15) implies that

Under conditions of thermal isolation ($dQ = 0$) and no exchange of matter, the entropy of a system always increases (i.e., never decreases) until total thermodynamic equilibrium is established where the entropy reaches its maximum value.

Combining (C.12)–(C.15) (and choosing for simplicity $dW = PdV$), we have

$$dU \leq TdS - PdV + \mu dN, \quad (\text{C.16})$$

with the equality holding only if there are no irreversible processes taking place within the system.³ From (C.16) and the definitions (C.2), (C.3), and (C.5), we have corresponding inequalities for the other thermodynamic potentials. For example:

$$dF \leq -SdT - PdV + \mu dN, \quad (\text{C.17})$$

$$dG \leq -SdT + VdP + \mu dN, \quad (\text{C.18})$$

$$d\Omega \leq -SdT - PdV - Nd\mu. \quad (\text{C.19})$$

Under equilibrium conditions, for which the equality sign holds, several new relations can be produced. For example:

$$S = - \left(\frac{\partial F}{\partial T} \right)_{V,N} = - \left(\frac{\partial \Omega}{\partial T} \right)_{V,\mu}, \quad (\text{C.20})$$

$$P = - \left(\frac{\partial F}{\partial V} \right)_{T,N} = - \left(\frac{\partial \Omega}{\partial V} \right)_{T,\mu} = - \frac{\Omega}{V}, \quad (\text{C.21})$$

$$\left(\frac{\partial V}{\partial T} \right)_{P,N} = - \left(\frac{\partial S}{\partial P} \right)_{T,N}, \quad (\text{C.22})$$

etc. With more complicated manipulations and – usually – with the help of Jacobians (see below), we can prove the following useful relations

$$a_b \equiv \frac{1}{B_T} \left(\frac{\partial P}{\partial T} \right)_{V,N}, \quad (\text{C.23})$$

$$B_S = \frac{C_P}{C_V} B_T, \quad (\text{C.24})$$

$$C_P - C_V = TVB_T a_b^2. \quad (\text{C.25})$$

If we have two functions $u(x, y)$ and $v(x, y)$ of the independent variables x, y , the Jacobian is defined as follows:

³ It is worthwhile to point out that ideal changes involving only equilibrium states produces no irreversible processes and consequently are associated with the equality sign in relations (C.16)–(C.19).

$$\frac{\partial(u, v)}{\partial(x, y)} \equiv \det \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\ \frac{\partial v}{\partial x} & \frac{\partial v}{\partial y} \end{vmatrix} \equiv \frac{\partial u}{\partial x} \frac{\partial v}{\partial y} - \frac{\partial u}{\partial y} \frac{\partial v}{\partial x}, \quad (\text{C.26})$$

The Jacobian has the following important properties:

$$\begin{aligned} \frac{\partial(u, x)}{\partial(y, x)} &= -\frac{\partial(u, x)}{\partial(x, y)} = \left(\frac{\partial u}{\partial y} \right)_x, \\ \frac{\partial(u, v)}{\partial(x, y)} &= \frac{\partial(u, v)}{\partial(r, t)} \frac{\partial(r, t)}{\partial(x, y)}. \end{aligned}$$

For example, the proof of (C.23) goes as follows:

$$\begin{aligned} a_b &\equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{1}{V} \frac{\partial(V, P)}{\partial(T, P)} = \frac{1}{V} \frac{\partial(V, P)}{\partial(V, T)} \frac{\partial(V, T)}{\partial(T, P)} = \frac{1}{V} \left(\frac{\partial P}{\partial T} \right)_V \\ &\times (-1) \left(\frac{\partial V}{\partial P} \right)_T = \frac{1}{B_T} \left(\frac{\partial P}{\partial T} \right)_V. \end{aligned}$$

C.2 Basic Relations of Statistical Mechanics

In this subsection we consider only *statistically independent* (see footnote 4) systems in *thermodynamic equilibrium*. Let Ψ_I be the eigenfunctions of the Hamiltonian of such a system with eigenenergies E_I and number of particles N_I . The quantity of central importance in Statistical Mechanics is the *probability*, P_I , to find such a system⁴ in the eigenstate Ψ_I . For an *open* such system exchanging both energy and particles with the environment, and, hence, having no fixed energy and number of particles, E_I , N_I , P_I depends only on these eigenvalues E_I , and N_I with the temperature T and the chemical potential μ as parameters

$$P_I = \frac{1}{Z_G} e^{-\beta(E_I - \mu N_I)}. \quad (\text{C.27})$$

β is the inverse of the product of Boltzmann's constant, k_B , times T .

$$\beta \equiv \frac{1}{k_B T}, \quad (\text{C.28})$$

and (as a result of $\sum_I P_I = 1$)

$$Z_G = \sum_I e^{-\beta(E_I - \mu N_I)}. \quad (\text{C.29})$$

⁴ Statistically independent means that P_I does not depend on the value of the probability Q_J for any neighboring system to be in its state Φ_J , so that the joint probability $\Pi_{IJ} = P_I \cdot Q_J$ and $\ln \Pi_{IJ} = \ln P_I + \ln Q_J$.

The basic equation (C.27) follows from the fact that the quantity $\ln P_I$ is additive (due to statistical independence) and conserved for a closed system (Liouville's theorem). As such, $\ln P_I$ is a linear combination of the independent, additive, and conserved quantities (for a closed system) such as the energy and the number of particles. (The latter are conserved in the absence of "chemical" reactions).

The connection with thermodynamics is obtained through the relation between the P_I s (as given by (C.27)) and the entropy:

$$S \equiv -k_B \sum_I P_I \ln P_I, \quad (\text{C.30})$$

from which it follows (using (C.2) and (C.5), $U \equiv \sum_I P_I E_I$, and $N \equiv \sum_I P_I N_I$) that

$$\Omega = -k_B T \ln Z_G. \quad (\text{C.31})$$

If there is no exchange of particles with the environment, N_I is fixed, $N_I = N$, and

$$P_I = \frac{1}{Z} e^{-\beta E_I}, \quad (\text{C.32})$$

where

$$Z = Z_G e^{-\beta \mu N} = \sum_I e^{-\beta E_I}, \quad (\text{C.33})$$

and

$$-k_B T \ln Z = -k_B T \ln Z_G + k_B T \beta \mu N = \Omega + \mu N \equiv F. \quad (\text{C.34})$$

Finally, if the system exchanges neither particles nor energy with the environment, both E_I and N_I are fixed, $E_I = U$ and $N_I = N$ and consequently

$$P_I = \frac{1}{\Delta \Gamma}, \quad (\text{C.35})$$

where

$$\Delta \Gamma = Z e^{\beta U}, \quad (\text{C.36})$$

and

$$k_B \ln \Delta \Gamma = k_B \ln Z + k_B \beta U = -\frac{F}{T} + \frac{U}{T} = \frac{TS}{T} = S. \quad (\text{C.37})$$

Equation (C.35) means that all eigenstates of equal energy and equal number of particles are of equal probability to occur (for a statistically independent system in thermodynamic equilibrium). Furthermore, (C.37) implies that their total number, $\Delta \Gamma$, is directly connected to the entropy through the famous relation $S = k_B \ln \Delta \Gamma$. This relation follows also by combining (C.30) and (C.35).

C.3 Non-Interacting Particles

When the system consists of noninteracting particles, the general formulae of Subsect. C.2 are drastically simplified, because they can be expressed in terms of the eigenenergies, ε_i , of a *single*-particle instead of the eigenenergies, E_I , of the *whole system*.

C.3.1 Non-Interacting Electrons

We consider the single particle eigenstate ψ_i (including the spin variable) with eigenenergy ε_i . According to (C.27), the probability of having zero electrons in this state is

$$P_0 = \frac{1}{Z_{Gi}}, \quad (\text{C.38})$$

since in this case $n_i = 0$ and consequently $n_i \varepsilon_i = 0$. The probability of having one electron in this state is, according to (C.27),

$$P_1 = \frac{1}{Z_{Gi}} e^{-\beta(\varepsilon_i - \mu)}. \quad (\text{C.39})$$

Because of Pauli's principle, the probability of having n particles in the state ψ_i , where $n \geq 2$, is zero. Hence, $P_0 + P_1 = 1$ and consequently

$$Z_{Gi} = 1 + e^{-\beta(\varepsilon_i - \mu)}. \quad (\text{C.40})$$

Combining (C.39) and (C.40), we find the average number of particles in the eigenstate ψ_i , $\bar{n}_i = 0 \cdot P_0 + 1 \cdot P_1 = P_1$, (the so-called *Fermi distribution* valid for any fermionic particle):

$$\bar{n}_i = \frac{1}{e^{\beta(\varepsilon_i - \mu)} + 1}. \quad (\text{C.41})$$

It follows that the total average number of particles N is

$$N = \sum_i \bar{n}_i = \sum_i \frac{1}{e^{\beta(\varepsilon_i - \mu)} + 1}, \quad (\text{C.42})$$

and the total average energy U is

$$U = \sum_i \bar{n}_i \varepsilon_i = \sum_i \frac{\varepsilon_i}{e^{\beta(\varepsilon_i - \mu)} + 1}. \quad (\text{C.43})$$

Combining (C.40), (C.31), and (C.5), we have

$$-k_B T \sum_i \ln \left(1 + e^{-\beta(\varepsilon_i - \mu)} \right) = \Omega = -PV. \quad (\text{C.44})$$

The summations in (C.42), (C.43), and (C.44), which are over all *single* particle eigenstates, can be transformed into integrals by introducing the single-particle density of states (DOS) *per spin*, $\rho(\varepsilon)$ and the number, $R(\varepsilon)$,

of eigenstates *per spin* with eigenenergy less than ε . (Obviously, $dR(\varepsilon) \equiv R(\varepsilon + d\varepsilon) - R(\varepsilon) = \rho(\varepsilon) d\varepsilon$).

$$N = 2 \int_{\varepsilon_{\min}}^{\infty} \frac{d\varepsilon \rho(\varepsilon)}{e^{\beta(\varepsilon-\mu)} + 1}, \quad (\text{C.45})$$

$$U = 2 \int_{\varepsilon_{\min}}^{\infty} \frac{d\varepsilon \varepsilon \rho(\varepsilon)}{e^{\beta(\varepsilon-\mu)} + 1}, \quad (\text{C.46})$$

and

$$\begin{aligned} -\Omega = PV &= 2k_B T \int_{\varepsilon_{\min}}^{\infty} d\varepsilon \rho(\varepsilon) \ln \left[1 + e^{-\beta(\varepsilon-\mu)} \right] \\ &= 2 \int_{\varepsilon_{\min}}^{\infty} \frac{d\varepsilon R(\varepsilon)}{e^{\beta(\varepsilon-\mu)} + 1}. \end{aligned} \quad (\text{C.47})$$

The relation (C.42) or (C.45) is very important because it allows the determination of the chemical potential μ in terms of the (average) number of particles, N , the parameters (such as the volume) in $\rho(\varepsilon)$, and the temperature T . In particular for $T = 0$ (i.e., $\beta = \infty$)

$$\begin{aligned} \bar{n}_i &= 1 \quad \text{for } \varepsilon_i < \mu(0), \\ &= 0 \quad \text{for } \varepsilon_i > \mu(0), \end{aligned} \quad (\text{C.48})$$

which, in view of Fig. 1.2, implies that

$$E_F = \lim_{T \rightarrow 0} \mu(T). \quad (\text{C.49})$$

We conclude this subsection by pointing out that integrals of the type

$$I \equiv 2 \int_{\varepsilon_{\min}}^{\infty} \frac{d\varepsilon g(\varepsilon)}{e^{\beta(\varepsilon-\mu)} + 1}, \quad (\text{C.50})$$

such as the ones in (C.45) till (C.47) can be approximated at low temperatures ($k_B T \ll E_F - \varepsilon_{\min}$) by the first two terms in a series expansion in powers of T^2 :

$$I = 2 \int_{\varepsilon_{\min}}^{\mu} d\varepsilon g(\varepsilon) + \frac{\pi^2}{3} g'(\mu) (k_B T)^2 + \dots \quad (\text{C.51})$$

Equation (C.51) is valid under the condition that $g(\varepsilon)$ is analytic with nonzero derivative at $\varepsilon = \mu$. For metals, where $(E_F - \varepsilon_{\min})/k_B$ is of the order 10^5 K, while the melting or the boiling temperature is no higher than 6×10^3 K, the first two terms of the rhs of (C.51) constitute usually a very good approximation for all temperatures at which the metals exist. Exceptions appear in

cases where the function $g(\varepsilon)$ (which practically means the DOS or $R(\varepsilon)$) exhibits strong variations within a range, $\delta\varepsilon$ around E_F comparable to $k_B T$. In contrast, for semiconductors (C.51) is not valid and one has to return to the full (C.50).

Application: For a metal using (C.51), calculate $\mu(T)$, $S(T)$, $U(T)$, and $C_V(T)$ assuming that $\varepsilon_{\min} = 0$.

Answer: From (C.51) and (C.45), we have

$$N = 2 \int_0^{\mu} d\varepsilon \rho(\varepsilon) + \frac{\pi^2}{3} \rho'(\mu) (k_B T)^2. \quad (\text{C.52})$$

Comparing (C.52) with its $T = 0$ limit we obtain

$$\mu(T) = E_F - \frac{\pi^2}{6} \frac{\rho'(E_F)}{\rho(E_F)} (k_B T)^2. \quad (\text{C.53})$$

Equations (C.51) and (C.47) give

$$\Omega = -2 \int_0^{\mu} d\varepsilon R(\varepsilon) - \frac{\pi^2}{3} R'(\mu) (k_B T)^2. \quad (\text{C.54})$$

Then (C.20) gives the entropy

$$\begin{aligned} S &= -(\partial\Omega/\partial T)_{V,\mu} = \frac{2\pi^2}{3} R'(\mu) k_B^2 T \\ &= \frac{2\pi^2}{3} R'(E_F) k_B^2 T = \frac{2\pi^2}{3} \rho(E_F) k_B^2 T. \end{aligned} \quad (\text{C.55})$$

In obtaining (C.55), we have used the fact that, in view of (C.53), $R'(\mu) = R'(E_F) + \mathcal{O}(T^2)$; we have omitted terms of the order of T^3 in S (which is consistent with omitting terms $\mathcal{O}(T^4)$ in (C.54)) and we have taken into account that $R'(\varepsilon) = \rho(\varepsilon)$. Now using (C.55) and (C.6), we obtain

$$C_V = \frac{2\pi^2}{3} \rho(E_F) k_B^2 T, \quad (\text{C.56})$$

and

$$U = U_0 + \frac{\pi^2}{3} \rho(E_F) (k_B T)^2. \quad (\text{C.57})$$

If the DOS $\rho(\varepsilon)$ is proportional to $\varepsilon^{1/2}$, we have that $\rho'(E_F)/\rho(E_F) = 1/2E_F$ and $\rho(E_F) = 3N/4E_F$; then, (C.53), (C.56), and (C.57) become

$$\mu(T) = E_F \left[1 - \frac{\pi^2}{12} \left(\frac{T}{T_F} \right)^2 \right], \quad (\text{C.58})$$

$$C_V = \frac{\pi^2}{2} N k_B \frac{T}{T_F}, \quad (\text{C.59})$$

$$U = \frac{3}{5} N E_F \left[1 + \frac{5\pi^2}{12} \frac{T^2}{T_F^2} \right], \quad (\text{C.60})$$

where

$$T_F = \frac{E_F}{k_B}. \quad (\text{C.61})$$

C.3.2 Phonons

For an independent one-dimensional harmonic oscillator of eigenenergies $\varepsilon_i (n + \frac{1}{2})$, where $\varepsilon_i = \hbar\omega_i$ and $n = 0, 1, 2, 3$ and in equilibrium with a heat bath of temperature $T = 1/k_B\beta$, we have according to (C.33):

$$Z_i = \sum_{n=0}^{\infty} e^{-\beta\varepsilon_i(n+\frac{1}{2})} = e^{-\beta\varepsilon_i/2} \sum_{n=0}^{\infty} (e^{-\beta\varepsilon_i})^n = \frac{e^{-\beta\varepsilon_i/2}}{1 - e^{-\beta\varepsilon_i}}. \quad (\text{C.62})$$

Hence, the corresponding free energy, F_i , is according to (C.34):

$$F_i = \frac{\varepsilon_i}{2} + k_B T \ln(1 - e^{-\beta\varepsilon_i}). \quad (\text{C.63})$$

Since the system of harmonically vibrating ions is equivalent to $3N_\alpha$ independent 1D harmonic oscillators, we have for the total free energy, F , of the ions

$$F = \sum_{i=1}^{3N_\alpha} F_i = \frac{1}{2} \sum_{i=1}^{3N_\alpha} \varepsilon_i + k_B T \sum_{i=1}^{3N_\alpha} \ln(1 - e^{-\beta\varepsilon_i}). \quad (\text{C.64})$$

The first term of the rhs of (C.64) is the zero point contribution to the ionic energy. The second term, which vanishes at $T = 0$ K, is the phonon contribution to the ionic free energy

$$F_{\text{ph}} \equiv k_B T \sum_{i=1}^{3N_\alpha} \ln(1 - e^{-\beta\varepsilon_i}) = k_B T \int_0^{\varepsilon_{\max}} d\varepsilon \phi(\varepsilon) \ln(1 - e^{-\beta\varepsilon}) = - \int_0^{\varepsilon_{\max}} \frac{d\varepsilon \Phi(\varepsilon)}{e^{\beta\varepsilon} - 1}. \quad (\text{C.65})$$

To obtain the last two equations in (C.65), we have introduced the phononic density of states, $\phi(\varepsilon)$, and the number, $\Phi(\varepsilon)$, of phonon states with ε_i less than ε . Obviously, $d\Phi \equiv \Phi(\varepsilon + d\varepsilon) - \Phi(\varepsilon) = \phi(\varepsilon) d\varepsilon$; $\Phi(\varepsilon) = \Phi(\hbar\omega) \equiv \tilde{\Phi}(\omega)$. The latter gives the number of eigenmodes with frequency ω_i less than ω . In the JM and for $\varepsilon \leq \varepsilon_D$ or $\omega \leq \omega_D$, $\Phi(\varepsilon) = 3N_a \varepsilon^3 / \varepsilon_D^3$ and $\tilde{\Phi}(\omega) = 3N_a \omega^3 / \omega_D^3$, for $\omega \leq \omega_D$, where $\omega_D = \tilde{c}q_D$, $q_D = (6\pi^2 n_\alpha)^{1/3}$, $\tilde{c}$ is a properly averaged sound velocity (see Chap. 4), $\varepsilon_D = \hbar\omega_D$, and ω_D is the upper cutoff in the vibrational spectrum $\hbar\omega_D = \varepsilon_{\max}$. For $\omega > \omega_D$ or $\varepsilon > \varepsilon_D$, $\Phi(\varepsilon) = \tilde{\Phi} = 3N_a$.

From (C.65) and (C.20), we obtain the phononic contribution to the entropy

$$S_{\text{ph}} = \frac{1}{T} \int_0^{\varepsilon_{\max}} \frac{d\varepsilon \phi(\varepsilon) \varepsilon}{e^{\beta\varepsilon} - 1} - k_B \int_0^{\varepsilon_{\max}} d\varepsilon \phi(\varepsilon) \ln(1 - e^{-\beta\varepsilon}). \quad (\text{C.66})$$

Then the phononic contribution to the energy is according to (C.2)

$$U_{\text{ph}} = F_{\text{ph}} + TS_{\text{ph}} = \int_0^{\varepsilon_{\text{max}}} \frac{d\varepsilon \varepsilon \phi(\varepsilon)}{e^{\beta\varepsilon} - 1}. \quad (\text{C.67})$$

The phononic contribution to the pressure is obtained by combining (C.65) and (C.21)

$$P_{\text{ph}} = - \left(\frac{\partial F_{\text{ph}}}{\partial V} \right)_{T, N_{\alpha}} = - \sum_{i=1}^{3N_{\alpha}} \frac{\partial \varepsilon_i}{\partial V} \frac{1}{e^{\beta\varepsilon_i} - 1} = \int_0^{\varepsilon_{\text{max}}} d\varepsilon \frac{\partial \Phi}{\partial V} \frac{1}{e^{\beta\varepsilon} - 1}. \quad (\text{C.68})$$

The phononic contribution to the specific heat C_V is calculated by differentiating U_{ph} with respect to the temperature

$$C_{V\text{ph}} = \left(\frac{\partial U_{\text{ph}}}{\partial T} \right)_{V, N_{\alpha}} = k_B \int_0^{\varepsilon_{\text{max}}} d\varepsilon \phi(\varepsilon) \frac{(\beta\varepsilon)^2 e^{\beta\varepsilon}}{(e^{\beta\varepsilon} - 1)^2}. \quad (\text{C.69})$$

The expression

$$U_{\text{ph}} = \int_0^{\varepsilon_{\text{max}}} \frac{d\varepsilon \varepsilon \phi(\varepsilon)}{e^{\beta\varepsilon} - 1} = \sum_{i=1}^{3N_{\alpha}} \frac{\varepsilon_i}{e^{\beta\varepsilon_i} - 1}, \quad (\text{C.70})$$

compared with the expression $U_{\text{ph}} = \sum_{i=1}^{3N_{\alpha}} \bar{n}_i \varepsilon_i$ allows us to determine the average number $\bar{n}_i$ of vibrational quanta each of energy $\varepsilon_i = \hbar\omega_i$:

$$\bar{n}_i = \frac{1}{e^{\beta\varepsilon_i} - 1}. \quad (\text{C.71})$$

Since each quantum of the eigenmode i is called *phonon*, (C.71) gives the average number of phonons in the phononic state i . Equation (C.71) is valid for any bosonic particle (or quasi-particle) with ε_i replaced by $\varepsilon_i - \mu$, where ε_i is the eigenenergy of the orbital-spin single particle eigenstate $|i\rangle$ and μ is the chemical potential. The chemical potential for phonons, as for any quantum of classical field, is zero.

Further Reading

- L. D. Landau & E. M. Lifshitz, *Statistical Physics*, Vol.I, 3rd ed., Pergamon Press, Oxford, 1980 [ST35].

D

Dielectric Function, $\varepsilon(\mathbf{k}, \omega)$: Formulas and Uses

In Appendix A we defined the dielectric function, $\varepsilon(\mathbf{k}, \omega)$, and we connected it with the electric conductivity, $\sigma(\mathbf{k}, \omega)$, the electric susceptibility, $\chi_e(\mathbf{k}, \omega)$, and the electric polarizability, $\alpha_e(\mathbf{k}, \omega)$ of atoms, or ions, or molecules:

$$\begin{aligned}\varepsilon(\mathbf{k}, \omega) &= \varepsilon_0 I + \frac{i\sigma(\mathbf{k}, \omega)}{\omega}, \quad \text{SI,} \\ &= I + \frac{4\pi i\sigma(\mathbf{k}, \omega)}{\omega}, \quad \text{G-CGS,}\end{aligned}\tag{D.1}$$

$$\begin{aligned}\varepsilon(\mathbf{k}, \omega) &= \varepsilon_0 I + \varepsilon_0 \chi_e(\mathbf{k}, \omega), \quad \text{SI,} \\ &= I + 4\pi \chi_e(\mathbf{k}, \omega), \quad \text{G-CGS,}\end{aligned}\tag{D.2}$$

where I is the unit tensor. We remind the readers that the susceptibility, χ_e , is defined through the relation

$$\begin{aligned}\mathbf{P} &= \varepsilon_0 \chi_e \mathbf{E}, \quad \text{SI,} \\ &= \chi_e \mathbf{E}, \quad \text{G-CGS,}\end{aligned}\tag{D.3}$$

and it is connected to the polarizability α_e as follows

$$\begin{aligned}\chi_e &= \frac{\sum_i \alpha_{ei}}{\varepsilon_0 \Delta V} \frac{E_{\text{loc}}}{E}, \quad \text{SI,} \\ &= \frac{\sum_i \alpha_{ei}}{\Delta V} \frac{E_{\text{loc}}}{E}, \quad \text{G-CGS.}\end{aligned}\tag{D.4}$$

Usually, in insulators, $\mathbf{E}_{\text{loc}} = (\varepsilon + 2)\mathbf{E}/3$, (in SI, ε must be replaced by $\varepsilon_r \equiv \varepsilon/\varepsilon_0$), while in metals $\mathbf{E}_{\text{loc}} \simeq \mathbf{E}$.

In Appendix A we have also outlined how the principle of causality leads to the Kramers–Kronig dispersion relations (A.53) and (A.54) connecting the real and imaginary part of the dielectric function.

D.1 Uses

In this section, we point out and demonstrate that the dielectric function is a powerful tool for calculating and understanding a wide range of important effects in solids; it is probably the most efficient bridge between microscopic features and macroscopic properties. More specifically, the dielectric function is of crucial importance in obtaining:

(a) *the linear electromagnetic response of condensed matter, including its optical properties.*

The propagation of electromagnetic waves in matter is determined mainly by the complex index of refraction, n , which is given by

$$n = n_1 + in_2 = \sqrt{\varepsilon_r \mu_r}, \quad (\text{D.5})$$

where $\varepsilon_r = \varepsilon/\varepsilon_0$ in SI and $\varepsilon_r \equiv \varepsilon$ in G-CGS; similarly, $\mu_r = \mu/\mu_0$ in SI and $\mu_r \equiv \mu$ in G-CGS. Usually, at high frequencies, $\mu_r \simeq 1$, and consequently, $n \simeq \sqrt{\varepsilon_r}$. The spatial and temporal dependence of a plane EM wave propagating along the x -direction is determined by Maxwell's equation and is given by the expression

$$\mathbf{E}, \mathbf{H} \sim \exp(ikx - i\omega t), \quad (\text{D.6})$$

where the wave number k is complex and is related to the angular frequency, ω , and the index of refraction, n , as follows:

$$k \equiv k_1 + ik_2 = \frac{\omega}{c} (n_1 + in_2) = \frac{2\pi}{\lambda_0} (n_1 + in_2); \quad (\text{D.7})$$

λ_0 is the wavelength in vacuum of an EM wave of frequency ω .

The real part, $k_1 = \omega n_1/c$, of k determines the phase velocity, c' , of propagation of an EM wave in the medium: $c' = \omega/k_1 = c/n_1$; the imaginary part, $k_2 = \omega n_2/c$, leads to a decay of the fields inside the material $|\mathbf{E}|$, $|\mathbf{H}| \sim \exp(-k_2 x)$. The energy density, which is proportional to $|\mathbf{E}|^2$ and $|\mathbf{H}|^2$, decays as $\exp(-2k_2 x)$. We define the *absorption coefficient*, α' , of a material as minus the constant multiplying x in the exponent of this last relation

$$\begin{aligned} \alpha' \equiv 2k_2 &= \frac{2\omega n_2}{c} = \frac{4\pi n_2}{\lambda_0} = \frac{\omega \varepsilon_{r2}}{cn_1} = \frac{\sigma_1}{\varepsilon_0 cn_1}, \quad \text{SI}, \\ &= \frac{\omega \varepsilon_2}{cn_1} = \frac{4\pi \sigma_1}{cn_1}, \quad \text{G-CGS}. \end{aligned} \quad (\text{D.8})$$

The last equation in (D.8) follows from the squaring¹ of (D.5) and taking into account (D.1). Some authors define the absorption coefficient, α , as $4\pi n_2/\lambda$,

¹ Assuming that $\mu_r = 1$, we have $n^2 = (n_1 + in_2)^2 = n_1^2 - n_2^2 + 2in_1 n_2 = \varepsilon_r \mu_r = \varepsilon_r = \varepsilon_{r1} + i\varepsilon_{r2}$. Thus, $n_2 = \varepsilon_{r2}/2n_1$, which in combination with $\alpha' = 2\omega n_2/c$, gives $\alpha' = \omega \varepsilon_{r2}/n_1 c = \omega \varepsilon_2/\varepsilon_0 n_1 c$ (SI) or $\alpha' = \omega \varepsilon_2/n_1 c$ (G-CGS).

where λ is the wavelength in the medium, i.e., $\lambda = 2\pi/k_1 = \lambda_0/n_1$. It follows from (D.8) that

$$\begin{aligned}\alpha &= n_1 \alpha' = \frac{\omega \varepsilon_{r2}}{c} = \frac{\sigma_1}{\varepsilon_0 c}, \quad \text{SI,} \\ &= \frac{\omega \varepsilon_2}{c} = \frac{4\pi \sigma_1}{c}, \quad \text{G-CGS.}\end{aligned}\quad (\text{D.9})$$

Thus measuring α , we obtain directly the imaginary part of the dielectric function or the real part of the conductivity (assuming that $\mu_r \simeq 1$). Note that α is directly connected with the transmission coefficient, T , of an EM wave through a thin film of thickness d under conditions of normal incidence²:

$$T \simeq 1 - \alpha d, \quad |n|\omega d/c \ll 1. \quad (\text{D.10})$$

(b) *The energy loss per unit length of a high-energy charged particle of known trajectory, $\mathbf{r}(t)$, propagating inside a material of dielectric function $\varepsilon(\omega)$ is expressed in terms of $\varepsilon(\omega)$.*

This energy loss per unit length along the particle's trajectory is given by the formula (for a proof see the book by Landau and Lifshitz, [E15], pp. 399–405):

$$\left| \frac{dW}{dx} \right| = \frac{iq^2}{2\pi^2} \int d^3k \frac{(\omega_k/v) - (\omega_k v \varepsilon(\omega_k)/c^2)}{[k^2 - \omega_k^2 \varepsilon(\omega_k)/c^2] \varepsilon(\omega_k)}, \quad \text{G-CGS,} \quad (\text{D.11})$$

where $\mathbf{v} \equiv d\mathbf{r}/dt$ is the velocity of the particle, q is its electric charge, and $\omega_k \equiv \mathbf{v} \cdot \mathbf{k}$. In the electrostatic limit, $v/c \rightarrow \infty$, (D.11) is simplified:

$$\left| \frac{dW}{dx} \right| = -\frac{q^2}{2\pi^2} \int d^3k \frac{\omega_k}{v k^2} \text{Im} \frac{1}{\varepsilon(\omega_k)}, \quad \text{G-CGS.} \quad (\text{D.12})$$

To end up with (D.12), we take into account that the $\text{Re } \varepsilon(\omega)$ is an even function, while the $\text{Im } \varepsilon(\omega)$ is an odd function of ω , and that $\omega_k \equiv \mathbf{v} \cdot \mathbf{k} = -\omega_{-\mathbf{k}}$.

(c) *The equation $\varepsilon(\mathbf{k}, \omega) = 0$ gives the longitudinal collective eigenoscillations of a material.*

Indeed, when $\varepsilon(\mathbf{k}, \omega) = 0$, it is possible to have a nontrivial solution of Maxwell's equations (A.17–A.20) in the absence of external charges and currents such that $\mathbf{D} = \mathbf{B} = \mathbf{H} = 0$, while $\mathbf{E} \neq 0$; this can be verified by a simple inspection of (A.17)–(A.20). The physical meaning of this solution

² See, e.g. the book by Ibach and Lüth [SS79] (1991), p. 243, or the book by Landau and Lifshitz, *Electrodynamics of Continuous Media*, 2nd ed. [E15], p. 299. In general the transmission coefficient through a film of thickness d of an EM wave polarized parallel or normal to the plane of incidence is given by $T = |t|^2$ where $t = (1 - r^2)/(e^{-i\varphi} - r^2 e^{i\varphi})$ and $\phi = (\omega d/c)(\varepsilon_r \mu_r - \sin^2 \theta_0)^{1/2}$. In the equations above r is the reflection amplitude from a *single* interface between vacuum and the material characterized by ε_r and μ_r , and θ_0 is the angle of incidence; for normal incidence and $\mu_r = 1$, r is given by $(1 - n)/(1 + n)$.

is that internal charges of the material move periodically, disturbing locally the electrical neutrality and setting up electrostatic (i.e., longitudinal) electric fields, which acting on the charges sustain their oscillating motion.

Another way to convince ourselves that the statement (c) is correct is to notice that the integrand in (D.12) blows up³ when $\varepsilon = 0$. However, the blowing up of a response function, such as the integrand in (D.12), implies a resonance condition, i.e., the coincidence of the external frequency, $\omega_{\mathbf{k}} \equiv \mathbf{v} \cdot \mathbf{k}$, with an eigenfrequency of the system for the same $\mathbf{k}$; this eigenfrequency is of longitudinal nature, since in (D.12) only electrostatic fields were taken into account (which by their very nature are of longitudinal character, since $\nabla \times \mathbf{E}_{\text{electrostatic}} = 0$).

Employing the observation that a response function blows up when the external frequency coincides with an eigenfrequency of the system, we see from (D.11) that

(d) *The equation*

$$\varepsilon(\mathbf{k}, \omega) = \frac{c^2 k^2}{\omega^2}, \quad (\text{D.13})$$

which in the electrostatic limit, $c k/\omega \rightarrow \infty$, reduces to

$$\varepsilon(\mathbf{k}, \omega) = \infty, \quad (\text{D.14})$$

gives the transverse collective oscillations of a material of dielectric function $\varepsilon(\mathbf{k}, \omega)$. Indeed, the integrand in (D.11) blows up not only when the external frequency $\omega_{\mathbf{k}}$ coincides with the frequency ω such that $\varepsilon(\mathbf{k}, \omega) = 0$, but also when $\omega_{\mathbf{k}}$ coincides with a frequency satisfying (D.13), which is identical to (D.7), since $n = \sqrt{\varepsilon_r}$. In other words, (D.13) determines the phase velocity $c' = \omega/k = c/n$ of a self-sustained transverse EM wave propagating in a material of dielectric function, $\varepsilon(\mathbf{k}, \omega)$. When this velocity c' turns out to be much smaller than the velocity of light in vacuum, we can use (D.14) for its determination instead of the exact (D.13); Then this wave is essentially a transverse collective oscillation of the particles of the material driven by the internal electrostatic field. Of course, a small coupling of this oscillation to the full EM field is always present.

We can conclude that, in the framework of the electrostatic approximation, $c \rightarrow \infty$, the vanishing of the dielectric function $\varepsilon(\mathbf{k}, \omega)$ gives the eigenfrequency(ies) of the longitudinal collective oscillation(s) of the particles of the material, while the infinities of $\varepsilon(\mathbf{k}, \omega)$ give the eigenfrequencies of the transverse collective oscillations (assuming that the resulting ω/k is much smaller than c). It is obvious that the existence of such collective electrostatic oscillations implies a strong dependence of the dielectric function on the frequency.

³ The blow up of a response function can take place only when there are no losses, i.e., only when $\text{Im } \varepsilon = 0$. If $\text{Im } \varepsilon \neq 0$, instead of a blowing up we have a peak in $\text{Im } \varepsilon(\omega)$ the width of which is proportional to $\text{Im } \varepsilon$ and its height is proportional to $1/\text{Im } \varepsilon$.

In contrast, if the dielectric function were almost independent of the frequency, no electrostatic collective oscillations would be possible; in this case only pure electromagnetic waves can exist in the material; then, the only role of the material is to reduce their velocity from c (in the vacuum) to $c' = c/\sqrt{\epsilon}$. A fast-moving charged particle with velocity $\mathbf{v}$ larger than c' can excite these electromagnetic waves *resonantly*. Indeed, if the Fourier components $\mathbf{q}$ and $\omega_{\mathbf{q}} = \mathbf{v} \cdot \mathbf{q} = vq \cos \theta$ of the EM field of this particle match the EM wave's wavevector $\mathbf{k}$ and its eigenfrequency $\omega = c'k$, i.e., if

$$v \cos \theta = c, \quad (\text{D.15})$$

resonant excitation of EM waves takes place. According to (D.15), this excitation requires the velocity of the particle to exceed the velocity of light in the medium; the direction of propagation of these EM waves excited resonantly makes an angle θ with respect of the particle's velocity, $\mathbf{v}$, where $\cos \theta = c'/v$ according to (D.15). This is the famous *Cherenkov radiation*.

(e) *The differential cross section of inelastic scattering of a charged particle by a material can be expressed in terms of the dielectric function, $\epsilon(\mathbf{k}, \omega)$.*

Scattering of external beams of particles (either charged such as electrons, ions, or uncharged such as atoms, neutrons, photons) by a material is of central importance, because it is the main experimental tool for obtaining direct information about the static microscopic structure of the material as well as about the dynamic processes taking place within it. The main quantity of interest is the so-called inelastic differential scattering cross section, $d^2\sigma$, which gives the number of particles per unit time and per unit initial flux of the beam that are scattered within the solid angle, $d\Omega$, around a given direction and have energy between ε_f and $\varepsilon_f + d\varepsilon_f$. Let us assume that each particle of the beam has electrical charge q and mass m . Before the scattering, its momentum is $\hbar\mathbf{k}_i$ and its energy, $\varepsilon_i = \hbar^2 k_i^2 / 2m$. After the scattering, the momentum of some particles is $\hbar\mathbf{k}_f$ and their energy, $\varepsilon_f = \hbar^2 k_f^2 / 2m$; the direction of $\mathbf{k}_f$ determines the direction of scattering of those particles, while its magnitude fixes the final energy of each of those particles. Furthermore, we denote by V the volume of the material and by $\hbar\mathbf{k}$ and $\hbar\omega$ the differences $\hbar\mathbf{k}_i - \hbar\mathbf{k}_f$ and $\varepsilon_i - \varepsilon_f$ respectively; $\hbar\mathbf{k}$ is the momentum transfer (from an external particle to the material) and $\hbar\omega$ is the energy transfer. With this notation, the differential scattering cross section $d^2\sigma$ per unit solid angle and per unit final energy is given by the following formula:

$$\frac{d^2\sigma}{d\Omega d\varepsilon_f} = -\frac{Vm^2 k_f q^2}{\pi^2 \hbar^4 k_i k^2} \text{Im} \left\{ \frac{1}{\epsilon(\mathbf{k}, \omega)} \right\}, \quad \text{G-CGS.} \quad (\text{D.16})$$

(f) *The exact potential energy and the exact total energy of the Jellium Model (JM) can be expressed in terms of the dielectric function.*

The formula giving the potential energy E_P , in terms of $\varepsilon(\mathbf{k}, \omega)$, is:

$$E_P = -\hbar \sum_{\mathbf{k}} \int_0^\infty \frac{d\omega}{2\pi} \text{Im} \left\{ \frac{1}{\varepsilon(\mathbf{k}, \omega)} \right\} - \sum_{\mathbf{k}} \frac{2\pi e^2 n_e}{4\pi\varepsilon_0 k^2}, \quad (\text{D.17})$$

where n_e is the electron concentration.

The total energy E_t is then:

$$E_t(e^2) = E_t(0) + \int_0^{e^2} d(e'^2) \frac{E_P(e'^2)}{e'^2}, \quad (\text{D.18})$$

where $E_t(0) = 0$, $6N_e E_F$ is the total energy, if the electric charge of the electrons and the ionic background was zero and $E_P(e'^2)$ is the potential energy as given by (D.17) if everywhere instead of e^2 we set e'^2 . *The Fourier transform, $4\pi q_1 q_2 / 4\pi\varepsilon_0 k^2$, of the bare Coulomb interaction, $q_1 q_2 / 4\pi\varepsilon_0 r$, between two charges q_1, q_2 is connected to the Fourier transform, $\mathcal{V}_s(\mathbf{k}, \omega)$, of the screened Coulomb interaction through the following simple formula involving the dielectric function:*

$$\mathcal{V}_s(\mathbf{k}, \omega) = \frac{4\pi q_1 q_2}{4\pi\varepsilon_0 k^2 \varepsilon(\mathbf{k}, \omega)}. \quad (\text{D.19})$$

The screening of the bare Coulomb repulsion between two electrical charges q_1, q_2 placed within a material is due to the presence of all other particles of the material (both electrons and ions), which rearrange themselves to minimize the energy. The proof of (D.19) follows directly from (A.17), (A.47), and (A.21). Note that in the static limit, $\omega \rightarrow 0$, a familiar approximate expression for the screened Coulomb interaction (in real space) is as follows

$$\mathcal{V}_s(r) = \frac{q_1 q_2}{4\pi\varepsilon_0 r} e^{-k_s r}, \quad (\text{D.20})$$

where k_s^{-1} is the so-called *screening length*. The Fourier transform of (D.20) is $\mathcal{V}_s(\mathbf{k}) = 4\pi q_1 q_2 / 4\pi\varepsilon_0 (k^2 + k_s^2)$. Comparing this expression with (D.19), we conclude that the static dielectric function, which produces in real space a screened Coulomb interaction as in (D.20), has the form: $\varepsilon(\mathbf{k}, 0) = 1 + (k_s^2/k^2)$.

D.2 Expressions for $\varepsilon(\mathbf{k}, \omega)$ within the JM

Given the importance of the dielectric function in so many aspects of the behavior of solids, it is obvious that we must try to obtain expressions for $\varepsilon(\mathbf{k}, \omega)$. Even within the simplest possible model, that of JM, it is not possible to find exact *explicit* formulae for the dielectric function. We have an exact but not explicit expression and we have several explicit but approximate formulae.

It is proved in [MB45], pp. 172–182 that the exact general formula of the dielectric function *within the Jellium Model* (JM) can be expressed in terms of an infinite sum involving the exact eigenstates, Ψ_n , and eigenenergies, E_n , of the JM:

$$\frac{1}{\varepsilon(\mathbf{k}, \omega)} = 1 - \frac{4\pi e^2}{4\pi\varepsilon_0 k^2} \sum_n |\langle \Psi_n | \hat{n}_{\mathbf{k}} | \Psi_0 \rangle|^2 \times \left[\frac{1}{E_n - E_0 - \hbar\omega - i\eta} + \frac{1}{E_n - E_0 + \hbar\omega + i\eta} \right], \quad (\text{D.21})$$

where $\eta \rightarrow 0^+$, $|\Psi_0\rangle$ is the ground state of the JM, and

$$\hat{n}_{\mathbf{k}} = \frac{1}{\sqrt{V}} \int d^3r e^{-i\mathbf{k}\cdot\mathbf{r}} [\hat{n}(\mathbf{r}) - \zeta n_i]. \quad (\text{D.22})$$

In (D.22), $\hat{n}(\mathbf{r})$ is the electronic concentration operator, and n_i is the (constant) ionic concentration of the JM. From (D.21) or by other means, one can obtain an approximation, which is called *random phase approximation* (RPA), for the dielectric function

$$\varepsilon(\mathbf{k}, \omega) = 1 - \frac{8\pi e^2}{4\pi\varepsilon_0 k^2} \int \frac{d^3k'}{(2\pi)^3} \frac{f_{\mathbf{k}'} - f_{\mathbf{k}'+\mathbf{k}}}{\hbar\omega + \varepsilon_{\mathbf{k}'} - \varepsilon_{\mathbf{k}'+\mathbf{k}} + i\eta}, \quad (\text{D.23})$$

where f_q is the Fermi distribution

$$f_q = \frac{1}{e^{\beta(\varepsilon_q - \mu)} + 1}, \quad \mathbf{q} = \mathbf{k}', \mathbf{k}' + \mathbf{k}, \quad (\text{D.24})$$

and $\varepsilon_q \equiv \hbar^2 q^2 / 2m_e$ ($\mathbf{q} = \mathbf{k}', \mathbf{k}' + \mathbf{k}$) is the kinetic energy of a single electron. For the JM and for all realistic temperatures, $\beta = (k_B T)^{-1}$ can be taken as infinite and μ as equal to E_F . In [MB45], pp. 172–182, (D.23) is deduced from the general expression (D.21). Equation (D.23) in the limit $\mathbf{k} \rightarrow 0$ and $\omega \neq 0$, is reduced to

$$\varepsilon(k, \omega) \rightarrow 1 - \frac{\omega_{\text{pf}}^2}{\omega^2}, \quad (\text{D.25})$$

where⁴ $\omega_{\text{pf}}^2 = 4\pi e^2 n_e / 4\pi\varepsilon_0 m_e$; ω_{pf} is the so-called *electronic plasma frequency*. Equation (D.25) is exact in the limit $\omega \rightarrow \infty$; furthermore, it can be derived very easily in the framework of a phenomenological approach to be presented in D-3. In the opposite limit $k \neq 0$ and $\omega \rightarrow 0$, (D.23) gives

$$\varepsilon(\mathbf{k}, \omega) \rightarrow 1 + \frac{k_{\text{TF}}^2}{k^2} f\left(\frac{k}{k_F}\right), \quad (\text{D.26})$$

where the Thomas–Fermi screening constant k_{TF} satisfies the relation

$$k_{\text{TF}}^2 = \frac{4k_F}{\pi a_B}, \quad (\text{D.27})$$

⁴ In SI $\omega_{\text{p}}^2 = e^2 n_e / \varepsilon_0 m_e$. To distinguish between ω_{pf} and ω_{p} see (5.25) and Fig. 5.1.

k_F is the Fermi wavenumber, and

$$f(x) = \frac{1}{2} \left[1 - \frac{1}{x} \left(1 - \frac{1}{4}x^2 \right) \ln \left| \frac{1 - \frac{1}{2}x}{1 + \frac{1}{2}x} \right| \right], \quad x = \frac{k}{k_F}, \quad (\text{D.28})$$

$f(x)$ decreases monotonically from 1 at $x = 0$ to zero at $x = \infty$ passing through $1/2$ at $x = 2$, at which point its derivative exhibits a singularity. We can conclude that, when $\omega \gg v_F k$ and within the JM, (D.25) is a good approximation to (D.23), while, when $\omega \ll v_F k$, then (D.26) is a good approximation of (D.23).

Problem D.1t. Prove (D.26), starting from (D.23) and as $T \rightarrow 0$.

D.3 Phenomenological Expressions for the Dielectric Function

The dielectric function of a solid depends on the response to an applied electric field by the charged particles of the solid, i.e., by the electrons and the ions. The electrons can be classified in two groups: Those that are free to move and produce an electric current under the influence of the total static electric field and those that do not produce an electric current under the influence of a static electric field. The conventional view of the charges of the second group is that they are bound and that their displacement from their equilibrium positions causes a restoring force⁵. For the ions too, we have to distinguish two cases: The first refers to one ion per primitive cell. In the second case, we have more than one ion per primitive cell; in this second case, we have to consider instead of the displacements $\mathbf{r}_i$ of each individual ion in the primitive cell the normal mode variables, i.e., such linear combinations $\mathbf{w}_\alpha = \sum_i \lambda_{\alpha i} \mathbf{r}_i$ that the equation of motion for each $\mathbf{w}_\alpha$ decouples from all other $\mathbf{w}_\alpha$ s; e.g., if we have two ions per primitive cell, we may consider under certain conditions $\mathbf{w}_r = \mathbf{r}_1 - \mathbf{r}_2$ and $\mathbf{w}_{cm} = (m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2)/(m_1 + m_2)$.

We denote by $\mathbf{u}_n$ either the displacement of an electron from its equilibrium position, or the ionic displacement $\mathbf{r}_i$ (if there is only one ion per primitive cell), or the normal mode ionic variable $\mathbf{w}_i$ (if there are more than one ion per unit cell). The Newtonian equation of motion for $\mathbf{u}_n$ has the following general form:

$$m_n^* \ddot{\mathbf{u}}_n = q_n^* \mathbf{E}_\ell - \kappa_n \mathbf{u}_n + i\omega m_n \mathbf{u}_n / \tau_n. \quad (\text{D.29})$$

In (D.29), $m_n^* = m_e$ (m_e is the electronic mass) if $\mathbf{u}_n$ is an electronic displacement, $m_n^* = m_i$ if $\mathbf{u}_n$ is a single ionic displacement, and m_n^* is an appropriate

⁵ Electrons in a completely full valence band of a semiconductor behave as if they were bound although their wave functions extend over the whole solid.

combination of ionic masses if $\mathbf{u}_n \equiv \mathbf{w}_n$; $q_n^* \mathbf{E}_1$ is the force exercised by the local electric field $\mathbf{E}_1$ on the effective charge q_n^* ($q_n^* = -e$, if we examine electronic displacement, $q_n^* = \zeta e$, if we study displacement of a single ion of valence ζ , and q_n^* is an appropriate combination of ionic charges, if $\mathbf{u}_n = \mathbf{w}_n$); $-\kappa_n \mathbf{u}_n$ is the restoring force which is connected with an eigenfrequency ω_n through the relation $-\kappa_n = -m_n^* \omega_n^2$ (quantum mechanically, ω_n is connected with properly averaged excitation energy, $\varepsilon_n = \hbar \omega_n$). Finally, the last term describes phenomenologically a friction force (proportional to the velocity, $\mathbf{v}_n = \dot{\mathbf{u}}_n = -i\omega \mathbf{u}_n$); the size of this force is characterized by the relaxation time τ_n (the time dependence is assumed to be of the form $\exp(-i\omega t)$). Solving (D.29) for the velocity $\mathbf{v}_n = -i\omega \mathbf{u}_n$, we find

$$\mathbf{v}_n = \frac{i\omega q_n^*}{m_n^*(\omega^2 - \omega_n^2 + i\omega/\tau_n)} \mathbf{E}_1. \quad (\text{D.30})$$

The corresponding electrical current density, $\mathbf{j}_n$, is given by

$$\mathbf{j}_n = q_n^* n_n \mathbf{v}_n, \quad (\text{D.31})$$

where n_n is the concentration of each species (be it free electron, or bound electron, or ion). The contribution to the conductivity σ_n of the species n is given by the ratio j_n/E or by combining (D.31) and (D.30),

$$\sigma_n = \frac{i\omega n_n q_n^{*2}}{m_n^*(\omega^2 - \omega_n^2 + i\omega/\tau_n)} \frac{E_1}{E}, \quad (\text{D.32})$$

where E is the macroscopic electric field. Taking into account (D.1) and summing the contributions over all species, we have for the dielectric function

$$\varepsilon(\mathbf{k}, \omega) = 1 - \sum_n \frac{4\pi n_n q_n^{*2}}{m_n^*(\omega^2 - \omega_n^2 + i\omega/\tau_n)} \frac{E_1}{E}, \quad \text{G-CGS.} \quad (\text{D.33})$$

(In SI replace 4π by $1/\varepsilon_0$ and ε by $\varepsilon/\varepsilon_0 = \varepsilon_r$). For each particular type of solids, we have to determine which the various contributions to the sum in (D.33) are, and for each contribution we must estimate the ratio E_1/E and the parameters ω_n and τ_n , which in general are functions of $\mathbf{k}$. For example, for metals with a single ion per primitive cell we have:

- A contribution from the free electrons for which $\omega_n \simeq 0$, $q_n^* = -e$, $m_n^* = m_e$, $n_n = n_e = n_f$, and $E_1/E = 1$. This contribution coincides with the $-\omega_p^2/\omega^2$ term in (D.25), if we omit the friction term $-i\omega/\tau_n$. Notice that $\omega_n \simeq 0$, only if ω and k satisfy the inequality $\omega \gg v_F k$; in the opposite case, $\omega \ll v_F k$, $\omega_n^2 \simeq \omega_{\text{pf}}^2 k^2/k_{\text{TF}}^2 f(k/k_F)$ in order to recapture (D.26).
- Contributions for the various types of bound electrons occupying the various ionic shells and subshells.
- Contribution from the ionic displacement.

Thus for a metal we have (for $\omega \gg v_F k$ and assuming $E_l/E = 1$ for the bound electrons as well).

$$\varepsilon(\mathbf{k}, \omega) = 1 - \frac{\omega_{\text{pf}}^2}{\omega^2 + i\omega/\tau_f} - \sum_b \frac{\omega_{\text{pb}}^2}{\omega^2 - \omega_b^2 + i\omega/\tau_b} - \frac{\omega_{\text{pi}}^2}{\omega^2 - \omega_i^2 + i\omega/\tau_i}, \quad (\text{D.34})$$

where the free-electron plasma frequency, ω_{pf} , is given by

$$\omega_{\text{pf}}^2 = \frac{4\pi e^2 n_f}{4\pi \varepsilon_0 m_{e4}}, \quad (\text{D.35})$$

(in G-CGS set $4\pi \varepsilon_0$ equal to 1), while

$$\omega_{\text{pb}}^2 = \frac{4\pi e^2 n_b}{4\pi \varepsilon_0 m_e}, \quad (\text{D.36})$$

and

$$\omega_{\text{pi}}^2 = \frac{4\pi (e\zeta)^2 n_i}{4\pi \varepsilon_0 m_i} = \frac{4\pi e^2 \zeta n_f}{4\pi \varepsilon_0 m_i}, \quad (\text{D.37})$$

In these relations, n_f is the free-electron concentration, $n_i = n_f/\zeta$ is the ionic concentration and n_b is the electronic concentration of the bound electrons occupying the various subshells of the ion. Notice that the plasma frequency, ω_p , at which $\varepsilon(0, \omega_p) = 0$, does not in general coincides with ω_{pf} . For low frequencies, $\omega \ll \omega_{b,\text{min}}$, we can omit both ω^2 and $i\omega/\tau_b$ in the bound electron contribution, so that the latter becomes $\sum_b \omega_{\text{pb}}^2/\omega_b^2$. Then, the dielectric function takes the form $\varepsilon(\omega) = 1 + \tilde{\chi}_b - \omega_{\text{pf}}^2/(\omega^2 + i\omega/\tau_f)$, and hence, $\omega_p = \omega_{\text{pf}}/\sqrt{1 + \tilde{\chi}_b}$ (provided that $\omega_p \ll \omega_{b,\text{min}}$), where $\tilde{\chi}_b = \sum_b \omega_{\text{pb}}^2/\omega_b^2$. In the opposite case, where $\omega_{b,\text{min}}^2 \ll \omega_{\text{pf}}^2 + \omega_{\text{pb}}^2$, we have $\omega_p^2 \simeq \omega_{\text{pf}}^2 + \omega_{\text{pb}}^2$. For example, in Si, where $\omega_{\text{pf}} = 0$ and $\omega_{b,\text{min}} \ll \omega_{\text{pb}}$, we have $\omega_p \simeq \omega_{\text{pb}}$. Comparing this expression with (D.2) and (D.4), we find that $\sum_b \omega_{\text{pb}}^2/\omega_b^2 = 4\pi(\sum_l \alpha_{\text{el}})/\Delta V$ (G-CGS; in SI replace 4π by $1/\varepsilon_0$). The ionic quantity ω_i is a function of $\mathbf{k}$: $\omega_i = c_t k$, where c_t is the velocity of the transverse acoustic wave.

Problem D.2t. Determine the transverse collective eigenoscillations of a metal.

Problem D.3t. Find the zeros of $\varepsilon(\mathbf{k}, \omega)$ for a metal in the case $\omega \gg v_F k$, ignoring the bound electron contributions. The same for the opposite case $v_i k \ll \omega \ll v_F k$ where $v_i = v_F (m_e/m_i)^{3/4}$. Plot for a metal the longitudinal collective eigenfrequencies as a function of k .

E

Waves in Continuous Elastic Media

E.1 Strains

Let $\mathbf{u}(\mathbf{r}, t)$ be the displacement of a point $\mathbf{r}$ at time t of a continuous medium. The medium is deformed as a result of $\mathbf{u}$ being non-uniform. Hence, the deformation will depend on the derivatives $\partial u_\nu / \partial x_\mu$ ($\mu, \nu = 1, 2, 3$ are the Cartesian coordinates). If the quantities $\partial u_\nu / \partial x_\mu$ are small, the change of the distance between two neighboring points depends on the symmetrized derivatives $u_{\nu\mu}$ (see [AW60]), which is given by

$$u_{\nu\mu} = \frac{1}{2} \left(\frac{\partial u_\nu}{\partial x_\mu} + \frac{\partial u_\mu}{\partial x_\nu} \right). \quad (\text{E.1})$$

This so-called *strain tensor* $u_{\nu\mu}$ fully characterizes the deformation of the medium. In particular, one can show that the relative variation $\Delta(\Delta V) / \Delta V$ of a small volume element ΔV is given by

$$\frac{\Delta(\Delta V)}{\Delta V} = \sum_{\nu} u_{\nu\nu} = \nabla \cdot \mathbf{u}. \quad (\text{E.2})$$

We can separate the strain tensor $u_{\nu\mu}$ into two components: the first one, $(\nabla \cdot \mathbf{u}) \delta_{\nu\mu} / 3$, represents pure isotropic compression and the second one, $u'_{\nu\mu}$, pure shear deformation without any change in the local volume elements:

$$u_{\nu\mu} = \frac{1}{3} (\nabla \cdot \mathbf{u}) \delta_{\nu\mu} + u'_{\nu\mu}, \quad (\text{E.3})$$

$$u'_{\nu\mu} = u_{\nu\mu} - \frac{1}{3} (\nabla \cdot \mathbf{u}) \delta_{\nu\mu}. \quad (\text{E.4})$$

E.2 Equations of Motion

In order to determine the displacement $\mathbf{u}(\mathbf{r}, t)$ and the strain tensor, we have to use Newton's equation of motion for a small volume ΔV of mass $\Delta m = \rho_M \Delta V$ around the point $\mathbf{r}$:

$$\Delta m \ddot{\mathbf{u}} = \Delta \mathbf{F}, \quad (\text{E.5})$$

or by dividing with the small volume element ΔV :

$$\rho_M \ddot{\mathbf{u}} = \mathbf{f}, \quad (\text{E.6})$$

where $\mathbf{f} \equiv \Delta \mathbf{F} / \Delta V$. Now we define the *stress tensor* $T_{\mu\nu}$ such that the total force $\Delta \mathbf{F}$ on the volume element ΔV due to the deformation is given by integrating $T_{\mu\nu}$ over the surface surrounding the volume element ΔV :

$$\Delta F_\mu = \sum_\nu \int T_{\mu\nu} dS_\nu. \quad (\text{E.7})$$

This surface integral can be transformed into a volume integral using Gauss' theorem:

$$\Delta F_\mu = \int_{\Delta V} dV \sum_\nu \left(\frac{\partial T_{\mu\nu}}{\partial x_\nu} \right). \quad (\text{E.8})$$

Since $f_\mu \equiv \Delta F_\mu / \Delta V$, we have from (E.8) that

$$f_\mu = \sum_\nu \frac{\partial T_{\mu\nu}}{\partial x_\nu}. \quad (\text{E.9})$$

E.3 Connecting Stress and Strain

The stress tensor $T_{\mu\nu}$ must be expressed in terms of the strain tensor $u_{\mu\nu}$ in order to obtain an equation involving only the displacement $\mathbf{u}$ and its derivatives. The first step is to use the relation between the stress tensor and the deformation potential energy per unit volume, Δ :

$$T_{\mu\nu} = \frac{\partial \Delta}{\partial u_{\mu\nu}}. \quad (\text{E.10})$$

Equation (E.10) is the analog of the single particle equation $F = -\partial E_P / \partial x$ connecting the potential energy E_P with the force F . (The difference in sign is due to the convention that $T_{\mu\nu} dS_\nu$ is the elementary force exercised on the body and not by the body, as in the usual definition of pressure.)

The next step is to express Δ in terms of strain tensor $u_{\mu\nu}$. Assuming that Hooke's law is valid (which means that Δ depends on the squares of $u_{\mu\nu}$) and taking into account that Δ is a scalar, we conclude that Δ must be proportional to scalar square functions of $u_{\mu\nu}$. For an isotropic medium, there are only two such functions: $(\sum_\nu u_{\nu\nu})^2$ and $\sum_{\mu\nu} (u_{\mu\nu}^2)$. Hence,

$$\Delta = \frac{1}{2} \lambda \left(\sum_\nu u_{\nu\nu} \right)^2 + \mu_s \sum_{\mu\nu} (u_{\mu\nu}^2), \quad (\text{E.11})$$

where λ and μ_s are two constants (called Lamé's coefficients) characterizing the elastic properties of the medium. If we replace (E.3) in (E.11), we obtain

$$\Delta = \frac{1}{2} \left(\lambda + \frac{2}{3} \mu_s \right) (\nabla \cdot \mathbf{u})^2 + \mu_s \sum_{\mu, \nu=1}^3 (\mathbf{u}'_{\mu\nu})^2. \quad (\text{E.12})$$

The first term in the rhs of (E.12) represents the potential deformation energy density due to pure hydrostatic (i.e. isotropic) compression and the second one represents the one due to pure shear strain. From the definition of the bulk modulus B , we have for an isotropic compression that $\Delta = \frac{1}{2} B (\nabla \cdot \mathbf{u})^2$. Hence, the following connection between B and the Lamé's coefficients is established:

$$B = \lambda + \frac{2}{3} \mu_s. \quad (\text{E.13})$$

From (E.10–E.12), we obtain the desired relation between the stress and the strain tensors

$$T_{\nu\mu} = \lambda (\nabla \cdot \mathbf{u}) \delta_{\nu\mu} + 2\mu_s u_{\nu\mu} = B (\nabla \cdot \mathbf{u}) \delta_{\nu\mu} + 2\mu_s u'_{\nu\mu}. \quad (\text{E.14})$$

E.4 The Elastic Wave Equation

The combination of (E.6), (E.9), and (E.14) leads to the elastic wave equation in an isotropic continuous medium:

$$\rho_M \ddot{\mathbf{u}} = (\lambda + \mu_s) \nabla (\nabla \cdot \mathbf{u}) + \mu_s \nabla^2 \mathbf{u}. \quad (\text{E.15})$$

For a pure transverse (i.e. shear) wave for which $\nabla \cdot \mathbf{u} = 0$, (E.15) becomes

$$\rho_M \ddot{\mathbf{u}}_t = \mu_s \nabla^2 \mathbf{u}_t. \quad (\text{E.16})$$

For a pure longitudinal wave for which $\nabla \times \mathbf{u}_\ell = 0$, we have that $\nabla (\nabla \cdot \mathbf{u}_\ell) = \nabla^2 \mathbf{u}_\ell$ and (E.15) becomes

$$\rho_M \ddot{\mathbf{u}}_\ell = (\lambda + 2\mu_s) \nabla^2 \mathbf{u}_\ell. \quad (\text{E.17})$$

Assuming a plane wave, $\mathbf{u} \sim \exp(i\mathbf{k} \cdot \mathbf{r} - i\omega t)$, we have from (E.16) $-\rho_M \omega^2 = -\mu_s k^2$. Hence, the velocity c_t of transverse waves in elastic isotropic media is

$$c_t \equiv \frac{\omega}{k} = \sqrt{\frac{\mu_s}{\rho_M}}. \quad (\text{E.18})$$

In a similar way, we find from (E.17) that the velocity of longitudinal waves in elastic isotropic media is

$$c_l = \sqrt{\frac{\lambda + 2\mu_s}{\rho_M}} = \sqrt{\frac{B + \frac{4}{3}\mu_s}{\rho_M}}. \quad (\text{E.19})$$

Note that transverse plane waves involve only shear deformations and consequently their velocity depends on the shear modulus and not on bulk modulus B . In contrast, longitudinal plane waves involve compression in the direction of propagation only (i.e. non-isotropic compression). As a result, both B and μ_s appear in the velocity of propagation of longitudinal waves.

We conclude this appendix by pointing out that quite often in the theory of elasticity, instead of λ and μ_s or instead of B and μ_s the so-called *Young modulus*, E , is used where

$$E \equiv \frac{9B\mu_s}{3B + \mu_s} = \frac{9x}{3+x}B, \quad x = \frac{\mu_s}{B}, \quad (\text{E.20})$$

as well as the so-called *Poisson ratio*, σ , where

$$\sigma \equiv \frac{1}{2} \frac{3B - 2\mu_s}{3B + \mu_s} = \frac{1}{2} \frac{3 - 2x}{3 + x}. \quad (\text{E.21})$$

The quantities E , σ are directly related to the elongation and the radius reduction of a rod under the influence of a uniform stretching force per unit area, p . If the rod is in the z -direction, we have that $u_{zz} = p/E$ and $u_{xx} = u_{yy} = -\sigma u_{zz}$. In terms of E and σ , the sound velocities are given by (see [AW60])

$$c_l = \sqrt{\frac{E(1-\sigma)}{\rho_M(1+\sigma)(1-2\sigma)}}, \quad (\text{E.22})$$

$$c_t = \sqrt{\frac{E}{2\rho_M(1+\sigma)}}. \quad (\text{E.23})$$

We also have $B = E/3(1-2\sigma)$ and $\mu_s = E/2(1+\sigma)$.

F

The Method LCAO Applied to Molecules

F.1 Formulation of the LCAO Method

The main step in the calculation of the properties of atoms, molecules, and solids is finding the solution to the time-independent Schrödinger equation

$$\hat{H}\psi = E\psi, \quad (\text{F.1})$$

where $\hat{H}$ is the single-electron Hamiltonian operator:

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \mathcal{V}(\mathbf{r}). \quad (\text{F.2})$$

The solution to this partial differential equation is often facilitated if we express the unknown function $\psi(\mathbf{r})$ as a linear combination of an appropriate complete set of orthogonal normalized functions $\phi_n(\mathbf{r})$ (such that $\int \phi_m^*(\mathbf{r}) \phi_n(\mathbf{r}) d^3r = \delta_{mn}$):

$$\psi(\mathbf{r}) = \sum_n c_n \phi_n(\mathbf{r}). \quad (\text{F.3})$$

Then, as it was shown in (B.35), Schrödinger's equation is transformed into a system of linear, homogeneous equations for the coefficients $\{c_n\}$

$$\sum_{n=-\infty}^{\infty} (H_{mn} - E\delta_{mn}) c_n = 0, \quad m = 1, 2, 3, \dots, \quad (\text{F.4})$$

where

$$H_{mn} = \left\langle m \left| \hat{H} \right| n \right\rangle \equiv \int \phi_m^*(\mathbf{r}) \hat{H} \phi_n(\mathbf{r}) d^3r. \quad (\text{F.5})$$

Strictly speaking, the system (F.4) consists of an infinite number of equations and unknowns $\{c_n\}$. In practice, we restrict ourselves to a finite number of ϕ_n s, creating thus some inevitable errors, which we try to keep as small as possible.

As it was mentioned in Appendix B, one set of basis functions ϕ_n (widely used in solid state physics) is that of plane waves (see (B.17)); another is that of atomic (or atomic-like) orbitals, which is of central importance in chemistry. Indeed the method based on equations (F.3–F.5), with ϕ_n being atomic (or atomic-like) orbitals and known as **linear combination of atomic orbitals** (LCAO), is the basic tool for understanding the stereochemistry and other properties of molecules. The advantages of the LCAO method are as follows:

1. Qualitative and semi-quantitative results can be obtained by keeping a small number of equations (and unknowns) in the set (F.4); quite often this set is reduced to the elementary problem of two equations with two unknown coefficients.
2. The physical interpretation of the obtained results is easy, since the molecular orbitals and energy levels are directly related to the corresponding orbitals and levels of the participating atoms.
3. The method can handle large molecules (and solids with a large number of atoms in the unit cell), i.e., systems where more accurate methods cannot be applied.

The main disadvantage of the LCAO is that accurate determination of the matrix elements H_{mn} from first principles is at best very laborious and at worse unattainable. To face this problem, we follow two approaches: the first determines the required H_{mn} s by fitting to accurate results obtained through other methods; the second, is less accurate but much simpler: it identifies the diagonal matrix elements, H_{mm} , with the atomic levels as given in Table B.3¹ of Appendix B. The off-diagonal elements $H_{mn}(m \neq n)$ among s and p orbitals belonging to *nearest neighbor* atoms are assumed to be proportional to the inverse square of the bond length d :

$$H_{mn} = \eta \frac{\hbar^2}{m_e d^2}, \quad (\text{F.6})$$

where the numerical factor η depends in general on the angular type of the atomic orbitals ϕ_m, ϕ_n and the direction cosines, ℓ_x, ℓ_y, ℓ_z of the vector that starts from the atom of the orbital m and ends at the atom of the orbital n . The values of η for s and p_x, p_y, p_z atomic orbitals are given according to Harrison¹ [SS76] by the following expressions:

¹ A modified and extended version for the diagonal and off-diagonal matrix elements, H_{mn} , is presented in a paper by L. Shi and D.A. Papaconstantopoulos, Phys. Rev. B **70**, 205101 (2004) and in a review article by D.A. Papaconstantopoulos and J.M. Mehl in *Encyclopaedia of Condensed Matter Physics*, ed. by F. Bassani, G.L. Liedl, and P. Wyder, Elsevier, 2005, Vol. **6**, p. 194.

$$\eta_{s,s} = -1.32, \quad (\text{F.7})$$

$$\eta_{s,i} = 1.42\ell_i, \quad i = p_x, p_y, p_z, \quad (\text{F.8})$$

$$\eta_{i,i} = 2.22\ell_i^2 - 0.63(1 - \ell_i^2), \quad i = p_x, p_y, p_z, \quad (\text{F.9})$$

$$\eta_{i,j} = 2.85\ell_i\ell_j, \quad i \neq j, \quad i, j = p_x, p_y, p_z. \quad (\text{F.10})$$

Note that $\eta_{j,s} = -1.42\ell_j$, since reversing the order of the orbitals multiplies each ℓ_i by minus one (ℓ_i are the direction cosines of the vector that starts from the atom, which corresponds to the first subscript in η and ends at the one corresponding to the second). If we choose $\ell_x = 1$ and $\ell_y = \ell_z = 0$, we have $\eta_{s,x} = 1.42$, $\eta_{x,x} = 2.22$, $\eta_{y,y} = \eta_{z,z} = -0.63$ as shown in Fig. F.1.

$$\eta_{s,s} = -1.32, \quad (\text{F.11})$$

$$\eta_{s,x} = 1.42, \quad (\text{F.12})$$

$$\eta_{x,x} = 2.22, \quad (\text{F.13})$$

$$\eta_{y,y} = -0.63. \quad (\text{F.14})$$

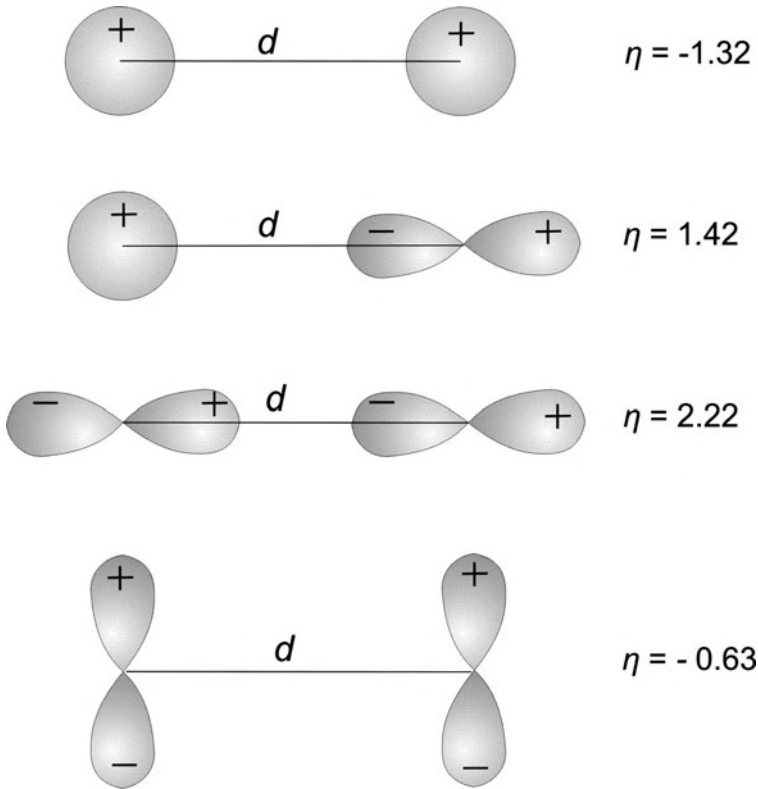


Fig. F.1. The values of the coefficient η for orbitals belonging to nearest neighbor atoms. The bond is along the x -axis (See Eqs. (F.6) to (F.14) in the text)

Notice that the first three figures remain invariant under rotations of one orbital around the bond axis (a symmetry denoted by the Greek letter σ), while the fourth is multiplied by -1 under a 180° degree rotation (a symmetry denoted by π). Notice also how the sign and the magnitude of the η 's in the figure are connected with the shape, orientation, and sign of the corresponding atomic orbitals.

To implement the LCAO method, we need to know which atomic orbitals to use for each atom. Obviously, the more atomic orbitals involved, the better the approximation is. The *minimum* number of atomic orbitals to be employed is as follows.

For atoms in columns IA (1) and IB (11) of the periodic table (alkalis and noble metals), we use the partially occupied s orbital; for atoms in columns IIA (2) and IIB (12), we use the highest fully occupied s orbital; for atoms in the columns IIIB (13)–VIIB (17), we use the partially occupied p orbital, the other two p orbitals of the same energy level, and the s orbital with the same principal quantum number.

We conclude this subsection by pointing out that atomic orbitals belonging to different atoms are not orthogonal to each other; furthermore, there are non-negligible matrix elements between atomic orbitals belonging to atoms that are second or third neighbors. The simplified version of the LCAO based on (F.6–F.10) ignores these complications at the expense of the quantitative accuracy of the results.

F.2 Some Important Examples

F.2.1 Covalent Diatomic Molecule

The simplest such molecule is one consisting of two identical alkalis, e.g., Na_2 . In this case only two, ϕ_1 , ϕ_2 , atomic orbitals are involved; ϕ_1 is the 3s atomic orbital of Na atom 1 and ϕ_2 is the 3s atomic orbital of Na atom 2. The diagonal matrix element of each is $\varepsilon_0 = -4.95$ eV according to Table B.3, while the off-diagonal denoted usually by V_2 is (according to (F.6) and (F.7)) equal to $-1.32\hbar^2/m_e d^2 \simeq -1.06$ eV (the experimental value of the bond length $d = 3.078$ Å was used for obtaining the numerical value of V_2). Then the system (F.4) takes the form (assuming that ϕ_1 and ϕ_2 are orthonormal)

$$(\varepsilon_0 - E) c_1 + V_2 c_2 = 0, \quad (\text{F.15})$$

$$V_2 c_1 + (\varepsilon_0 - E) c_2 = 0. \quad (\text{F.16})$$

In order to have non-zero solutions, the determinant $(\varepsilon_0 - E)^2 - V_2^2$ must be set equal to zero, which leads to two eigenvalues of energy:

$$E_b = \varepsilon_0 + V_2, \quad (\text{F.17})$$

$$E_a = \varepsilon_0 - V_2. \quad (\text{F.18})$$

The solution corresponding to the eigenenergy E_b (which is the lowest one, since V_2 is negative) is the symmetric one; $c_1 = c_2$, i. e.,

$$\psi_b = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2), \quad (\text{F.19})$$

while the one corresponding to the higher eigenenergy, E_a , is the antisymmetric one; $c_1 = -c_2$, i.e.,

$$\psi_a = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2). \quad (\text{F.20})$$

The separation energy between the ground state ψ_b and the excited state ψ_a is $2|V_2| \simeq 2.12 \text{ eV}$ (the corresponding experimental value is 2.6 eV).

Now, if we place the two valence electrons (one was originally in the atomic orbital ϕ_1 and the other in ϕ_2) on the molecular orbital ψ_b , their energy would be $2E_b + U$; the additional positive term U is due partly to the Coulomb repulsion of the two electrons being now on the same molecular orbital and partly to the overlap of the ionic electronic clouds. Hence, the lowering of the total energy due to the formation of the molecule is $2\varepsilon_0 - 2E_b - U = 2|V_2| - U$; usually, U is in the range $(0.5-1.55)|V_2|$, which implies that the dissociation energy, D_0 , is in the range

$$D_0 = (0.45 - 1.5)|V_2|, \quad (\text{F.21})$$

the larger values of the coefficient in (F.21) are often associated with long single bonds in solids and the smaller with shorter multiple bonds in molecules.

The conclusion is that the doubly occupied molecular orbital ψ_b leads to a lowering of the total energy, and hence, to the formation of the molecule. For this reason, ψ_b is called *bonding* molecular orbital and the corresponding eigenenergy, E_b , bonding molecular level. In contrast, if we place both electrons in the molecular orbital ψ_a , the total energy will be raised by $2|V_2| + U'$ (where U' is positive and similar but not identical to U), and consequently, no molecule will be formed. For this reason, ψ_a and E_a are called *antibonding* molecular orbital and molecular level respectively. Notice also that in the case where both ϕ_1 and ϕ_2 were originally doubly occupied (as in alkaline earths), we have to place the four electrons in such a way that two are in the bonding states and two in the antibonding states. Hence, no energy gain will result and consequently no molecular orbitals will be formed² in the ground state.

² The absence of molecular *orbital* formation in the ground state does not necessarily imply the absence of molecule formation. It was mentioned in Sect. 2.2 that as two atoms approach each other, there is always at large relative distance rearrangement of electrons *within each atom*, which leads to the van der Waals attraction. If there is eventually energetically favorable molecular orbital formation (i. e., *spreading of each electron to both atoms*), this dominates over the van der Waals attraction; otherwise the molecule formation and survival at finite temperature will be determined by the weak van der Waals attraction on the one hand, and the various increases in the total kinetic energy on the other.

As another example of covalent diatomic molecule, let us consider N_2 . Here we have eight atomic orbitals involved: ϕ_{1a}, ϕ_{2a} ($a = s, p_x, p_y, p_z$; the indices 1,2 refer to atom 1 and atom 2 respectively; axis x coincides with the molecular axis). Each of the atomic orbitals ϕ_{1s} and ϕ_{2s} is doubly occupied and consequently we can, as a first approximation, omit these orbitals, since they do not lead to the lowering of the total energy by molecular orbital formation.³ Furthermore, based on (F.9) and (F.10), the sets (ϕ_{1x}, ϕ_{2x}) , (ϕ_{1y}, ϕ_{2y}) , and (ϕ_{1z}, ϕ_{2z}) are decoupled from each other (because $\ell_x = 1, \ell_y = \ell_z = 0$). Hence, to a first approximation, the electronic structure of N_2 was reduced to the solution to three independent 2×2 systems as in (F.15) and (F.16) with $\varepsilon_0 = -13.84 \text{ eV}$ and $V_2 = 2.22\hbar^2/m_e d^2 = 14.12 \text{ eV}$ for the set (ϕ_{1x}, ϕ_{2x}) and $V_2 = -0.63\hbar^2/m_e d^2 = -4 \text{ eV}$ for the sets (ϕ_{1y}, ϕ_{2y}) and (ϕ_{1z}, ϕ_{2z}) . Thus in the molecule N_2 , the two atoms are held together by a triple bond consisting of a strong σ bond (strength⁴ of about 6.35 eV) and 2 weak π bonds (strength of each of about 1.8 eV) adding to a dissociation energy of about 9.95 eV vs. 9.75 eV for the experimental value.

F.2.2 Ionic Diatomic Molecule

As an example, let us consider the molecule NaCl. For the Na atom, we shall employ the singly occupied $3s$ atomic orbital denoted by ϕ_1 and for Cl atom only the singly occupied $3p_x$ denoted by ϕ_2 (the orbitals $3p_y$ and $3p_z$ of Cl are doubly occupied and not coupled to ϕ_1 , while the $3s$ of Cl is also doubly occupied). As a result of using only two atomic orbitals, (F.4) becomes:

$$(\varepsilon_1 - E)c_1 + V_2 c_2 = 0, \quad (\text{F.22})$$

$$V_2 c_1 + (\varepsilon_2 - E)c_2 = 0, \quad (\text{F.23})$$

where $\varepsilon_1 = -4.95 \text{ eV}$, $\varepsilon_2 = -13.78 \text{ eV}$ and $V_2 \equiv V_{s,p_x} = 1.42\hbar^2/m_e d^2 = 1.94 \text{ eV}$ (using the experimental value of $d = 2.36 \text{ \AA}$).

By defining

$$\varepsilon \equiv \frac{\varepsilon_1 + \varepsilon_2}{2}, \quad (\text{F.24})$$

and

$$V_3 \equiv \frac{\varepsilon_1 - \varepsilon_2}{2}, \quad (\text{F.25})$$

and by setting the determinant of (F.22 and F.23) equal to zero, we find the bonding and antibonding molecular eigenenergies

$$E_b = \varepsilon - \sqrt{V_2^2 + V_3^2}, \quad (\text{F.26})$$

$$E_a = \varepsilon + \sqrt{V_2^2 + V_3^2}, \quad (\text{F.27})$$

³ However, there is a coupling of the ϕ_{1s} orbital with the ϕ_{2x} orbital and a coupling of the ϕ_{1x} orbital to the ϕ_{2s} orbital. These couplings are also omitted for the sake of simplicity.

⁴ We took the lowest value of the coefficient in (F.21), because this is a very short triple bond.

the corresponding molecular orbitals are

$$\psi_b = \frac{1}{\sqrt{2}} \left[(1 - a_p)^{1/2} \phi_1 + (1 + a_p)^{1/2} (-\phi_2) \right], \quad (\text{F.28})$$

$$\psi_a = \frac{1}{\sqrt{2}} \left[(1 + a_p)^{1/2} \phi_1 - (1 - a_p)^{1/2} (-\phi_2) \right], \quad (\text{F.29})$$

where $-\phi_2$ has the positive lobe pointing towards the Na atom and

$$a_p \equiv \frac{V_3}{\sqrt{V_2^2 + V_3^2}}. \quad (\text{F.30})$$

The quantity a_p is called the *polarity* index and gives the electronic charge transfer (in units of $-e$) from the Na atom to the Cl atom when the two electrons are placed in the lowest energy molecular orbital ψ_b . Indeed, according to (F.28) the probability of finding an electron in the atomic orbital ϕ_2 (i.e., in the $3p_x$ orbital of Cl) is $(1 + a_p)/2$; hence, the average total electronic charge in ϕ_2 is $-2e(1 + a_p)/2 = -e(1 + a_p)$ and consequently the excess negative charge in Cl is $-ea_p$, which is the same as the missing electronic charge from the Na atom. If we place the two electrons in the antibonding state ψ_a , the electronic charge transfer is again $-ea_p$, but this time the transfer is from the Cl to the Na atom: an energetically unfavorable situation that explains the higher energy of the ψ_a orbital.

The energy gain resulting from the placing of the two electrons in the bonding molecular orbital is given by $2\varepsilon - 2E_b - U'' = 2\sqrt{V_2^2 + V_3^2} - U''$, where U'' is similar to the quantity U introduced in Sect. F.2.1.⁵

The energy levels before and after the formation of the molecule NaCl are shown in Fig. F.2.

F.3 Hybridization of Atomic Orbitals

Examining the molecule N_2 , we have shown that the system of eight equations with eight unknown was reduced to three sets of two equation with two unknowns each, plus two unmodified atomic orbitals. This was achieved by omitting some small matrix elements of the Hamiltonian in comparison with the dominant ones. Usually we are not so lucky: there are no small matrix elements such that their omission reduces the problem to simpler ones as, for example, to independent sets of two equations with two unknowns. In these

⁵ When the polarity index a_p is close to one, we can estimate the value of the dissociation energy D_0 as $D_0 = a_p e^2 / 4\pi\epsilon_0 d - a_p \Delta E$, where ΔE is the energy cost of transferring one electron from the Na to the Cl atom when their distance is infinite; $\Delta E = I - E_{\text{af}}$, where I is the ionization energy of Na ($I = 5.14$ eV) and E_{af} is the electron affinity of the Cl atom ($E_{\text{af}} = 3.61$ eV). The *electron affinity* of an atom is defined as the minimum energy required to extract an electron from the ground state of the singly charged anion of that atom (assuming that such an anion exists). Notice that in our estimates of the dissociation energy, we have omitted the zero point motion of the ions, which reduces D_0 by $\hbar\omega_0/2$.

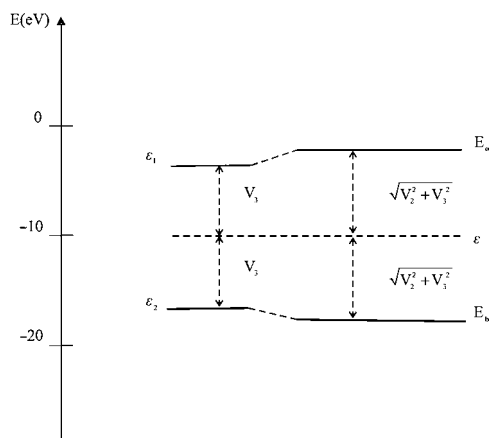


Fig. F.2. Atomic and molecular levels of *Na*, *Cl*, and *NaCl*

common cases, there are two options. The first one is to solve the problem numerically in the computer without any further approximations beyond that of the LCAO. The second one aims at simplicity and physical clarity at the expense of accuracy; the idea is to make a change of the basis from the atomic orbitals to a *predefined* combination of atomic orbitals belonging to the same atom. These combinations are known as *hybrid* atomic orbitals. The hope is that the matrix elements of the Hamiltonian in the new basis can be separated in two groups: the large ones and the small ones. Omitting the latter, the problem may be simplified and even be reduced to independent sets of two equations with two unknowns as it happened naturally in the N_2 molecule.

For atoms belonging to the III B (13)–VIIB (17) columns of the periodic table of the elements, where s and p_x, p_y, p_z orbitals are involved in molecular formation, there are *three widely used predefined hybrid atomic orbitals*.

We stress that the hybrids do not provide exact solutions to the stereochemistry or any other property of the molecules; nevertheless, they are quite often reasonable approximations.

F.3.1 sp^1 Hybrid Atomic Orbitals

In this case the hybrids involve an equal weight combination of the s and one of the p orbitals (e. g. the p_x orbital). Thus, the four member atomic orbital basis, s, p_x, p_y, p_z , is replaced by the following four member basis:

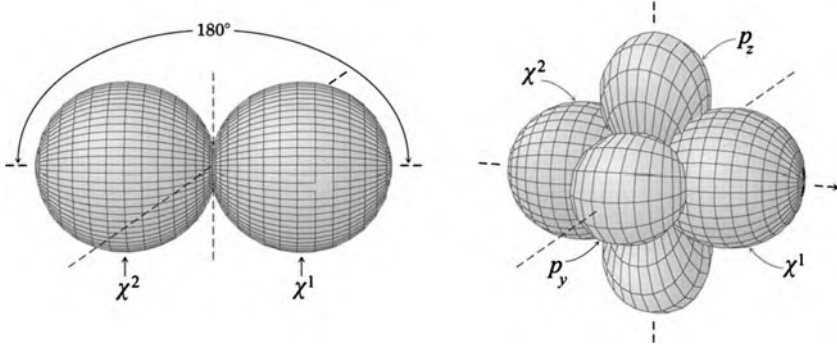


Fig. F.3. Schematic representations of the two hybrid atomic orbitals sp^1 (left) and the four member basis χ^1, χ^2, p_y, p_z . (after [C66])

$$\chi^1 = \frac{1}{\sqrt{2}}(\phi_s + \phi_x), \quad (\text{F.31})$$

$$\chi^2 = \frac{1}{\sqrt{2}}(\phi_s - \phi_x), \quad (\text{F.32})$$

$$p_y, \quad (\text{F.33})$$

$$p_z, \quad (\text{F.34})$$

which is shown schematically in Fig. F.3. ($p_i \equiv \phi_i, i = x, y, z$)

The next step is to calculate the matrix elements of the Hamiltonian in the new basis. We have the following results for orbitals of the same atom:

$$\varepsilon_h \equiv \langle \chi^1 | \hat{H} | \chi^1 \rangle = \frac{1}{2} \left[\langle \phi_s | \hat{H} | \phi_s \rangle + \langle \phi_x | \hat{H} | \phi_x \rangle \right] = \frac{\varepsilon_s + \varepsilon_p}{2}, \quad (\text{F.35})$$

$$\varepsilon_h \equiv \langle \chi^2 | \hat{H} | \chi^2 \rangle = \frac{1}{2} \left[\langle \phi_s | \hat{H} | \phi_s \rangle + \langle \phi_x | \hat{H} | \phi_x \rangle \right] = \frac{\varepsilon_s + \varepsilon_p}{2}, \quad (\text{F.36})$$

$$-V_1 \equiv \langle \chi^2 | \hat{H} | \chi^1 \rangle = \frac{1}{2} \left[\langle \phi_s | \hat{H} | \phi_s \rangle - \langle \phi_x | \hat{H} | \phi_x \rangle \right] = \frac{\varepsilon_s - \varepsilon_p}{2}, \quad (\text{F.37})$$

$$\langle p_y | \hat{H} | p_y \rangle = \langle p_z | \hat{H} | p_z \rangle = \varepsilon_p. \quad (\text{F.38})$$

All other matrix elements of the Hamiltonian between orbitals (hybrids or not) of the same atom are zero. Notice that the off-diagonal matrix element $\langle \chi^2 | \hat{H} | \chi^1 \rangle = (\varepsilon_s - \varepsilon_p)/2$ is not zero. This is a disadvantage of the new basis compared with the original atomic orbitals. To see its advantages, let us consider the molecule C_2H_2 , the hybrids and non-hybrids atomic orbitals of which are shown in Fig. F.4.

Let us consider the matrix element of the Hamiltonian between the hybrids χ_1^1 and χ_2^2 :

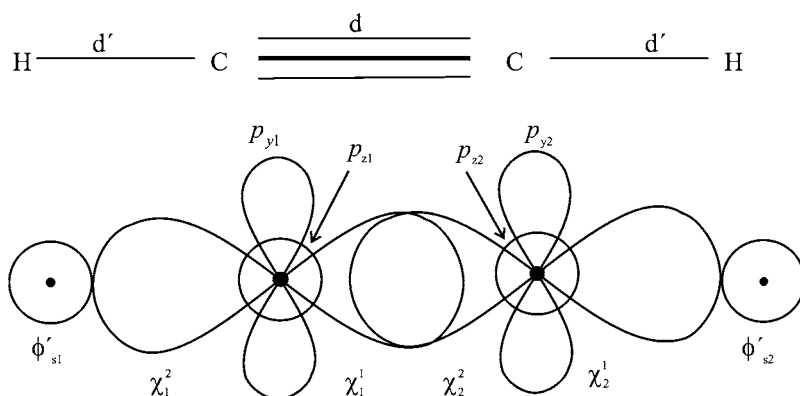


Fig. F.4. The molecule C_2H_2 and its ten atomic orbitals (four hybrids and six non-hybrids) involved in the molecule formation. There are five molecular bonding orbitals (shown as straight segments in the figure above) and five antibonding. The strong C–C bond (thick line) is due to the molecular bonding orbital involving χ_1^1 and χ_2^2 , while the two weaker C–C bonds involve the two pairs (p_{y1}, p_{y2}) and (p_{z1}, p_{z2}) . There are also two bonds between carbon hybrid and the hydrogen s

$$\begin{aligned}
 \langle \chi_1^1 | \hat{H} | \chi_2^2 \rangle &= \frac{1}{2} \left[\langle \phi_{s1} | \hat{H} | \phi_{s2} \rangle - \langle \phi_{s1} | \hat{H} | \phi_{x2} \rangle + \langle \phi_{x1} | \hat{H} | \phi_{s2} \rangle \right. \\
 &\quad \left. - \langle \phi_{x1} | \hat{H} | \phi_{x2} \rangle \right] \\
 &= \frac{1}{2} [-1.32 - 1.42 - 1.42 - 2.22] \frac{\hbar^2}{m_e d^2} = -3.19 \frac{\hbar^2}{m_e d^2}. \quad (F.39)
 \end{aligned}$$

We see that this matrix element is larger (in absolute value) than any other we have encountered so far. All the other matrix elements of the hybrid orbital χ_1^1 are considerably smaller.

Indeed we have, by employing (F.37), (F.11–F.14), (F.31), and (F.32),

$$\langle \chi_1^1 | \hat{H} | \chi_1^2 \rangle = \frac{\varepsilon_s - \varepsilon_p}{2}, \quad (F.40)$$

$$\langle \chi_1^1 | \hat{H} | \phi'_{s1} \rangle = \frac{1}{\sqrt{2}} [-1.32 + 1.42] \frac{\hbar^2}{m_e d'^2} = 0.07 \frac{\hbar^2}{m_e d'^2}, \quad (F.41)$$

$$\langle \chi_1^1 | \hat{H} | \chi_2^1 \rangle = \frac{1}{2} [-1.32 + 1.42 - 1.42 + 2.22] \frac{\hbar^2}{m_e d^2} = 0.45 \frac{\hbar^2}{m_e d^2}, \quad (F.42)$$

$$\begin{aligned}
 \langle \chi_1^1 | \hat{H} | \phi_{s2}' \rangle &= \frac{1}{\sqrt{2}} [-1.32 - 1.42] \frac{\hbar^2}{m_e (d + d')^2} = -1.94 \frac{\hbar^2}{m_e (d + d')^2}. \\
 &\quad (F.43)
 \end{aligned}$$

Furthermore,

$$\langle \chi_1^2 | \hat{H} | \chi_2^2 \rangle = \frac{1}{2} [-1.32 + 1.42 + 1.42 - 2.22] \frac{\hbar^2}{m_e d^2} = -0.35 \frac{\hbar^2}{m_e d^2}. \quad (F.44)$$

Although formulae (F.6–F.10) and (F.11–F.14) are not applicable to hydrogen and to second nearest neighbors, it is clear that all matrix elements in (F.40–F.44) are much smaller than the one in (F.39). This is explained by simple inspection of Fig. F.4, and by taking into account that, if the overlap of two orbitals is very small, the corresponding matrix element of the Hamiltonian will also be very small.

Thus by omitting as a first approximation all the matrix elements in (F.40–F.44) and the ones that are equal to them, we end up with five independent systems of two equations with two unknowns each, i.e., $(\phi'_{s1}$ and $\chi_1^2)$, $(p_{y1}$ and $p_{y2})$, $(p_{z1}$, $p_{z2})$, $(\chi_1^1$ and $\chi_2^2)$, $(\chi_2^1$ and $\phi'_{s2})$. The solution to these five 2×2 systems leads to five bonding and five antibonding molecular orbitals. The three pairs of bonding and antibonding orbitals between the carbon atoms employ the χ_1^1 , χ_2^2 hybrids, the p_{y1} , p_{y2} , and the p_{z1} , p_{z2} atomic orbital respectively. The other two pairs of bonding and antibonding molecular orbitals are between the hydrogen and the carbon atoms and employ the ϕ'_{s1} , χ_1^2 and the χ_2^1 and ϕ'_{s2} orbitals respectively. The readers may write down the wave functions of all ten molecular orbitals and the corresponding molecular levels in analogy with (F.15 and F.16), (F.19 and F.20), (F.26 and F.27), and (F.28 and F.29), where V_2 is equal to $-3.19\hbar^2/m_e d^2$ for the strong carbon–carbon σ bond and $-0.63\hbar^2/m_e d^2$ for the other two weaker carbon–carbon π bonds. For the two hydrogen–carbon σ bonds, V_2 can be taken⁶ as $-1.94\hbar^2/m_e d^2$ and $V_3 = (\varepsilon_H - \varepsilon_h)/2$, where $\varepsilon_H = -13.6$ eV and $\varepsilon_h = (\varepsilon_{cs} + \varepsilon_{cp})/2 = -15.22$ eV.

Let us return to the small matrix elements (F.40–F.44) that we have ignored so far. These matrix elements will create a coupling between the σ C–C molecular orbitals and the σ H–C and C–H molecular orbitals to the left and the right respectively. For example, the matrix element V_{2bb} of the Hamiltonian between the bonding H–C σ molecular orbital, $\psi_{HCb} = [(1 - a_p)^{1/2} \phi'_{1s} + (1 + a_p)^{1/2} \chi_1^2] / \sqrt{2}$, and the bonding C–C σ molecular orbital, $\psi_{ccb} = [\chi_1^1 + \chi_2^2] / \sqrt{2}$, is approximately⁷ equal to

$$V_{2bb} \equiv \langle \psi_{HCb} | \hat{H} | \psi_{CCb} \rangle = \langle \psi_{CCb} | \hat{H} | \psi_{CHb} \rangle \simeq -\frac{(1 + a_p)^{1/2}}{2} V_1, \quad (\text{F.45})$$

where

⁶ We remind the readers that formulae (F.6–F.10) and (F.11–F.14) produce large errors when applied to hydrogen (see [SS76]).

⁷
$$\begin{aligned} \langle \psi_{HCb} | \hat{H} | \psi_{CCb} \rangle &= \frac{1}{2} \left[(1 - a_p)^{1/2} \langle \phi'_{1s} | \hat{H} | \chi_1^1 \rangle + (1 + a_p)^{1/2} \langle \phi'_{1s} | \hat{H} | \chi_2^2 \rangle \right. \\ &\quad \left. + (1 + a_p)^{1/2} \langle \chi_1^2 | \hat{H} | \chi_1^1 \rangle + (1 + a_p)^{1/2} \langle \chi_1^2 | \hat{H} | \chi_2^2 \rangle \right] = \\ &= \frac{(1 - a_p)^{1/2} \hbar^2}{2m_e} \left[\frac{0.07}{d^2} - \frac{1.97}{(d + d')^2} \right] + \frac{(1 + a_p)^{1/2}}{2} \left[\frac{\varepsilon_s - \varepsilon_p}{2} + \frac{0.45\hbar^2}{m_e d^2} \right] \end{aligned}$$

It turns out that among the matrix elements in (F.40–F.44) the largest one is the one in (F.40). Hence, to a first approximation, we have (F.45–F.46).

$$V_1 \equiv \frac{\varepsilon_p - \varepsilon_s}{2}. \quad (\text{F.46})$$

F.3.2 sp^2 Hybrid Atomic Orbitals

In this case the hybrids involve a combination of s and two of the three p orbitals (e.g., p_x and p_y). In all hybrids, the probability of the s orbital is half the probability of the two p orbitals taken together. This means that the hybrids are of the form

$$\chi^i = \frac{1}{\sqrt{3}} [\phi_s + \lambda_{xi}\phi_x + \lambda_{yi}\phi_y], \quad i = 1, 2, 3, \quad (\text{F.47})$$

with

$$\lambda_{xi}^2 + \lambda_{yi}^2 = 2. \quad (\text{F.48})$$

The demand for orthogonality of the three hybrids implies that

$$1 + \lambda_{xi}\lambda_{xj} + \lambda_{yi}\lambda_{yj} = 0, \quad i \neq j = 1, 2, 3. \quad (\text{F.49})$$

Without loss of generality, we can choose the direction of the x -axis so that $\lambda_{y1} = 0$; then (F.48) implies that $\lambda_{x1} = \pm\sqrt{2}$. If we choose the upper sign, it follows from (F.49) that $\lambda_{xj} = -1/\sqrt{2}$ for $j = 2, 3$ and $\lambda_{y2} = \sqrt{3/2}$, while $\lambda_{y3} = -\sqrt{3/2}$.

Thus the new full basis has the form

$$\chi^1 = \frac{1}{\sqrt{3}} (\phi_s + \sqrt{2}p_x), \quad (\text{F.50})$$

$$\chi^2 = \frac{1}{\sqrt{3}} \left(\phi_s - \frac{1}{\sqrt{2}}p_x + \sqrt{\frac{3}{2}}p_y \right), \quad (\text{F.51})$$

$$\chi^3 = \frac{1}{\sqrt{3}} \left(\phi_s - \frac{1}{\sqrt{2}}p_x - \sqrt{\frac{3}{2}}p_y \right), \quad (\text{F.52})$$

$$p_z. \quad (\text{F.53})$$

The three sp^2 hybrids of (F.50–F.52) as well as the p_z are shown schematically in Fig. F.5.

If we had chosen the lower sign in $\lambda_{x1} = \pm\sqrt{2}$, we would have obtained a picture resulting from Fig. F.5 by a reflection with respect to the origin; this means that in the formulae (F.50–F.52) p_x should go to $-p_x$ and p_y should go to $-p_y$. In Fig. F.6 we show how the sp^2 hybrids are involved in the structure of the molecule C_2H_4 .

Let us calculate the matrix elements of the Hamiltonian in the basis (F.50–F.53). We find the following results between hybrids of the same atom (see Fig. F.5):

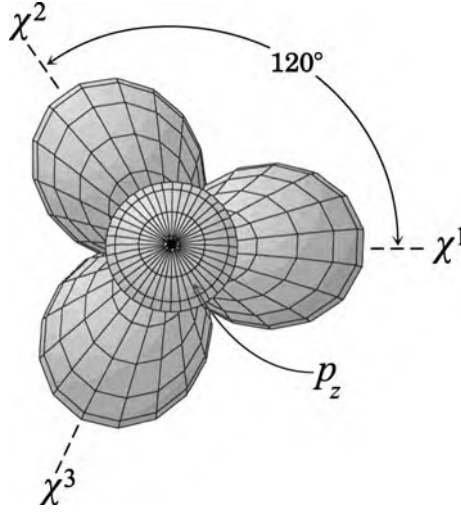


Fig. F.5. The three sp^2 atomic hybrids (consisting of linear combinations of the ϕ_s , p_x , p_y orbitals of the same atom as in (F.50–F.52) are coplanar and form angles of 120° among themselves. The unhybridized orbital p_z is perpendicular to this page (after [C66])

$$\langle \chi^i | \hat{H} | \chi^i \rangle = \frac{1}{3} \left[\langle \phi_s | \hat{H} | \phi_s \rangle + 2 \langle p_x | \hat{H} | p_x \rangle \right] = \frac{\varepsilon_s + 2\varepsilon_p}{3}, \quad i = 1, 2, 3, \quad (\text{F.54})$$

$$\langle \chi^i | \hat{H} | \chi^j \rangle = \frac{1}{3} \left[\langle \phi_s | \hat{H} | \phi_s \rangle - \langle p_x | \hat{H} | p_x \rangle \right] = \frac{\varepsilon_s - \varepsilon_p}{3}, \quad i \neq j. \quad (\text{F.55})$$

The big matrix element between oppositely directed sp^2 orbitals (belonging to *neighboring* atoms), such as the χ^1 , $\chi^{1'}$ in Fig. F.6, is equal to

$$\begin{aligned} \langle \chi^1 | \hat{H} | \chi^{1'} \rangle &= \frac{1}{3} \left[\langle \phi_s | \hat{H} | \phi'_s \rangle - \sqrt{2} \langle \phi_s | \hat{H} | p'_x \rangle + \sqrt{2} \langle p_x | \hat{H} | \phi'_s \rangle \right. \\ &\quad \left. - \sqrt{2} \langle p_x | \hat{H} | p'_x \rangle \right] = \frac{1}{3} \left[-1.32 - 1.42\sqrt{2} - 1.42\sqrt{2} - 2 \times 2.22 \right] \frac{\hbar^2}{m_e d^2} \\ &= -3.26 \frac{\hbar^2}{m_e d^2}. \end{aligned} \quad (\text{F.56})$$

F.3.3 sp^3 Hybrid Atomic Orbitals

In this case the hybrids involve a combination of s and all three of the p orbitals; the latter collectively have three times the probability compared with that of the s orbital.

Thus the hybrids have the form

$$\chi^i = \frac{1}{2} [\phi_s + \lambda_{xi} p_x + \lambda_{yi} p_y + \lambda_{zi} p_z], \quad i = 1, 2, 3, 4, \quad (\text{F.57})$$

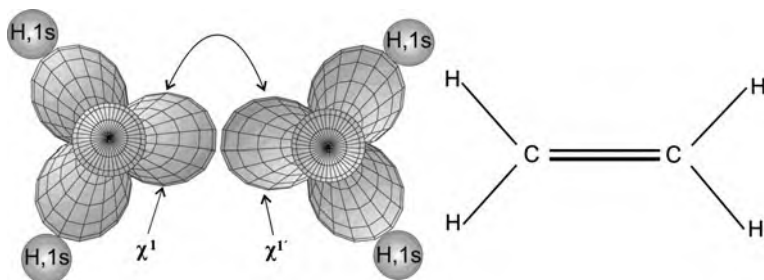


Fig. F.6. Using the sp^2 hybrid atomic orbitals of the two carbon atoms, we can reduce to a first approximation the problem of the 12 atomic orbitals involved in the formation of the molecule C_2H_4 to six independent sets of two equations with two unknowns of the form of (F.15 and F.16) (between the two sp^2 , χ^1 and $\chi^{1'}$ and the two p_z of the two carbon atoms) and (F.22 and F.23) (four equivalent sets between 1s of hydrogen and the nearby sp^2 of carbon). By simple inspection, one can deduce that C_2H_4 is a planar molecule with the hydrogenic bonds forming approximately 120° angles. Matrix elements as the one in (F.55) would create couplings among the resulting molecular orbitals

with

$$\lambda_{xi}^2 + \lambda_{yi}^2 + \lambda_{zi}^2 = 3, \quad i = 1, \dots, 4. \quad (\text{F.58})$$

The orthogonality of the four χ^i s leads to the equations

$$1 + \lambda_{xi}\lambda_{xj} + \lambda_{yi}\lambda_{yj} + \lambda_{zi}\lambda_{zj} = 0, \quad i \neq j, \quad i, j = 1, \dots, 4. \quad (\text{F.59})$$

If we choose for $i = 1$ the set $\lambda_{x1} = \lambda_{y1} = \lambda_{z1} = 1$, then the other three sets satisfying (F.58) and (F.59) are $\{\lambda_{x2} = 1, \lambda_{y2} = \lambda_{z2} = -1\}$, $\{\lambda_{x3} = \lambda_{z3} = -1, \lambda_{y3} = 1\}$, $\{\lambda_{x4} = \lambda_{y4} = -1, \lambda_{z4} = 1\}$.

Hence, according to this choice of the λ 's, the four sp^3 hybrids (Fig. F.7) are

$$\chi^1 = \frac{1}{2} [\phi_s + p_x + p_y + p_z], \quad (\text{F.60})$$

$$\chi^2 = \frac{1}{2} [\phi_s + p_x - p_y - p_z], \quad (\text{F.61})$$

$$\chi^3 = \frac{1}{2} [\phi_s - p_x + p_y - p_z], \quad (\text{F.62})$$

$$\chi^4 = \frac{1}{2} [\phi_s - p_x - p_y + p_z]. \quad (\text{F.63})$$

Another common set of sp^3 results from the one in (F.60–F.63) by reflection with respect to the origin, i.e., by the replacements, $p_x \rightarrow -p_x$, $p_y \rightarrow -p_y$, and $p_z \rightarrow -p_z$. In general, any rigid rotation or reflection of the cartesian axes relative to the four sp^3 hybrids ($x, y, z \rightarrow x', y', z'$) produce different but

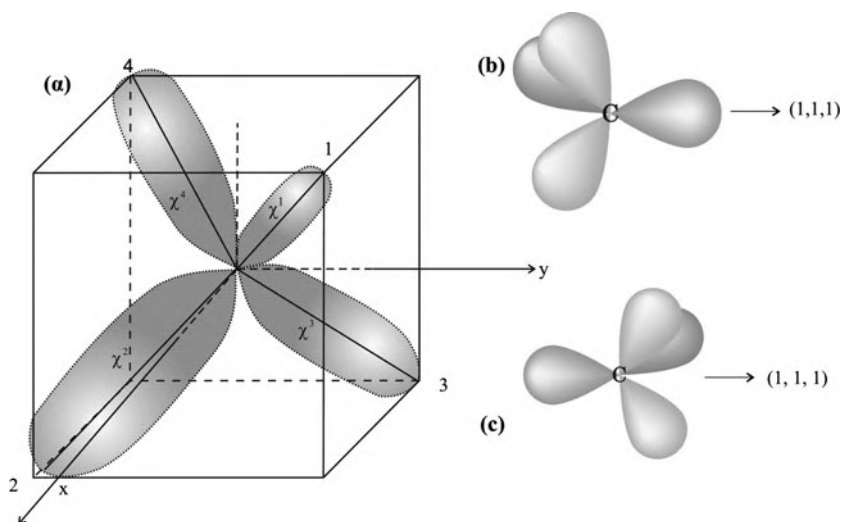


Fig. F.7. (a) Schematic representation of the four sp^3 hybrid orbitals $\chi^1, \chi^2, \chi^3, \chi^4$, which point along the direction $(1, 1, 1), (1, \bar{1}, \bar{1}), (\bar{1}, 1, \bar{1})$, and $(\bar{1}, \bar{1}, 1)$ from the center of the cube to the apexes denoted by 1, 2, 3, and 4 respectively. The $\cos \phi$, where ϕ is the angle between any pair of sp^3 hybrids, is $-1/3$ which means that $\phi = 109.47^\circ$ (this value is the same for any set of λ 's satisfying (F.58, 59)). (b) and (c) rigid rotation and rotation/reflection respectively of the four sp^3 orbitals shown in (a)

equivalent expressions of the sp^3 hybrids in terms of p_x, p_y, p_z ⁸. A case where both sets of sp^3 orbitals are employed is that of the molecule C_2H_6 shown in Fig. F.8.

The matrix elements of the Hamiltonian between sp^3 orbitals of the same atom are given by the following expressions:

$$\begin{aligned} \langle \chi^i | \hat{H} | \chi^i \rangle &= \frac{1}{4} \left[\langle \phi_s | \hat{H} | \phi_s \rangle + \langle p_x | \hat{H} | p_x \rangle \right. \\ &\quad \left. + \langle p_y | \hat{H} | p_y \rangle + \langle p_z | \hat{H} | p_z \rangle \right] = \frac{\varepsilon_s + 3\varepsilon_p}{4}, \quad i = 1, \dots, 4, \end{aligned} \quad (F.64)$$

$$\begin{aligned} \langle \chi^i | \hat{H} | \chi^j \rangle &= \frac{1}{4} \left[\langle \phi_s | \hat{H} | \phi_s \rangle + \langle p_x | \hat{H} | p_x \rangle \right. \\ &\quad \left. - \langle p_y | \hat{H} | p_y \rangle - \langle p_z | \hat{H} | p_z \rangle \right] = \frac{\varepsilon_s - \varepsilon_p}{4}, \quad i \neq j, \quad i, j = 1, \dots, 4. \end{aligned} \quad (F.65)$$

⁸ E.g., a less symmetric but more convenient for calculations form of the four sp^3 hybrids (F.60–F.63) results if we choose the x' axis along $1, 1, 1$ and y' axis such that χ^2 to be in x', y' plane. We have then $\chi^1 = (s + \sqrt{3}p_{x'})/2$, $\chi^2 = (s - \sqrt{1/3}p_{x'} - \sqrt{8/3}p_{y'})/2$, $\chi^3 = (s - \sqrt{1/3}p_{x'} + \sqrt{2/3}p_{y'} - \sqrt{2}p_{z'})/2$, $\chi^4 = (s - \sqrt{1/3}p_{x'} + \sqrt{2/3}p_{y'} + \sqrt{2}p_{z'})/2$. The readers may easily verify that this set satisfies (F.58) and (F.59).

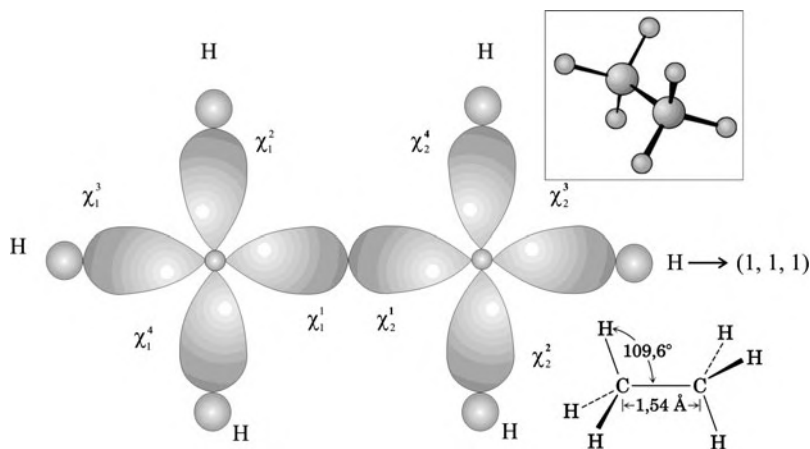


Fig. F.8. Schematic 2D representation of the eight sp^3 non-coplanar (see insert) hybrid orbitals associated with the two carbon atoms and the six s orbitals associated with the six hydrogen atoms of the molecule C_2H_6 . With the use of the sp^3 orbitals, the problem of the 14 coupled atomic orbitals is reduced approximately to seven sets of two equations with two unknowns. The stereochemistry of the molecule is also determined since all angles between pairs of bonds ending at each carbon atom are approximately 110° . The bold subscript in χ_2^n means that $n = -1, \dots, -4$

The big matrix element between oppositely directed sp^3 orbitals belonging to *nearest neighboring* atoms, such as χ_1^1 and χ_2^1 in Fig. F.8, is obtained as follows:

We find first the values of the various $\eta_{s,j}$ as defined in (F.6)

$$\eta_{s,s} = -1.32, \quad (F.66)$$

$$\eta_{s,x} = \eta_{s,y} = \eta_{s,z} = \frac{1.42}{\sqrt{3}} = 0.8198, \quad (F.67)$$

$$\eta_{i,i} = 2.22\frac{1}{3} - 0.63\frac{2}{3} = 0.32, \quad i = x, y, z, \quad (F.68)$$

$$\eta_{i,j} = 2.85\frac{1}{3} = 0.95, \quad i \neq j, \quad i, j = x, y, z, \quad (F.69)$$

and, then we write:

$$\begin{aligned} \langle \chi_1^1 | \hat{H} | \chi_2^1 \rangle &= \frac{1}{4} \left[\langle \phi_s + p_x + p_y + p_z | \hat{H} | \phi'_s - p'_x - p'_y - p'_z \rangle \right] \\ &= \frac{1}{4} \{ -1.32 - 3 \times 0.8198 - [0.8198 + 0.32 + 2 \times 0.95] 3 \} \frac{\hbar^2}{2m_e d^2} \\ &= -3.22 \frac{\hbar^2}{2m_e d^2}. \end{aligned} \quad (F.70)$$

A much easier way to obtain (F.70) is to use the rotated system, x', y', z' ; then we have

$$\begin{aligned}\langle \chi_1^1 | \hat{H} | \chi_2^{\bar{1}} \rangle &= \frac{1}{4} \langle (s_1 + \sqrt{3}p_{x1}^1) | \hat{H} | (s_2 - \sqrt{3}p_{x'2}) \rangle \\ &= \frac{1}{4} [V_{ss\sigma} - \sqrt{3}V_{sp\sigma} + \sqrt{3}V_{ps\sigma} - 3V_{pp\sigma}] \\ &= \frac{1}{4} [-1.32 - 2\sqrt{3} \times 1.42 - 3 \times 2.22] \hbar^2/md^2 = -3.22 \hbar^2/md^2.\end{aligned}$$

We summarize the main results for the most important matrix elements between hybrid orbitals:

- the diagonal matrix element ε_h is given by:

$$\varepsilon_h = \frac{\varepsilon_s + \varepsilon_p}{2}, \quad \text{for sp hybrids,} \quad (\text{F.71})$$

$$\varepsilon_h = \frac{\varepsilon_s + 2\varepsilon_p}{3}, \quad \text{for sp}^2 \text{ hybrids,} \quad (\text{F.72})$$

$$\varepsilon_h = \frac{\varepsilon_s + 3\varepsilon_p}{4}, \quad \text{for sp}^3 \text{ hybrids.} \quad (\text{F.73})$$

- the off-diagonal matrix element between hybrids of the same atom is as follows:

$$-V_1 = \frac{\varepsilon_s - \varepsilon_p}{2}, \quad \text{for sp hybrids,} \quad (\text{F.74})$$

$$-V_1 = \frac{\varepsilon_s - \varepsilon_p}{3}, \quad \text{for sp}^2 \text{ hybrids,} \quad (\text{F.75})$$

$$-V_1 = \frac{\varepsilon_s - \varepsilon_p}{4}, \quad \text{for sp}^3 \text{ hybrids.} \quad (\text{F.76})$$

- the large matrix element, V_{2h} , between similar, oppositely directed hybrids belonging to nearest neighbor atoms (according to Harrison's choices, (F.11–F.13)) is given by:

$$V_{2h} = -3.19 \frac{\hbar^2}{m_e d^2}, \quad \text{for sp hybrids,} \quad (\text{F.77})$$

$$V_{2h} = -3.26 \frac{\hbar^2}{m_e d^2}, \quad \text{for sp}^2 \text{ hybrids,} \quad (\text{F.78})$$

$$V_{2h} = -3.22 \frac{\hbar^2}{m_e d^2}, \quad \text{for sp}^3 \text{ hybrids.} \quad (\text{F.79})$$

We point out that if the bonding is between different atoms and one or two hybrids are involved, ε_1 or ε_2 or both in (F.22–F.23) are replaced by ε_{h1} or ε_{h2} or by both respectively.

Finally we must stress that *the hybridization* of atomic orbitals of the same atom *costs energy*. The readers may verify that the increase in energy δE_h (named *promotion energy*) in *singly* populating the hybrids by the maximum number of electrons instead of the unhybridized atomic orbitals is given by

$$\delta E_h = (\varepsilon_p - \varepsilon_s) \quad m + 1 \leq n \leq 7 - m, \quad (\text{F.80})$$

where m refers to the type of hybrid, sp^m , $m = 1, 2, 3$, and n is the number of electrons per atom in the s and p orbitals; $3 \leq n \leq 7$.

Problem 4. Show that $\delta E_h = b(\varepsilon_p - \varepsilon_s)$, where $b = 5/4$, if $m = n = 3$, $b = nm/(m + 1)$, if $n \leq m + 1$ but not $m = n = 3$, and $b = (8 - n)/(m + 1)$, if $n \geq 7 - m$.

This energy increase is expected to be more than compensated for by the large energy decrease due to the strong bonding energy associated with the large matrix element V_{2h} between hybrids. Thus, δE_h is an energy investment that is expected to pay back by increasing $|V_{2h}|$ and strengthening the bonding energy. If δE_h is larger than the expected gain, hybridization is energy-unfavorable and it will not take place.

Question 1. Consider the water molecule H_2O . If unhybridized atomic orbitals of oxygen are used, what would be the value of the angle HOH? If sp^3 oxygen hybrids are used what would be the value of the angle HOH? What would the bonding energy be in each case?

Further Readings

- J. McMurry, *Organic Chemistry*, Brooks/Cole Publishing Company 1996, Chapter 1 [C66]. Some of the drawings in App. F were taken from this book.
- W.A. Harrison, *Electronic Structure and the Properties of Solids*, W.H. Freeman, San Francisco, 1980, Chapter 1 [SS76]; see also W.A. Harrison, *Elementary Electronic Structure*, World Scientific, Singapore, 1999, pp. 9–16, 22–31, 57–65 [SS84].

G

Boltzmann's Equation

The function to be determined by employing Boltzmann's equation (BE) is the density $f(\mathbf{r}, \mathbf{k}; t)$ of particles in a $2 \times D$ -dimensional phase space; $f(\mathbf{r}, \mathbf{k}, t)$ is defined by the relation

$$dN \equiv (2s + 1) \frac{d^D r d^D k}{(2\pi)^D} f(\mathbf{r}, \mathbf{k}; t),$$

where dN is the number of particles in the phase space volume element $d^D r d^D k$ around the point $\mathbf{r}, \mathbf{k}$ at time t . In what follows, we shall assume that the spin $s = 1/2$ for fermions and $s = 1$ for bosons. Since we specify both the position, $\mathbf{r}$, and the (crystal) momentum, $\hbar \mathbf{k}$, it is clear that we work within the framework of the semiclassical approximation.

If there were no interactions among the particles or collisions with defects and other departures from periodicity, the total time derivative, df/dt , would be equal to zero according to Liouville's theorem

$$\frac{df}{dt} \equiv \frac{\partial f}{\partial t} + \frac{\partial f}{\partial \mathbf{r}} \cdot \frac{d\mathbf{r}}{dt} + \frac{\partial f}{\partial \mathbf{k}} \cdot \frac{d\mathbf{k}}{dt} = 0. \quad (\text{G.1})$$

However, because of collisions with defects and particle interactions, the rhs of (G.1) is not zero but equal to $(\partial f / \partial t)_c$, where the subscript c indicates any kind of collision or interaction. The simplest expression of $(\partial f / \partial t)_c$ is through the introduction of a phenomenological relaxation time τ :

$$\left(\frac{\partial f}{\partial t} \right)_c \simeq -\frac{f - f_0}{\tau} \equiv -\frac{f_1}{\tau}, \quad f_1 \equiv f - f_0, \quad (\text{G.2})$$

where f_0 is the expression of f in a state of thermodynamic equilibrium,

$$f_0(E_{\mathbf{k}}) = \frac{1}{\exp[\beta(E_{\mathbf{k}} - \mu)] \pm 1}, \quad (\text{G.3})$$

and the chemical potential μ is determined by the condition

$$(2s + 1) \int \frac{d\mathbf{r} d\mathbf{k}}{(2\pi)^D} f_0(E_{\mathbf{k}}) = N.$$

In Chap. 5, we have shown that¹

$$\frac{1}{\tau} = v n_s \sigma_s = v n_s \int \frac{d\sigma_s}{d\Omega} (1 - \cos \theta) d\Omega, \quad (\text{G.4})$$

where v is an average of $\mathbf{v}_\mathbf{k} = \partial E_n(\mathbf{k}) / \hbar \partial \mathbf{k}$ over the solid angle. Notice that all quantities depend in general on the wave vector $\mathbf{k}$ and the band index n ; however, usually we assume that τ depends on $E_\mathbf{k}$ and n (for metals the assumption is that τ depends on E_F).

In (G.1) $d\mathbf{r}/dt = \mathbf{v}_\mathbf{k}$ and $d\mathbf{k}/dt = \hbar^{-1}q(\mathbf{E} + \mathbf{v}_\mathbf{k} \times \mathbf{B}/c)$, where $\mathbf{E}$ and $\mathbf{B}$ are the imposed electric and magnetic fields respectively and q is the charge of the carrier ($-e$ for electrons). Hence,

$$\begin{aligned} \frac{df}{d\mathbf{k}} \cdot \frac{d\mathbf{k}}{dt} &= \left(\frac{df_0}{d\mathbf{k}} + \frac{\partial f_1}{\partial \mathbf{k}} \right) \cdot \left(\mathbf{E} + \frac{\mathbf{v}_\mathbf{k}}{c} \times \mathbf{B} \right) \hbar^{-1}q \\ &\quad \cdot \left(\frac{\partial f_0}{\partial E_\mathbf{k}} \cdot \frac{\partial E_\mathbf{k}}{\partial \mathbf{k}} + \frac{\partial f_1}{\partial \mathbf{k}} \right) \cdot \left(\mathbf{E} + \frac{\mathbf{v}_\mathbf{k}}{c} \times \mathbf{B} \right) \hbar^{-1}q \quad (\text{G.5}) \\ &= q \frac{\partial f_0}{\partial E_\mathbf{k}} \mathbf{v}_\mathbf{k} \cdot \mathbf{E} + \frac{q}{\hbar c} \frac{\partial f_1}{\partial \mathbf{k}} \cdot (\mathbf{v}_\mathbf{k} \times \mathbf{B}). \end{aligned}$$

In the last relation we have used the fact that $(\partial E_\mathbf{k} / \partial \mathbf{k}) \cdot (\mathbf{v}_\mathbf{k} \times \mathbf{B}) = 0$, since $\partial E_\mathbf{k} / \partial \mathbf{k} = \hbar \mathbf{v}_\mathbf{k}$ and we have omitted the term $(\partial f_1 / \partial \mathbf{k}) \cdot \mathbf{E} \hbar^{-1}q$, since it is of second order in $\mathbf{E}$ (take into account that f_1 is of first order in $\mathbf{E}$). In calculating quantities as the conductivity, which represent linear response to $\mathbf{E}$, there is no need to keep terms of higher order than the first in $\mathbf{E}$.

If the fields $\mathbf{E}$ and $\mathbf{B}$ are taken as $\mathbf{r}$ - and t -independent, the density $f(\mathbf{r}, \mathbf{k}; t)$ does not depend on $\mathbf{r}$ and t and the linearized Boltzmann's equation takes the form

$$\frac{q}{\hbar c} \frac{\partial f_1}{\partial \mathbf{k}} \cdot (\mathbf{v}_\mathbf{k} \times \mathbf{B}) + \frac{f_1}{\tau} = -q \frac{\partial f_0}{\partial E_\mathbf{k}} \mathbf{v}_\mathbf{k} \cdot \mathbf{E}. \quad (\text{G.6})$$

We examine first the case of no magnetic field, $\mathbf{B} = 0$. Equation (G.6) gives immediately the solution

$$f_1(\mathbf{k}) = -q \tau \frac{\partial f_0}{\partial E_\mathbf{k}} \mathbf{v}_\mathbf{k} \cdot \mathbf{E}. \quad (\text{G.7})$$

We return now to the case where there is a nonzero magnetic field, $\mathbf{B}$, the direction of which is taken as the z -axis. We assume further that the collision term is given by (G.2) and (G.4). Instead of the triad k_x, k_y, k_z , we shall use the triad $\phi, E_\mathbf{k}, k_z$, where the phase $\phi = \phi(t) + \phi_0$ is given by the formula

$$\phi = \phi(t) + \phi_0 = \omega_c t + \phi_0,$$

and ω_c is the cyclotron frequency, $\omega_c = |q| B / m^* c$ (in SI $\omega_c = |q| B / m^*$).

¹ In Ch. 9, sect. 9.4 we have generalized the scattering cross-section σ_s to include inelastic collisions.

In the new variables, only ϕ changes with $\mathbf{B}$:

$$\frac{\partial f_1}{\partial \mathbf{k}} \cdot \left(\frac{d\mathbf{k}}{dt} \right)_B = \frac{\partial f_1}{\partial \phi} \left(\frac{\partial \phi}{\partial t} \right)_B = \omega_c \frac{\partial f_1}{\partial \phi}. \quad (\text{G.8})$$

Substituting (G.8) in (G.6), we have

$$\omega_c \frac{\partial f_1}{\partial \phi} + \frac{f_1}{\tau} = -q \frac{\partial f_0}{\partial E_{\mathbf{k}}} \mathbf{v}_{\mathbf{k}} \cdot \mathbf{E}. \quad (\text{G.9})$$

This equation can be solved by employing Green's function techniques. This means that we solve first the following equation

$$\omega_c \frac{\partial G}{\partial \phi} + \frac{G}{\tau} = \delta(\phi - \phi'). \quad (\text{G.10})$$

Its solution is

$$G(\phi - \phi') = \theta(\phi - \phi') \frac{\exp[(\phi' - \phi)/\omega_c \tau]}{\omega_c}. \quad (\text{G.11})$$

Then the solution to (G.9) is

$$\begin{aligned} f_1(\phi, E_{\mathbf{k}}, k_z) &= -q \frac{\partial f_0}{\partial E_{\mathbf{k}}} \int_{-\infty}^{\infty} d\phi' G(\phi - \phi') \mathbf{v}_{\mathbf{k}}(\phi', E_{\mathbf{k}}, k_z) \cdot \mathbf{E} \\ &= \frac{q}{\omega_c} \left(-\frac{\partial f_0}{\partial E_{\mathbf{k}}} \right) \int_{-\infty}^{\phi} d\phi' \exp\left(\frac{\phi' - \phi}{\omega_c \tau}\right) \mathbf{v}_{\mathbf{k}}(\phi', E_{\mathbf{k}}, k_z) \cdot \mathbf{E}. \end{aligned} \quad (\text{G.12})$$

Assuming that $E_{\mathbf{k}} = \hbar^2 k^2 / 2m^*$, we have that

$$d^3 k = \left(\frac{m^*}{\hbar^2} \right) d\phi dE_{\mathbf{k}} dk_z. \quad (\text{G.13})$$

Substituting this last relation in the expression for the electronic current density,

$$\mathbf{j} = 2q \int \frac{d^3 k}{(2\pi)^2} \mathbf{v}_{\mathbf{k}} f_1(\mathbf{k}), \quad (\text{G.14})$$

and taking into account (G.12), we find for the conductivity tensor in the presence of magnetic field the following expression:

$$\begin{aligned} \sigma_{ij} &= \frac{q^2}{4\pi^3 \hbar^2} \int dE_{\mathbf{k}} \left(-\frac{\partial f_0}{\partial E_{\mathbf{k}}} \right) \int dk_z \frac{m^*}{\omega_c} \\ &\quad \times \int_0^{2\pi} d\phi \int_{-\infty}^0 d\phi' v_{\mathbf{k}i}(\phi) v_{\mathbf{k}j}(\phi + \phi') \exp\left(\frac{\phi'}{\omega_c \tau}\right). \end{aligned} \quad (\text{G.15})$$

Notice that both $v_{\mathbf{k}i}(\phi)$ and $v_{\mathbf{k}j}(\phi + \phi')$ depend also on $E_{\mathbf{k}}$ and k_z . For electrons in metals, where $-\partial f_0 / \partial E_{\mathbf{k}} = \delta(E_{\mathbf{k}} - E_F)$, (G.15) becomes

$$\sigma_{ij} = \frac{q^2}{4\pi^3\hbar^2} \int dk_z \frac{m^*}{\omega_c} \int_0^{2\pi} d\phi \int_{-\infty}^0 d\phi' v_{\mathbf{k}i}(\phi) v_{\mathbf{k}j}(\phi' + \phi) \exp(\phi'/\omega_c\tau), \quad (\text{G.16})$$

where $q = -e$ for electrons. Equations (G.15) and (G.16) are known as *Shockley's tube-integral formulas* and constitute the basis for calculating the magnetoresistance tensor. By returning to the variables k_x, k_y, k_z (through (G.13)) and changing variables from ϕ' to $t = \phi'/\omega_c$, we recapture (10.78) and (10.79). In the latter, the band index is shown explicitly.

H

Tables

Table H.1. Physical constants (numbers in parentheses give the standard deviation in the last two digits)

Quantity	Symbol	Value (year 2008)	Units
Planck constant over 2π	$\hbar = h/2\pi$	$1.054\,571\,628(53) \times 10^{-34}$	J s
	$\hbar$	$6.582\,118\,99(16) \times 10^{-16}$	eV s
Velocity of light	c	299 792 458	m s ⁻¹
Gravitational constant	G	$6.674\,28(67) \times 10^{-11}$	m ³ kg ⁻¹ s ⁻²
Proton charge	e	$1.602176487(40) \times 10^{-19}$	C
Electron mass	m_e or m	$9.10938215(45) \times 10^{-31}$	kg
Proton mass	m_p	$1.672621637(83) \times 10^{-27}$	kg
Neutron mass	m_n	$1.674927211(84) \times 10^{-27}$	kg
Atomic mass constant $\frac{1}{12}m(\text{C}^{12})$	m_u (or u)	$1.660538782(83) \times 10^{-27}$	kg
Vacuum permittivity	ε_0	$8.854187817 \dots \times 10^{-12}$	F m ⁻¹
Vacuum permeability	μ_0	$4\pi \times 10^{-7}$	N A ⁻²
Boltzmann constant	k_B	$1.3806504(24) \times 10^{-23}$	J K ⁻¹
Avogadro constant	N_A	$6.02214179(30) \times 10^{23}$	mol ⁻¹
Fine-structure constant	α^*	$(137.035999679(94))^{-1}$	
Magnetic flux quantum	Φ_0^*	$2.067833667(52) \times 10^{-15}$	Wb
Quantum Hall resistance	R_H^*	25 812.8075(80)	Ω
Bohr magneton	μ_B^*	$927.400915(23) \times 10^{-26}$	J T ⁻¹
Nuclear magneton	μ_N^*	$5.05078324(13) \times 10^{-27}$	J T ⁻¹

Table H.1. (Continued)

Quantity	Symbol	Value (year 2008)	Units
Electron magnetic moment	μ_e	$-1.00115965218111(74)$	μ_B
Proton magnetic moment	μ_p	$2.792847356(23)$	μ_N
Neutron magnetic moment	μ_n	$-1.91304273(45)$	μ_N
Gas constant	$R \equiv N_A k_B$	$8.314472(15)$	$\text{J mol}^{-1} \text{K}^{-1}$
Bohr radius	$a_B \equiv 4\pi\epsilon_0\hbar^2/m_e e^2$	$0.52917720859(36) \times 10^{-10}$	m

* $\alpha = e^2/4\pi\epsilon_0\hbar c$, $\Phi_0 = h/2e$, $R_H \equiv h/e^2$, $\mu_B \equiv e\hbar/2m_e$, $\mu_N \equiv (m_e/m_p)\mu_B$
(all in SI)
 $\alpha = e^2/\hbar c$, $\Phi_0 = hc/2e$, $a_B = \hbar^2/m_e e^2$, $\mu_B = e\hbar/2m_e c$, $\mu_N \equiv (m_e/m_p)\mu_B$
(all in G-CGS)

Table H.2. Atomic system of units ($m_e = 1$; $e = 1$; $a_B = 1$; $k_B = 1$) $c = 1/\alpha$ in G-CGS; $\varepsilon_0 = 1/4\pi$, $\mu_0 = 4\pi\alpha^2$ in SI.

Length	$l_0 \equiv a_B$
Mass	$m_0 \equiv m_e$
Charge	$q_0 \equiv e$
Time	$t_0 \equiv m_e a_B^2 / \hbar = 2.418884 \times 10^{-17} \text{ s}$
Energy	$E_0 \equiv \hbar^2 / m_e a_B^2 = 4.359744 \times 10^{-18} \text{ J} = 27.211384 \text{ eV}$
Angular frequency	$\omega_0 \equiv \hbar / m_e a_B^2 = 4.134137 \times 10^{16} \text{ rad/s}$
Velocity	$v_0 \equiv a_B / t_0 = \hbar / m_e a_B = \alpha c = 2\,187.691 \text{ km/s}$
Mass density	$\rho_0 \equiv m_e / a_B^3 = 6.147315 \text{ kg/m}^3$
Temperature	$T_0 \equiv E_0 / k_B = \hbar^2 / m_e a_B^2 k_B = 315\,775 \text{ K}$
Pressure	$P_0 \equiv E_0 / a_B^3 = \hbar^2 / m_e a_B^5 = 2.942101 \times 10^{13} \text{ N/m}^2 = 2.942101 \times 10^8 \text{ bar}$
Electrical resistance	$R_0 \equiv \hbar / e^2 = R_H / 2\pi = 4\,108.236 \, \Omega$
Resistivity	$\rho_{\rho 0} \equiv R_0 a_B = \hbar a_B / e^2 = 21.739\,848 \, \mu\Omega \times \text{cm}$
Conductivity	$\sigma_0 \equiv 1 / \rho_{c0} = e^2 / \hbar a_B = 4.599848 \times 10^7 \, \Omega^{-1} \text{m}^{-1}$
Electric current	$i_0 \equiv e / t_0 = 6.623618 \times 10^{-3} \text{ A}$
Voltage	$V_0 \equiv E_0 / e = 27.211384 \text{ V}$
Electric field	$\mathcal{E}_0 \equiv V_0 / a_B = 5.142\,206 \times 10^{11} \text{ V/m}$
Magnetic field ^a	$B_0 \equiv c \hbar / e a_B^2 = 2.350517 \times 10^5 \text{ T}$
Electric polarizability ^b	$a_{e0} \equiv 4\pi \varepsilon_0 a_B^3 = 1.648777 \times 10^{-41} \text{ Fm}^2$
Electric induction	$D_0 \equiv e / a_B^2 = 57.214762 \text{ C/m}^2$
Magnetic moment	$\mu_0 \equiv 2\mu_B = 1.854802 \times 10^{-23} \text{ J T}^{-1}$
Magnetization	$M_0 \equiv \mu_0 / a_B^3 = 1.251682 \times 10^8 \text{ A/m}$
Magnetic field	$H_0 \equiv M_0 = 1.251682 \times 10^8 \text{ A/m}$

For any quantity X we define $\bar{X} = X/X_0$ (see (1.16))

^aIn SI set $c = 1$

^bIn G-CGS set $4\pi\varepsilon_0 = 1$

Table H.3. Acronyms

AW	Atomic weight
AES	Auger electron spectroscopy
AFM	Atomic force microscopy
APS	Appearance potential spectroscopy
ARPES	Angle resolved photoemission spectroscopy
bcc	Body-centered cubic
BZ	Brilluin zone
CB	Conduction band
CMP	Condensed Matter physics
DLTS	Deep level transient spectroscopy
DOS	Density of states
EA	Electron affinity
EELS	Electron energy loss spectroscopy
ELS	Electron loss spectroscopy
EM	Electromagnetism
EPR	Electron paramagnetic resonance
ESCA	Electron spectroscopy for chemical analysis
ESR	Electron spin resonance
EXAFS	Extended X-ray absorption fine structure
fcc	Face-centered cubic
FEM	Field emission spectroscopy
FET	Field effect transistor
FIM	Field ionization microscopy
FQHE	Fractional quantum Hall effect
hcp	Hexagonal close-packed
HREM	High-resolution electron microscopy
INS	Inelastic neutron scattering
IP	Ionization potential
IPS	Inverse photoemission spectroscopy
IQHE	Integral quantum Hall effect
ISS	Ion scattering spectroscopy
JM	Jellium model
KE	Kinetic energy
LCAO	Linear combination of atomic orbitals
LEED	Low energy electron diffraction
LO	Longitudinal optical
LST	Lyddane–Sachs–Teller
MBE	Molecular beam epitaxy
MOS	Metal–oxide–semiconductor
MW	Molecular weight
MRI	Magnetic resonance imaging
NMR	Nuclear magnetic resonance
NQR	Nuclear quadrapole resonance
PE	Potential energy
PTE	Periodic table of the elements
QM	Quantum Mechanics
RHEED	Reflection high energy electron diffraction

Table H.3. (continued)

RJM	Revised Jellium model
RPA	Random phase approximation
SAM	Scanning Auger microscopy
sc	Simple cubic
SEM	Scanning electron microscopy
SES	Secondary electron spectroscopy
SEXAFS	Surface extended X-ray absorption fine structure
SIMS	Secondary ion mass spectroscopy
SLEED	Spin-polarized LEED
SM	Statistical mechanics
SP	Statistical physics
SSP	Solid state physics
STM	Scanning tunneling microscopy
TBA	Tight-binding approximation
TBM	Tight binding model
TDMS	Thermal desorption mass spectroscopy
TEM	Transmission electron microscopy
THEED	Transmission high energy electron diffraction
TO	Transverse optical
UPS	Ultraviolet photoelectron spectroscopy
UV	Ultraviolet
VB	Valence band
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

Table H.4. Numerical relations and correspondences

1 eV = 1.602176487(40) $\times 10^{-19}$ J
= 1.602176487(40) $\times 10^{-12}$ erg
= 3.829293 $\times 10^{-23}$ kcal ^a
= 3.674932540(92) $\times 10^{-2}$ Hartree
$\leftrightarrow 1.782661758(44) \times 10^{-36}$ kg ($m = E/c^2$)
$\leftrightarrow 1.23984187(17) \times 10^4$ A ($\lambda = hc/E$)
$\leftrightarrow 8.06554465(20) \times 10^5$ m ⁻¹ ($\frac{1}{\lambda} = \frac{E}{hc}$)
$\leftrightarrow 2.417989454(60) \times 10^{14}$ Hz ($\nu = \frac{E}{h}$)
$\leftrightarrow 1.51926758(38) \times 10^{15}$ rad $\times$ s ⁻¹ ($\omega = \frac{E}{h}$)
$\leftrightarrow 1.1604505(20) \times 10^4$ K ($T = \frac{E}{k_B}$)
$\leftrightarrow 1.073544188(27) \times 10^{-9}$ m_u ($m = E/c^2$)
1 eV/atom or molecule = 23.06052 kcal/mol ^a
1 J = 0.239006 cal ^a
= 6.24150965(16) $\times 10^{18}$ eV
= 10 ⁵ erg
$N_A m_u = 1$ g = 10 ⁻³ kg
$m_u = 1822.888 m_e$
$\frac{m_n}{m_p} = 1.001378419$
$T_0 = 27.211384$ eV $\times 1.1604505 \times 10^4$ K eV ⁻¹ = 315 775 K
1 bar = 0.987 atm = 10 ⁵ N/m ² = 10 ⁵ Pa
= 10 ⁶ dyn/cm ² = 750 torr = 750 mmHg

^aThis kcal is the thermochemical one which is equal to 4.184 $\times 10^3$ J; there is also the "International Table" kcal which is equal to 4.1868 $\times 10^3$ J.

TABLE H.5: PERIODIC TABLE OF THE ELEMENTS

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA	IB	IIB								VIII
1 H 1.00794 1.008 1.00784	2 He 4.002602 4.0026 4.002603	3 Li 6.941 6.94 6.941	4 Be 9.0122 9.012 9.0122	5 B 10.811 10.81 10.811	6 C 12.011 12.01 12.011	7 N 14.007 14.007 14.007	8 O 15.999 15.999 15.999	9 F 18.998 18.998 18.998	10 Ne 20.179 20.179 20.179	11 Na 22.990 22.99 22.990	12 Mg 24.305 24.305 24.305	13 Al 26.982 26.98 26.982	14 Si 28.086 28.086 28.086	15 P 30.974 30.974 30.974	16 S 32.06 32.06 32.06	17 Cl 35.453 35.45 35.453	18 Ar 39.948 39.948 39.948
19 K 39.0983 39.1 39.0983	20 Ca 40.078 40.078 40.078	21 Sc 44.956 44.956 44.956	22 Ti 47.88 47.88 47.88	23 V 50.942 50.942 50.942	24 Cr 52.004 52.004 52.004	25 Mn 54.938 54.938 54.938	26 Fe 55.845 55.845 55.845	27 Co 58.933 58.933 58.933	28 Ni 58.69 58.69 58.69	29 Cu 63.546 63.546 63.546	30 Zn 65.38 65.38 65.38	31 Ga 69.723 69.723 69.723	32 Ge 72.64 72.64 72.64	33 As 74.922 74.922 74.922	34 Se 78.96 78.96 78.96	35 Br 79.904 79.904 79.904	36 Kr 83.80 83.80 83.80
37 Rb 85.468 85.468 85.468	38 Sr 87.62 87.62 87.62	39 Y 88.906 88.906 88.906	40 Zr 91.224 91.224 91.224	41 Nb 92.906 92.906 92.906	42 Mo 95.94 95.94 95.94	43 Tc 98.906 98.906 98.906	44 Ru 101.07 101.07 101.07	45 Rh 102.905 102.905 102.905	46 Pd 106.42 106.42 106.42	47 Ag 107.868 107.868 107.868	48 Cd 112.411 112.411 112.411	49 In 114.818 114.818 114.818	50 Sn 118.710 118.710 118.710	51 Sb 121.757 121.757 121.757	52 Te 127.60 127.60 127.60	53 I 126.905 126.905 126.905	54 Xe 131.29 131.29 131.29
55 Cs 132.905 132.905 132.905	56 Ba 137.33 137.33 137.33	57 La 138.905 138.905 138.905	58 Ce 140.12 140.12 140.12	59 Pr 140.907 140.907 140.907	60 Nd 144.24 144.24 144.24	61 Pm 144.912 144.912 144.912	62 Sm 150.36 150.36 150.36	63 Eu 151.96 151.96 151.96	64 Gd 157.25 157.25 157.25	65 Tb 158.925 158.925 158.925	66 Dy 162.50 162.50 162.50	67 Ho 164.930 164.930 164.930	68 Er 167.26 167.26 167.26	69 Tm 168.934 168.934 168.934	70 Yb 173.054 173.054 173.054	71 Lu 174.967 174.967 174.967	72 Hf 178.49 178.49 178.49
87 Fr 223.021 223.021 223.021	88 Ra 226.025 226.025 226.025	89 Ac 227.028 227.028 227.028	90 Th 232.038 232.038 232.038	91 Pa 231.036 231.036 231.036	92 U 238.029 238.029 238.029	93 Np 237.048 237.048 237.048	94 Pu 239.052 239.052 239.052	95 Am 243.061 243.061 243.061	96 Cm 247.070 247.070 247.070	97 Bk 247.070 247.070 247.070	98 Cf 251.080 251.080 251.080	99 Es 252.083 252.083 252.083	100 Fm 257.103 257.103 257.103	101 Md 258.103 258.103 258.103	102 No 259.108 259.108 259.108	103 Lr 262.105 262.105 262.105	104 Ta 180.948 180.948 180.948

† For the gas phase (noted by the symbol *g*) the units is g/mol for T=273K and P=1 atm.

Table H.7: Radius of a sphere whose volume is the volume per atom.

Table H.7: Radius of a sphere whose volume is the volume per atom.

⁴ K																	² K	
H																	He ⁴	
1.64																	1.97	
3.09																	3.73	
⁷ 8K	Be											F	O	N	Diamond	C	B	Ne
Li	1.24															1.11	1.22	1.75
1.72	2.35															2.09	2.31	3.30
3.25																		
⁵ K	Mg											Cl	S	P	Si	Al	Ar	
Na	1.77														1.68	1.58	2.07	
2.08	3.34														3.18	2.99	3.92	
3.93																		
⁵ K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
K	2.18	1.81	1.61	1.49	1.42	1.43	1.43	1.38	1.38	1.41	1.54	1.67	1.75	1.73	1.87	1.99	2.20	
2.57	4.12	3.42	3.05	2.82	2.68	2.70	2.70	2.61	2.60	2.67	2.90	3.16	3.32	3.27	3.53	3.75	4.16	
4.86																		
⁵ K	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn (α)	Sb	Te	I	Xe	
Rb	2.38	1.99	1.77	1.63	1.55	1.50	1.48	1.49	1.52	1.60	1.73	1.84	2.01	1.93	2.01	2.17	2.40	
2.75	4.49	3.76	3.35	3.07	2.93	2.85	2.80	2.81	2.87	3.02	3.27	3.48	3.80	3.65	3.80	4.10	4.53	
5.20																		
⁵ K	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg (α)	Tl	Pb	Bi	Po	At	Rn	
Cs	2.47	2.07	1.74	1.63	1.56	1.52	1.50	1.50	1.53	1.59	1.78	1.90	1.93	2.04	2.07			
2.98	4.67	3.92	3.30	3.07	2.94	2.88	2.83	2.83	2.89	3.01	3.36	3.59	3.66	3.85	3.92			
5.62																		
Fr	Ra	Ac																
	2.62	2.08																
	4.95	3.92																
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
			2.02	2.02	2.01	2.07;	1.99	2.26	1.99	1.97	1.96	1.95	1.94	1.93	2.14	1.92		
			3.81	3.82	3.81	3.91;	3.77	4.26	3.76	3.72	3.70	3.69	3.67	3.65	4.05	3.62		
			Th	Pa	U (α)	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		
			1.99	1.81	1.70	1.66	1.66	2.01										
			3.75	3.42	3.22	3.14	3.14	3.79										

Al
1.58
2.99

$\leftarrow r_i$ in Å
 $\leftarrow r_i/a_B$

Table H.8: Atomic radius* R_a and $d/2R_a$ where d is the nearest neighbor distance.

Table H.8: Atomic radius* R_a and $d/2R_a$ where d is the nearest neighbor distance.																																					
H	0.529 —											He	0.291 6.13																								
Li	1.586 0.95	Be	1.040 1.09											F	0.396 —																						
Na	1.713 1.07	Mg	1.279 1.25											O	0.450 —																						
				Fe	1.227 1.01											N	0.521 —																				
				$\leftarrow$ atomic radius, R_a (in Å)* $\leftarrow$ ratio $d/2R_a$										C	0.620 1.24																						
K	2.162 1.05	Ca	1.690 1.17	Sc	1.57 1.05	Ti	1.477 1.0	V	1.401 0.94	Cr	1.453 0.86	Mn	1.278 0.88	Fe	1.227 1.01	Co	1.181 1.06	Ni	1.139 1.09	Cu	1.191 1.07	Zn	1.065 1.25	Ga	1.254 0.97	Ge	1.090 1.12	As	1.001 1.58	Se	0.918 1.26	Br	0.851 —	Kr	0.795 2.52		
Rb	2.287 1.06	Sr	1.836 1.17	Y	1.693 1.08	Zr	1.593 1.01	Nb	1.589 0.90	Mo	1.520 0.89	Tc	1.391 0.98	Ru	1.410 0.96	Rh	1.364 0.99	Pd	1.325 1.01	Ag	1.286 1.12	Cd	1.184 1.26	In	1.382 1.18	Sn (a)	1.240 1.13	Sb	1.193 1.22	Te	1.111 1.29	I	1.044 1.70	Xe	0.986 2.20		
Cs	2.518 1.04	Ba	2.060 1.06	La	1.915 0.98	Hf	1.476 1.08	Ta	1.413 1.01	W	1.360 1.00	Re	1.310 1.05	Os	1.266 1.08	Ir	1.227 1.10	Pt	1.221 1.13	Au	1.187 1.21	Hg (a)	1.126 1.34	Tl	1.319 1.31	Pb	1.215 1.44	Bi	1.295 1.19	Po	1.212 1.38	At	1.146 —	Rn	1.090 —		
Fr	2.447 —	Ra	2.042 —	Ac	1.895 0.99											Dy	1.75 —	Ho	1.727 —	Er	1.703 —	Tm	1.681 —	Yb	1.658 —	Lu	1.553 —										
						Ce	1.978 0.92	Pr	1.942 0.94	Nd	1.912 0.96	Pm	1.882 —	Sm	1.854 0.97	Eu	1.826 1.08	Gd	1.713 1.06	Tb	1.775 1.01	Dy	1.75 1.03	Ho	1.727 1.04	Er	1.703 1.05	Tm	1.681 1.05	Yb	1.658 1.17	Lu	1.553 1.13				
						Th	1.788 1.01	Pa	1.804 0.89	U (a)	1.775 0.77	Np	1.741 0.75	Pu	1.784 0.87	Am	1.757 1.03	Cm	1.657 —	Bk	1.626 —	Cf	1.598 —	Es	1.576 —	Fm	1.557 —	Md	1.527 —	No	1.581 —	Lr	—				

* The atomic radius is not a clearly measured quantity. Here R_a has been defined as the radius at which the main maximum of the density of the highest occupied atomic orbital appears. For small atoms their size extends well beyond R_a .

Table H.10: Cohesive energies (from the book by Kittel).

The minimum energy required to split the solid (under 1 atm and $T = 0$ K) into neutral atoms at their ground state.

neutral atoms at their ground state.																														
Li 158 1.63 37.7	Be 320 3.32 76.5	<table><tr><td>Al</td><td>← kJ/mol</td><td>← eV/atom</td><td>← kcal/mol</td></tr><tr><td>327 3.39 78.1</td><td></td><td></td><td></td></tr></table>															Al	← kJ/mol	← eV/atom	← kcal/mol	327 3.39 78.1				B 561 5.81 134	C 711 7.37 170	N 474 4.92 113.4	O 251 2.60 60.03	F 81.0 0.84 19.37	Ne 1.92 0.020 0.46
Al	← kJ/mol	← eV/atom	← kcal/mol																											
327 3.39 78.1																														
Na 107 1.113 25.67	Mg 145 1.51 34.7																Al 327 3.39 78.1	Si 446 4.63 106.7	P 331 3.43 79.16	S 275 2.85 65.75	Cl 135 1.40 32.2	Ar 7.74 0.080 1.85								
K 90.1 0.934 21.54	Ca 178 1.84 42.5	Sc 376 3.90 89.9	Ti 468 4.85 111.8	V 512 5.31 122.4	Cr 395 4.10 94.5	Mn 282 2.92 67.4	Fe 413 4.28 98.7	Co 424 4.39 101.3	Ni 428 4.44 102.4	Cu 336 3.49 80.4	Zn 130 1.35 31.04	Ga 271 2.81 64.8	Ge 372 3.85 88.8	As 237 2.96 68.2	Se 227 2.46 56.7	Br 118 1.22 28.18	Kr 11.2 0.116 2.68													
Rb 82.2 0.852 19.64	Sr 166 1.72 39.7	Y 422 4.37 100.8	Zr 603 6.25 144.2	Nb 730 7.57 174.5	Mo 658 6.82 157.3	Tc 661 6.74 158	Ru 650 6.74 155.4	Rh 554 5.75 132.5	Pd 376 3.89 89.8	Ag 284 2.95 68.0	Cd 112 1.16 26.73	In 243 2.52 58.1	Sn 303 3.14 72.4	Sb 265 2.75 63.4	Te 211 2.19 50.34	I 107 1.11 25.62	Xe 15.9 0.16 3.80													
Cs 77.6 0.804 18.54	Ba 183 1.90 43.7	La 431 4.47 103.1	Hf 621 6.44 148.4	Ta 782 8.10 186.9	W 859 8.90 205.2	Re 775 8.03 185.2	Os 788 8.17 188.4	Ir 670 6.94 160.1	Pt 564 5.84 134.7	Au 368 3.81 87.96	Hg 65 0.67 15.5	Tl 182 1.88 43.4	Pb 196 2.03 46.78	Bi 210 2.18 50.2	Po 144 1.50 34.5	At 19.5 0.202 4.66	Rn 15.9 0.16 3.80													
Fr	Ra 160 1.66 38.2	Ac 410 4.25 98																												
			Ce 417 4.32 99.7	Pr 357 3.70 85.3	Nd 328 3.40 78.5	Pm	Sm 206 2.14 49.3	Eu 179 1.86 42.8	Gd 400 4.14 95.5	Tb 391 4.05 93.4	Dy 294 3.04 70.2	Ho 302 3.14 72.3	Er 317 3.29 75.8	Tm 233 2.42 55.8	Yb 154 1.60 3.71	Lu 428 4.43 102.2														
			Th 598 6.20 142.9	Pa	U 536 5.55 128	Np 456 4.73 109	Pu 347 3.60 83.0	Am 264 2.73 63	Cm 385 3.99 92.1	Bk	Cf	Es	Fm	Md	No	Lr														

Table H.11: *Isothermal bulk modulus and compressibility at room temperature unless otherwise stated (from the book by Kittel).*

H [d] 0.002 500	Cu 1.37 0.73	He [d] 0.001 1168
Li 0.116 8.62	Be 1.003 0.997	F
Na 0.068 14.7	Mg 0.354 2.82	O
K 0.032 31	Ca 0.152 6.58	N [e] 0.012 80
Rb 0.031 32	Sr 0.116 8.62	C [d] 4.43 0.226
Cs 0.020 50	Ba 0.103 9.97	Al 0.722 1.385
Fr (0.020) (50)	Ra (0.132) (7.6)	Si 0.988 1.012
		P (b) 0.304 3.29
		S (r) 0.178 5.62
		Cl
		Ar [a] 0.013 79
		Br
		Se
		As
		Ge
		Ga [b] 0.569 1.76
		Zn 0.598 1.67
		Cu 1.37 0.73
		Ni 1.86 0.538
		Co 1.914 0.522
		Fe 1.683 0.594
		Mn 0.596 1.68
		Cr 1.901 0.526
		V 1.619 0.618
		Ti 1.051 0.951
		Sc 0.435 2.30
		Y 0.366 2.73
		Zr 0.833 1.20
		Nb 1.702 0.587
		Mo 2.725 0.366
		Ru 3.208 0.311
		Rh 2.704 0.369
		Pd 1.808 0.553
		Ag 1.007 0.993
		Cd 0.467 2.14
		In 0.411 2.43
		Sn (g) 1.11 0.901
		Sb 0.383 2.61
		Te 0.230 4.35
		I
		Xe
		Po (0.26) (3.8)
		Bi 0.315 3.17
		Pb 0.430 2.33
		Tl 0.359 2.79
		Hg [c] 0.382 2.60
		Au 1.732 0.577
		Pt 2.783 0.359
		Ir 3.55 0.282
		Os (4.18) (0.24)
		Re 3.72 0.269
		W 3.232 0.309
		Ta 2.00 0.50
		Hf 1.09 0.92
		La 0.243 4.12
		Ac (0.25) (4)
		Ce (γ) 0.239 4.18
		Pr 0.306 3.27
		Nd 0.327 3.06
		Pm (0.35) (2.85)
		Sm 0.294 3.40
		Eu 0.147 6.80
		Gd 0.383 2.61
		Tb 0.399 2.51
		Dy 0.384 2.60
		Ho 0.397 2.52
		Er 0.411 2.43
		Tm 0.397 2.52
		Yb 0.133 7.52
		Lu 0.411 2.43
		No
		Md
		Fm
		Es
		Cf
		Bk
		Cm
		Am
		Pu (0.68) (1.5)
		Np 0.987 1.01
		U (0.76) (1.3)
		Pa 0.543 1.84
		Th 0.543 1.84

Table H.12: First and second ionization potential, electron affinity (in eV) and values of L , S , J of atom

Table H.12: First and second ionization potential, electron affinity (in eV) and values of L , S , J of atom																													
H $^1S_{1/2}$		Li $^2S_{1/2}$		Be $^1S_0$		Na $^2S_{1/2}$		Mg $^1S_0$		Al $^2P_{1/2}$		Si $^3P_0$		P $^4S_{3/2}$		S $^3P_2$		Cl $^3P_{3/2}$		Ar $^1S_0$		Kr $^1S_0$		Xe $^1S_0$		Rn $^1S_0$			
13.5984	0.7542	5.3917	9.3227	5.3917	9.3227	5.3917	9.3227	5.3917	9.3227	5.3917	9.3227	5.3917	9.3227	5.3917	9.3227	5.3917	9.3227	5.3917	9.3227	5.3917	9.3227	5.3917	9.3227	5.3917	9.3227	5.3917	9.3227	5.3917	9.3227
75.640	0.62	5.3917	75.640	5.3917	75.640	5.3917	75.640	5.3917	75.640	5.3917	75.640	5.3917	75.640	5.3917	75.640	5.3917	75.640	5.3917	75.640	5.3917	75.640	5.3917	75.640	5.3917	75.640	5.3917	75.640	5.3917	75.640
$\leftarrow ^{2S+1}L_J$ $\leftarrow$ ionization energy of neutral atom $\leftarrow$ ionization energy of a cation with $\xi = +1$ $\leftarrow$ ionization energy of an anion with $\xi = -1$ (electron affinity) $\text{Li } ^2S_{1/2}$ 5.3917 75.640 0.62																													
4.3407	0.5479	6.8281	12.7998	6.8281	12.7998	6.8281	12.7998	6.8281	12.7998	6.8281	12.7998	6.8281	12.7998	6.8281	12.7998	6.8281	12.7998	6.8281	12.7998	6.8281	12.7998	6.8281	12.7998	6.8281	12.7998	6.8281	12.7998	6.8281	12.7998
31.63	0.5015	11.8717	12.7998	11.8717	12.7998	11.8717	12.7998	11.8717	12.7998	11.8717	12.7998	11.8717	12.7998	11.8717	12.7998	11.8717	12.7998	11.8717	12.7998	11.8717	12.7998	11.8717	12.7998	11.8717	12.7998	11.8717	12.7998	11.8717	12.7998
0.0246	0.188	0.079	0.525	0.079	0.525	0.079	0.525	0.079	0.525	0.079	0.525	0.079	0.525	0.079	0.525	0.079	0.525	0.079	0.525	0.079	0.525	0.079	0.525	0.079	0.525	0.079	0.525	0.079	0.525
6.5615	0.188	6.8281	12.7998	6.8281	12.7998	6.8281	12.7998	6.8281	12.7998	6.8281	12.7998	6.8281	12.7998	6.8281	12.7998	6.8281	12.7998	6.8281	12.7998	6.8281	12.7998	6.8281	12.7998	6.8281	12.7998	6.8281	12.7998	6.8281	12.7998
6.1132	0.3407	6.8281	12.7998	6.8281	12.7998	6.8281	12.7998	6.8281	12.7998	6.8281	12.7998	6.8281	12.7998	6.8281	12.7998	6.8281	12.7998	6.8281	12.7998	6.8281	12.7998	6.8281	12.7998	6.8281	12.7998	6.8281	12.7998	6.8281	12.7998
5.6949	0.110301	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131
0.048	0.307	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893
7.4859	0.048	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131
5.2117	0.10038	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131
5.27895	0.110301	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131
0.4859	0.048	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893
5.2117	0.10038	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131
5.27895	0.110301	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131
0.4859	0.048	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893
5.2117	0.10038	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131
5.27895	0.110301	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131
0.4859	0.048	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893
5.2117	0.10038	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131
5.27895	0.110301	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131
0.4859	0.048	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893
5.2117	0.10038	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131
5.27895	0.110301	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131
0.4859	0.048	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893
5.2117	0.10038	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131
5.27895	0.110301	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131
0.4859	0.048	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893
5.2117	0.10038	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131
5.27895	0.110301	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131
0.4859	0.048	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893
5.2117	0.10038	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131
5.27895	0.110301	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131
0.4859	0.048	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893	0.426	0.893
5.2117	0.10038	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131	7.4859	13.131
5.27895	0.110301	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131	6.6339	13.131
0.4859																													

Table H.14: Specific heat capacity and latent heats of melting and vaporization under 1 atm.

Table H.14: Specific heat capacity and latent heats of melting and vaporization under 1 atm.																			
H																			He
–																			–
0.0587																			0.0845
0.4494																			
Li	Be																	Ne	
24.86	16.44																		
3.00	12.20																	0.3317	
145.92	292.40																	1.7326	
		Li																	
		24.99																	
		3.00																	
		145.92																	
Na	Mg	Al	B	C	N	O	F							Ar					
28.23	24.87	29.340	11.09	8.52	0.3604	0.2226	0.2552							–					
2.60	8.95	10.79	50.20	–	2.7928	3.4099	0.3317							1.188					
96.96	127.40	293.40	489.70	355.8	–	–	1.7326							6.447					
								Si	P	S	Cl								
								19.99	23.82	22.70	–								
								50.55	0.657	1.718	3.203								
								384.22	12.129	–	10.20								
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Br	Se	As	Sb	Te	I	Xe	
29.60	25.93	25.52	25.06	24.89	23.35	26.32	25.10	24.81	26.07	24.44	25.39	26.03	23.22	24.64	25.36	27.70	27.16	–	
2.33	8.54	14.10	15.45	20.90	16.90	12.05	13.8	16.19	17.47	13.05	7.322	5.59	36.94	–	6.694	37.70	5.286	1.638	
79.87	153.60	314.20	421.0	452	344.30	226.0	349.6	376.5	370.4	300.3	115.3	258.7	330.9	34.76	37.70	15.438	9.029		
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Sn	Pb	Bi	Po	
31.06	26.79	26.53	25.36	24.60	24.06	20.58	24.06	24.98	25.98	25.35	26.02	26.74	26.99	25.23	25.73	27.16	–	–	
2.19	8.30	11.40	16.90	26.40	32.0	24.0	24.0	21.5	17.6	11.3	6.192	3.263	7.029	19.87	17.49	7.824	2.297		
72.22	144.0	363.0	582.0	682.0	598.0	660.0	595.0	493.0	357.0	250.58	99.57	231.5	295.8	77.14	52.55	20.752	12.636		
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn		
32.21	28.07	27.11	25.73	25.36	24.27	25.48	24.7	25.10	25.86	25.42	27.98	26.32	26.84	25.52	–	–	–	–	
2.09	7.75	6.20	24.06	31.60	35.40	33.20	31.80	26.10	19.6	12.55	2.295	4.142	4.799	11.30	–	2.89			
67.74	142.0	414.0	575.0	743.0	824.0	715	746.0	604.0	510.0	334.4	59.229	164.1	177.7	104.8	–	16.40			
Fr	Ra	Ac	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu			
		27.2	26.94	27.20	27.45		29.54	27.66	37.03	28.91	28.16	27.15	28.12	27.03	26.74	26.86			
			5.46	6.89	7.14		8.63	9.21	10.05	10.80	11.06	12.20	19.90	16.84	7.660	18.60			
			414.0	296.8	273.0		166.4	143.5	359.4	330.9	230.0	241.0	261.0	191.0	128.90	355.90			
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr			
			27.32	–	27.67	28.45	31.72	26.73	–										
			16.10	12.30	8.520	5.190	2.84	14.4	15.0										
			514.40	–	477.0	–	344.0	–	–										

Table H.17. Useful mathematical formulae

1. $\mathbf{A}_1 \cdot (\mathbf{A}_2 \times \mathbf{A}_3) = \mathbf{A}_3 \cdot (\mathbf{A}_1 \times \mathbf{A}_2) = \mathbf{A}_2 \cdot (\mathbf{A}_3 \times \mathbf{A}_1)$
2. $\mathbf{A}_1 \times (\mathbf{A}_2 \times \mathbf{A}_3) = \mathbf{A}_2(\mathbf{A}_1 \cdot \mathbf{A}_3) - \mathbf{A}_3(\mathbf{A}_1 \cdot \mathbf{A}_2)$
3. $\nabla(\psi_1\psi_2) = \psi_1\nabla\psi_2 + \psi_2\nabla\psi_1$
4. $\nabla(\mathbf{A}_1 \cdot \mathbf{A}_2) = \mathbf{A}_1 \times (\nabla \times \mathbf{A}_2) + \mathbf{A}_2 \times (\nabla \times \mathbf{A}_1) + (\mathbf{A}_1 \cdot \nabla) \mathbf{A}_2 + (\mathbf{A}_2 \cdot \nabla) \mathbf{A}_1$
5. $\nabla \cdot (\psi \mathbf{A}) = \psi (\nabla \cdot \mathbf{A}) + \mathbf{A} \cdot (\nabla \psi)$
6. $\nabla \cdot (\mathbf{A}_1 \times \mathbf{A}_2) = \mathbf{A}_2 \cdot (\nabla \times \mathbf{A}_1) - \mathbf{A}_1 \cdot (\nabla \times \mathbf{A}_2)$
7. $\nabla \times (\psi \cdot \mathbf{A}) = \psi (\nabla \times \mathbf{A}) - \mathbf{A} \times (\nabla \psi)$
8. $\nabla \times (\mathbf{A}_1 \times \mathbf{A}_2) = (\mathbf{A}_2 \cdot \nabla) \mathbf{A}_1 - (\mathbf{A}_1 \cdot \nabla) \mathbf{A}_2 + \mathbf{A}_1 (\nabla \cdot \mathbf{A}_2) - \mathbf{A}_2 (\nabla \cdot \mathbf{A}_1)$
9. $\nabla \times (\nabla \times \mathbf{A}) = \nabla(\nabla \cdot \mathbf{A}) - \nabla^2 \mathbf{A}$
10. $\nabla \cdot (\nabla \times \mathbf{A}) = 0; \quad \nabla \times (\nabla \psi) = 0$

Spherical coordinates^a r, θ, ϕ .

$$\text{grad } \psi(\mathbf{r}) \equiv \nabla \psi(\mathbf{r}) = \frac{\partial \psi}{\partial r} \mathbf{i}_r + \frac{1}{r} \frac{\partial \psi}{\partial \theta} \mathbf{i}_\theta + \frac{1}{r \sin \theta} \frac{\partial \psi}{\partial \phi} \mathbf{i}_\phi$$

$$\text{div } \mathbf{A}(\mathbf{r}) \equiv \nabla \cdot \mathbf{A}(\mathbf{r}) = \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 A_r) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} (\sin \theta A_\theta) + \frac{1}{r \sin \theta} \frac{\partial A_\phi}{\partial \phi}$$

$$\begin{aligned} \nabla \times \mathbf{A} = \frac{1}{r \sin \theta} \left[\frac{\partial}{\partial \theta} (\sin \theta A_\phi) - \frac{\partial A_\theta}{\partial \phi} \right] \hat{r} + \frac{1}{r} \left[\frac{1}{\sin \theta} \frac{\partial A_r}{\partial \phi} - \frac{\partial}{\partial r} (r A_\phi) \right] \hat{\theta} \\ + \frac{1}{r} \left[\frac{\partial}{\partial r} (r A_\theta) - \frac{\partial A_r}{\partial \theta} \right] \hat{\phi} \end{aligned}$$

$$\nabla^2 \psi(r) = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2}$$

Cylindrical coordinates z, ρ, ϕ .

$$\text{grad } \psi(\mathbf{r}) \equiv \nabla \psi(\mathbf{r}) = \frac{\partial \psi}{\partial z} \mathbf{i}_z + \frac{\partial \psi}{\partial \rho} \mathbf{i}_\rho + \frac{1}{\rho} \frac{\partial \psi}{\partial \phi} \mathbf{i}_\phi.$$

$$\text{div } \mathbf{A}(\mathbf{r}) \equiv \nabla \cdot \mathbf{A}(\mathbf{r}) = \frac{\partial A_z}{\partial z} + \frac{1}{\rho} \frac{\partial}{\partial \rho} (\rho A_\rho) + \frac{1}{\rho} \frac{\partial A_\phi}{\partial \phi}.$$

$$\nabla \times \mathbf{A} = \left[\frac{1}{r} \frac{\partial A_z}{\partial \phi} - \frac{\partial A_\phi}{\partial z} \right] \hat{r} + \left[\frac{\partial A_r}{\partial z} - \frac{\partial A_z}{\partial r} \right] \hat{\phi} + \frac{1}{r} \left[\frac{\partial}{\partial r} (r A_\phi) - \frac{\partial A_r}{\partial \phi} \right] \hat{z}$$

$$\nabla^2 \psi(\mathbf{r}) = \frac{\partial^2 \psi}{\partial z^2} + \frac{1}{\rho} \frac{\partial}{\partial \rho} \left(\rho \frac{\partial \psi}{\partial \rho} \right) + \frac{1}{\rho^2} \frac{\partial^2 \psi}{\partial \phi^2}$$

^aNote that $i\partial/\partial r$ is not hermetian, while $(i/r) \cdot (\partial/\partial r)r$ is hermetian for $0 \leq r \leq \infty$

Table H.18. Solutions of Helmholtz equation, $(\nabla^2 + k^2)\psi = 0$, in various coordinate systems**Cartesian Coordinates, x, y, z**

$$\begin{aligned} \psi(\mathbf{r}) = & \sum_{\ell m} \{ A_{\ell m} [\sin(\ell x_1) + b_\ell \cos(\ell x_1)] \\ & \times [\sinh(x_2 \sqrt{\ell^2 + m^2}) + c_{\ell m} \cosh(x_2 \sqrt{\ell^2 + m^2})] \\ & \times [\sin(x_3 \sqrt{m^2 + k^2}) + d_m \cos(x_3 \sqrt{m^2 + k^2})] \} \end{aligned}$$

$\{x_1, x_2, x_3\}$ any permutation of x, y, z .

Cylindrical Coordinates, z, ϕ, ρ

$$\begin{aligned} \psi(\mathbf{r}) = & \sum_{m,n} A_{mn} [\sinh(mz) + b_m \cosh(mz)] [\sin(n\phi) + c_n \cos(n\phi)] \\ & \times [J_n(\rho \sqrt{m^2 + k^2}) + d_{nm} Y_n(\rho \sqrt{m^2 + k^2})] \end{aligned}$$

instead of $J_n(w)$ and $Y_n(w)$, where $w = \rho \sqrt{m^2 + k^2}$, one may use $H_n^{(1)}(w) = J_n(w) + iY_n(w)$ and/or $H_n^{(2)}(w) = J_n(w) - iY_n(w)$.

Spherical Coordinates, r, θ, ϕ

$$\begin{aligned} \psi(\mathbf{r}) = & \sum_{\ell m} A_{\ell m} (e^{im\phi} + b_m e^{-im\phi}) [P_\ell^m(\cos \theta) + c_{\ell m} Q_\ell^m(\cos \theta)] \\ & \times [j_\ell(kr) + d_\ell y_\ell(kr)] \end{aligned}$$

where

$$\begin{aligned} j_\ell &= \sqrt{\frac{\pi}{2w}} J_{\ell + \frac{1}{2}}(w) \\ &\rightarrow \frac{w^\ell}{1 \times 3 \times \cdots \times (2\ell + 1)} \quad \text{as } w \rightarrow 0, \end{aligned}$$

$$\begin{aligned} y_\ell &= \sqrt{\frac{\pi}{2w}} Y_{\ell + \frac{1}{2}}(w) \\ &\rightarrow -\frac{1 \times 3 \times \cdots \times (2\ell - 1)}{w^{\ell+1}} \quad \text{as } w \rightarrow 0 \end{aligned}$$

The solution of Laplace equation, $\nabla^2 \psi = 0$, is obtained by taking the limit $k \rightarrow 0$. Properties of $J_n(w), Y_n(w), j_\ell(w), y_\ell(w), P_\ell^m(\cos \theta), Q_\ell^m(\cos \theta)$ can be found in the book by Abramowitz and Stegun [D4].

Solutions of Selected Problems and Answers

Chapter 1

Problem 1.5s

The sphere and the probability distribution have both inversion and rotation symmetry; the first implies $\langle x \rangle = \langle y \rangle = \langle z \rangle = 0$ and the second in combination with the first implies

$$\Delta x^2 = \langle x^2 \rangle = \Delta y^2 = \langle y^2 \rangle = \Delta z^2 = \langle z^2 \rangle = \frac{1}{3} \langle r^2 \rangle.$$

Hence,

$$\langle \varepsilon_k \rangle = \frac{1}{2m} 3 \Delta p_x^2 \geq \frac{3}{2m} \frac{\hbar^2}{4} \frac{1}{\Delta x^2} = \frac{9\hbar^2}{8m \langle r^2 \rangle}.$$

For a uniform probability, within the sphere of radius r_0 and volume $V = (4\pi/3) r_0^3$, $\langle r^2 \rangle = (3/5) r_0^2 = (3/5) (3/4\pi)^{2/3} V^{2/3} = 0.2309 V^{2/3}$. Thus $\langle \varepsilon_k \rangle = 4.87 \hbar^2 / m V^{2/3}$.

Problem 1.9s

The quantity λ_m must depend on:

- (a) $\hbar$, since black body's radiation is of quantum nature
- (b) c , since it is an electromagnetic phenomenon
- (c) $k_B T$, since T is the only parameter in the spectral distribution of this radiation; furthermore, absolute temperature is naturally associated with Boltzmann's constant, k_B , as a product $k_B T$ with dimensions of energy

Out of $\hbar, c, k_B T$, there is only one combination with dimensions of length $\hbar c / k_B T$ (remember that $\hbar c$ has dimensions of energy times length). Hence,

$$\lambda_m = c_1 \frac{\hbar c}{k_B T},$$

where the numerical constant $c_1 = 1.2655$

Problem 1.10s

The scattering cross-section has dimensions of length square. The photon scattering by electron must depend on:

- (a) The electron charge, $-e$, since, if this charge was zero, there would be no interaction and no scattering.
- (b) The velocity of light, since we are dealing with an electromagnetic phenomenon.
- (c) The mass of the electron, m_e , since if the mass was infinite, the electron would not oscillate under the action of the photon electromagnetic field and would not emit radiation.
- (d) The energy of the photon, $\hbar\omega$.

The quantity $e^2/4\pi\epsilon_0 m_e c^2$ has dimensions of length (since $e^2/4\pi\epsilon_0 r$ has dimensions of energy). Hence, the cross-section, σ , is of the form

$$\sigma = \left(\frac{e^2}{4\pi\epsilon_0 m_e c^2} \right)^2 f \left(\frac{\hbar\omega}{m_e c^2} \right),$$

where the function f of the dimensionless quantity $\hbar\omega/m_e c^2$ cannot be determined from dimensional analysis; it turns out that $f(x)$ is a monotonically decreasing function of x with $f(0) = 8\pi/3$, and $f(\infty) = 0$. (The formula for σ is known as the Klein–Nishina formula).

Problem 1.11s

The natural linewidth, ΔE , has dimensions of energy. It must depend on:

- (a) The dipole moment $p = e \cdot r$ (as suggested by the question).
- (b) The velocity of light, c since the decay is due to the emission of a photon.
- (c) The frequency of the emitted photon, since only an oscillating dipole emits radiation.

Hence, by finding the only combination of p , c , ω with dimensions of energy, we obtain

$$\Delta E = c_1 \frac{e^2 r^2 \omega^3}{4\pi\epsilon_0 c^3} \text{ and the lifetime } t_1 = \frac{\hbar}{\Delta E} = \frac{4\pi\epsilon_0 \hbar c^3}{c_1 e^2 r^2 \omega^3},$$

where the “constant” c_1 depends on the details of the initial and the final atomic level, since actually r^2 is the square of the matrix element of an appropriate projection of $\mathbf{r}$ between the initial and the final states. We expect that, for the transition 2p to 1s in hydrogen, r^2 to be of the order of a_B^2 . Choosing, arbitrarily, $c_1 = 1$ and $r^2 = a_B^2$, while $\hbar\omega = 13.6 \left(1 - \frac{1}{4}\right) \text{ eV} = 10.2 \text{ eV}$ we find for this transition

$$t_1 \simeq 1.17 \times 10^{-9} \text{ s},$$

while a detailed advanced calculation gives $t_1 = 1.59 \times 10^{-9} \text{ s}$.

Problem 1.12s

The effective absolute temperature, T , would appear as the product $k_B T$ of dimensions of energy. It must depend on:

- (a) The product GM , where G is the gravitational constant. The reason is that the strong gravitational field responsible for this radiation depends on the product GM .
- (b) Planck's constant $\hbar$, since the phenomenon is of quantum origin.
- (c) The velocity of light, c , since we are dealing with electromagnetic radiation.

The reader may convince himself that out of GM , $\hbar$ and c there is only one combination to give dimensions of energy, namely, $\hbar c^3/GM$. Hence

$$k_B T = c_1 \hbar c^3 / GM,$$

where the numerical constant c_1 turns out to be equal to $1/8\pi$.

Problem 1.13s

It is more convenient for dimensional analysis to employ the G-CGS system (to get rid of ε_0 and μ_0). The skin depth will depend on:

- (a) The frequency ω (see the statement of the problem).
- (b) The velocity of light c (EM phenomenon).
- (c) The conductivity σ (we are dealing with a good conductor). But $[\sigma] = [e^2/\hbar a_B] = [t]^{-1}$. Hence,

$$\delta = c \sqrt{\frac{1}{\omega \sigma}} f\left(\frac{\omega}{\sigma}\right); \text{ it turns out that } f\left(\frac{\omega}{\sigma}\right) = \frac{1}{\sqrt{2\pi}}.$$

Chapter 2**Problem 2.3s**

According to the book by Karplus and Porter [C65], the minimum of the curve appears at $d = 0.74 \text{ \AA} = 1.4 \text{ a.u.}$ and it is equal to -4.75 eV . Assuming that at $d' = 5 \text{ a.u.}$, the energy is still given by the van der Waals, we have

$$\varepsilon_{d=5} = 6.48/d'^6 \text{ a.u.} = 6.48/5^6 \text{ a.u.} = 11.3 \text{ meV}.$$

At $d' = 0.5 \text{ a.u.}$, the total energy (excluding the proton-proton repulsion) is expected to be slightly higher than the total electronic energy of the He atom. The latter energy is equal to minus the sum of the first and the second ionization potential of He, i.e., $-24.587 - 54.418 \text{ eV} = -79 \text{ eV}$. To this energy we must add $2 \times 13.6 \text{ eV}$ to be consistent with our choice of the zero of energy.

Thus the total energy at $d' = 0.5$ a.u. is higher than $-79 + 27.2 + \frac{e^2}{4\pi\epsilon_0 d'} = -51.8 + \frac{27.2}{0.5} \text{ eV} = 2.6 \text{ eV}$.

In Fig. 2.5, we plot the experimental curve and the two points we estimated above.

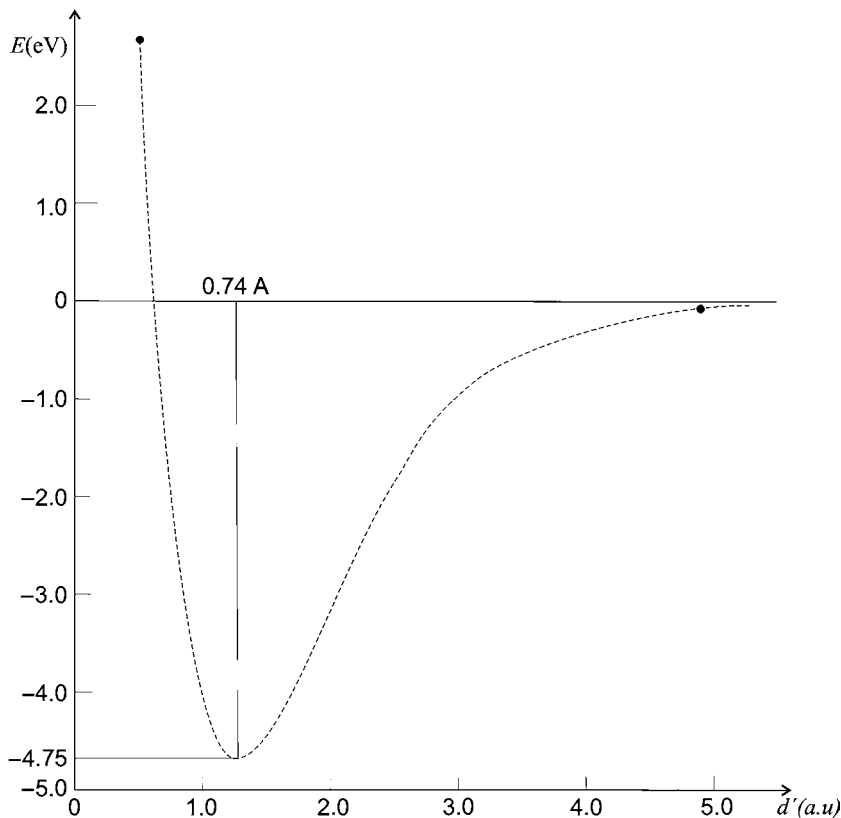


Fig. 2.5. Interaction energy of two hydrogen atoms vs their separation

Problem 2.5s

$$\begin{aligned}
 |\psi(r)|^2 &= A e^{-2r/a}, \quad \left\langle \frac{1}{r} \right\rangle = \int_0^\infty 4\pi r^2 dr |\psi|^2 \frac{1}{r} \\
 &= \frac{\int_0^\infty dr r e^{-2r/a}}{\int_0^\infty dr r^2 e^{-2r/a}} = \frac{1/(2/a)^2}{2/(2/a)^3} = \frac{1}{a}, \\
 \langle r^2 \rangle &= \frac{\int_0^\infty dr r^4 e^{-2r/a}}{\int_0^\infty dr r^2 e^{-2r/a}} = \frac{4!/(2/a)^5}{2!/(2/a)^3} = 4 \times 3 \left(\frac{a}{2} \right)^2 = 3a^2,
 \end{aligned}$$

$$\begin{aligned}\left\langle \frac{p^2}{2m} \right\rangle &= -\frac{\hbar^2}{2m} \int \psi \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\psi}{dr} \right) 4\pi r^2 dr = -\frac{4\pi\hbar^2}{2m} \int \psi \frac{d}{dr} \left(r^2 \frac{d\psi}{dr} \right) dr \\ &= -\frac{\hbar^2}{2m} \frac{\int_0^\infty e^{-r/a} \frac{d}{dr} \left(r^2 \frac{d}{dr} e^{-r/a} \right) dr}{\int_0^\infty dr r^2 e^{-2r/a}} = \frac{\hbar^2}{2m} \frac{a/4}{2a^3/8} = \frac{\hbar^2}{2ma^2},\end{aligned}$$

$$\langle \varepsilon \rangle = \frac{\hbar^2}{2ma^2} - \frac{e^2}{4\pi\varepsilon_0 a}, \quad \frac{\partial \langle \varepsilon \rangle}{\partial a} = 0 \Rightarrow a = \frac{4\pi\varepsilon_0 \hbar^2}{e^2 m} = a_B,$$

$$\Delta r = \sqrt{\langle r^2 \rangle} = \sqrt{3}a_B, \quad \Delta p_i^2 = \frac{1}{3} \langle p^2 \rangle = \frac{1}{3} \frac{\hbar^2}{a^2},$$

$$\Delta x_i^2 = \frac{1}{3} \langle r^2 \rangle = \frac{3}{3} a^2 = a^2, \quad \Delta p_i^2 \Delta x_i^2 = \frac{1}{3} \hbar^2,$$

$$\text{vs. } \Delta p_i^2 \Delta x_i^2 \geq \frac{\hbar^2}{4}.$$

Problem 2.6s

Solving the system

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2, \quad \mathbf{R} = (m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2) / (m_1 + m_2),$$

with respect to $\mathbf{r}_1$, $\mathbf{r}_2$, we find

$$\mathbf{r}_1 = \mathbf{R} + \frac{m_2}{M} \mathbf{r}, \quad \mathbf{r}_2 = \mathbf{R} - \frac{m_1}{M} \mathbf{r}.$$

Hence, taking into account that $\mathbf{p}_1 = m_1 \dot{\mathbf{r}}_1$, $\mathbf{p}_2 = m_2 \dot{\mathbf{r}}_2$, we have

$$\frac{\mathbf{p}_1^2}{2m_1} = \frac{m_1 \dot{\mathbf{R}}^2}{2} + \frac{\mu^2 \dot{\mathbf{r}}^2}{2m_1} + \mu \dot{\mathbf{R}} \dot{\mathbf{r}}, \quad \frac{\mathbf{p}_2^2}{2m_2} = \frac{m_2 \dot{\mathbf{R}}^2}{2} + \frac{\mu^2 \dot{\mathbf{r}}^2}{2m_2} - \mu \dot{\mathbf{R}} \dot{\mathbf{r}}.$$

Summing the two equations we find

$$\frac{\mathbf{p}_1^2}{2m_1} + \frac{\mathbf{p}_2^2}{2m_2} = \frac{1}{2} M \dot{\mathbf{R}}^2 + \frac{1}{2} \mu \dot{\mathbf{r}}^2 = \frac{\mathbf{P}^2}{2M} + \frac{\mathbf{p}^2}{2\mu}, \quad \text{QED.}$$

Problem 2.8s

From virial theorem $E = \left(1 + \frac{2}{\beta}\right) \bar{V}$, where $V(x) \sim \pm |x|^\beta$. According to the correspondence principle (valid for large n), to go from the level n to level $n+1$, $\bar{V}$ must go from $\bar{V}(x)$ to $\bar{V}(x+\delta x)$, where $\delta x = \lambda$; but $\lambda^{-2} \sim E_K \sim E$. Thus

$$\delta E \equiv E(n+1) - E(n) \sim \frac{\partial \bar{V}}{\partial x} \lambda \sim \frac{\partial \bar{V}}{\partial x} \frac{1}{\sqrt{E}}.$$

But

$$\delta E \simeq (dE/dn) = \alpha E/n \sim E/E^{1/a} = E^{1-(1/a)}, \quad \text{since } E \sim n^a,$$

$$\frac{\partial \bar{V}}{\partial x} \lambda \simeq \left(|\beta| |x|^\beta / |x| \right) \lambda \sim \bar{V}^{1-(1/\beta)} E^{-1/2}.$$

Substituting in $\delta E \sim (\partial \bar{V} / \partial x) \lambda$ the last two relations and taking into account that $E \sim \bar{V}$, we have

$$E^{1-\frac{1}{a}} \sim V^{1-\frac{1}{\beta}} E^{-\frac{1}{2}} \sim E^{1-\frac{1}{\beta}-\frac{1}{2}},$$

or

$$\frac{1}{a} = \frac{1}{2} + \frac{1}{\beta} \Rightarrow a = \left(\frac{1}{2} + \frac{1}{\beta} \right)^{-1}. \quad (1)$$

In spite of the hand-waving character of “deriving” (1), the latter is valid (for every n) for $\beta = 2$ (harmonic potential) and for $\beta = -1$ (Coulomb potential), since the exact results are $a = 1$ and $a = -2$ respectively.

The WKB approach (see Q34, p.447) gives that $|E| \sim (n + \frac{1}{2})^a$.

Problem 2.11s

We introduce the quantities q and k as follows:

$$\hbar^2 q^2 / 2m \equiv \varepsilon_b \text{ and } \hbar^2 k^2 / 2m \equiv |\varepsilon| - \varepsilon_b.$$

Then the ground state has the form:

$$\psi = A J_0(kr), r \leq a; \psi = B K_0(qr), r \geq a; \quad (1)$$

($K_0(z) = \frac{i\pi}{2} H_0^{(1)}(iz)$ is the modified Bessel function of zero-order; see Table H.18). The continuity of the logarithmic derivative ψ'/ψ at $r = a$ leads to the following relation

$$\frac{k J_0'(ka)}{J_0(ka)} = \frac{q K_0'(qa)}{K_0(qa)}, \quad (2)$$

where the prime denote differentiation with respect to the corresponding argument ka or qa respectively. For small values of ε_b and $|\varepsilon|$ (in comparison with $E_0 \equiv \hbar^2 / ma^2$), ka and qa are much smaller than one. Expanding $J_0(ka)$ and $K_0(qa)$ we have

$$J_0(ka) = 1 - \frac{1}{4}(ka)^2 + \mathcal{O}(k^4 a^4), \quad (3)$$

$$K_0(qa) = - \left[\ln \left(\frac{qa}{2} \right) + \gamma \right] \left[1 + \frac{(qa)^2}{4} \right] + \frac{(qa)^2}{4} + \mathcal{O} \left[\ln \left(\frac{qa}{2} \right) q^4 a^4 \right].$$

Substituting in (2) we have

$$- \frac{k^2 a^2}{2} = - \frac{1}{-\ln \left(\frac{1}{2} e^\gamma qa \right)}. \quad (4)$$

Taking into account that $q^2 a^2 = 2\varepsilon_b / E_0$ and $k^2 a^2 = 2(|\varepsilon| - \varepsilon_b) / E_0 \simeq 2|\varepsilon| / E_0$, we obtain the relation

$$\varepsilon_b \simeq \frac{2}{e^{2\gamma}} E_0 \exp \left(- \frac{2E_0}{|\varepsilon|} \right).$$

Chapter 3

Problem 3.1s

According to (3.1) the viscosity η is equal to $\mu_s t$, where μ_s is the shear modulus and t is a characteristic time of motion of each water molecule; t is expected to be of the order of the period of molecular vibration T in ice: $t = c_1 T = 2\pi c_1 / \omega$, where $\omega = (c_2 \hbar / m_e a_B^2 \bar{r}_w^2) \sqrt{m_e / m_w}$ and c_1, c_2 are numerical constants of the order of one. Substituting $m_w = 18 \times 1823 m_e$ and $\bar{r}_w = (2.68 \times 18)^{1/3} = 3.64$ we have $\omega = c_2 1.72 \times 10^{13}$ rad/s. The shear modulus μ_s (in ice) is expected to be around $0.3 B$ where B is the bulk modulus of water, where $B \simeq 0.2 \hbar^2 / m_e a_B^5 \bar{r}_w^5 = 9.2 \times 10^9$ N/m² (the numerical coefficient was taken 0.2 and not 0.6 as usually, because the hydrogen bond is much weaker than the strong bonds for which the 0.6 is a reasonable choice). Hence, the result for η is

$$\eta = (2\pi c_1 / c_2) (0.3 \times 9.2 \times 10^9 / 1.72 \times 10^{13}) = (c_1 / c_2) 10^{-3} \text{ kg/ms},$$

which coincides with the experimental result if $c_1 = c_2$.

Problem 3.2s

H₂O has larger cohesive energy, because H₂O possesses a dipole moment (being non-linear), while CO₂ is non-polar (being a symmetric linear molecule).

Problem 3.12s

Consider a rotation of a Bravais Lattice, by an angle θ , around the axis z , of an orthogonal Cartesian system, passing through a lattice point. The matrix $\sum(\theta)$ implementing this rotation has the form

$$\sum(\theta) = \begin{vmatrix} \cos \theta & \sin \theta & 0 \\ -\sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{vmatrix}. \quad (1)$$

Now we denote the same rotation in the system $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ by the matrix $\sum'(\theta)$. If $\sum'(\theta)$ is compatible with the translational symmetry of the lattice, each lattice point $\sum_i n_i \mathbf{a}_i$ will be mapped to another lattice point $\sum_i n'_i \mathbf{a}_i$: $[n'_i] = \sum'(\theta) [n_i]$; where $[n'_i]$ and $[n_i]$ are column matrices. For $\{n'_i\}$ ($i = 1, 2, 3$) to be integers, for any set of three integers n_1, n_2, n_3 the matrix elements of $\sum'(\theta)$, must be integers. Since $\sum(\theta)$ and $\sum'(\theta)$ describe the same rotation in different coordinate systems, they must be related by a transformation of the form

$$\sum'(\theta) = S^{-1} \sum(\theta) S, \quad (2)$$

where S is a 3×3 matrix, connecting the two coordinate systems. By taking the trace of (2), we have

$$\text{Tr} \sum'(\theta) = \text{Tr} S^{-1} \sum(\theta) S = \text{Tr} S S^{-1} \sum(\theta) = \text{Tr} \sum(\theta). \quad (3)$$

The $\text{Tr} \sum(\theta) = 2 \cos \theta + 1$ and the $\text{Tr} \sum'(\theta)$ is an integer, since all matrix elements of $\sum'(\theta)$ are integers. Hence

$$2 \cos \theta = \text{integer},$$

from which it follows that $\theta = 2\pi/n$, $n = 1, 2, 3, 4, 6$.

Chapter 4

Problem 4.7ts

For Cu , $\zeta = 2.57$, $\bar{r}_c = 1.113$, $\eta = 0.6025$, $a = 4.429 + 6.2687 = 10.70$, $\gamma = 1.97 + 5.944 = 7.916$, $\bar{r}_a = 2.70$, $B = 1.16 \text{ Mbar}$, $P_P = 294 \frac{\gamma}{4\pi \bar{r}_a^4} = \frac{185.2}{\bar{r}_a^4} = 3.48 \text{ Mbar}$.

Problem 4.1s

Binding energies in eV (Th.: Theory; Exp.: Experiment) Na (Th. 4.92; Exp. 6.25), K (Th. 4.07; Exp. 5.27), Mg (Th. 19.98; Exp. 24.19), Ca (Th. 15.73; Exp. 19.82), Fe (Th. 56.29; Exp. 59.02), Al (Th. 52.49; Exp. 56.65), Ti (Th. 69.36; Exp. 96.01).

Problem 4.2s

Debye temperature in degrees K according to the RJM for some solids:

Al (419), Cu (300), Au (142), Fe (497), Pb (80), Mg (344), Be (1322).

Problem 4.3s

Hint: Combine (C.25) with (4.100). At $T \geq \Theta_D$ use (4.51) for B and (4.66) for Θ_D .

Problem 4.7s

The constant electronic charge density is $\rho = -3\zeta e / 4\pi (r_a^3 - r_c^3)$, $r_c \leq r \leq r_a$; from Gauss theorem the electric field $\varepsilon(r)$ is $4\pi\varepsilon_0\varepsilon(r)r^2 = (4\pi/3)\rho(r^3 - r_c^3)$. The potential $\phi(r) = -\int \varepsilon(r)dr$ is $4\pi\varepsilon_0\phi(r) = -(2\pi/3)\rho r^2 - (4\pi\rho r_c^3/3r) +$

const. The const. is determined from $4\pi\epsilon_0\phi(r_a) = -\zeta e / r_a$: $\text{const} = -3\zeta e r_a^3 / 2 (r_a^3 - r_c^3)$. The classical electronic Coulomb self-energy is

$$E_{e-e} = \frac{1}{2} \int_{r_c}^{r_a} \phi(r) \rho(r) d^3r = \frac{3}{2} \frac{\zeta^2 e^2}{4\pi\epsilon_0 (1-x^2)^2 r_a} \left[\frac{4}{10} - x^3 + \frac{6}{10} x^5 \right], \quad x = \frac{r_c}{r_a}.$$

The electrostatic Coulomb electron-ion interaction is

$$E_{e-i} = \rho \int_{r_c}^{r_a} d^3r \frac{\zeta e}{4\pi\epsilon_0 r} = -\frac{3}{2} \frac{\zeta^2 e^2 (r_a^2 - r_c^2)}{4\pi\epsilon_0 (r_a^3 - r_c^3)}.$$

Adding E_{e-e} and E_{e-i} , we obtain the classical electrostatic energy per atom in agreement with the given formula.

Chapter 5

Problem 5.4s

Values of $\hbar\omega_{pf}$ (in eV) for some solids according to (5.27).

Li (8.39), Na (6.62), K (4.87), Rb (4.45), Mg (11.21), Al (14.98), Ag (9.33).

Problem 5.9s

For Si and from Table 4.4 (p. 98), we have $c_l = 8945$ m/s and $c_t = 5341$ m/s. We shall choose $\langle c \rangle \simeq 7500$ m/s. The Debye temperature $\Theta_D = 645$ K, so that $T / \Theta_D \simeq 300 / 645 = 0.465$ and $C_V \simeq 0.82 \times 3N_a k_B$; $V / N_a = 20 \text{ \AA}^3$; $\ell_{ph} \simeq 300 \text{ \AA}$. The result, according to (5.134), is $K_{ph} \simeq 127 \text{ Wm}^{-1}\text{K}^{-1} = 1.27 \text{ Wcm}^{-1}\text{K}^{-1}$ vs. $1.48 \text{ Wcm}^{-1}\text{K}^{-1}$ experimentally.

Problem 5.11s

The Fourier transform of $f(\mathbf{r}) = \exp(-k_s r) / r$ is

$$\begin{aligned} \tilde{f}(\mathbf{k}) &= \int d^3r \exp(-i\mathbf{k} \cdot \mathbf{r}) f(\mathbf{r}) \\ &= 2\pi \int_{-1}^1 d(\cos \theta) \exp(-ikr \cos \theta) dr r^2 f(r) \\ &= (4\pi/k) \int_0^\infty dr \sin kr \exp(-k_s r) = 4\pi / (k^2 + k_s^2). \end{aligned}$$

Problem 5.13s

The resistivity in SI is $\rho = v_F / \varepsilon_0 \omega_{\text{pf}}^2 \ell$, where $\ell^{-1} = n_s \int \frac{d\sigma}{d\Omega} (1 - \cos \theta) d\Omega$. We have $k^2 = 4k_F^2 \sin^2(\theta/2) = 2k_F^2(1 - \cos \theta)$, $2k dk = -2k_F^2 d(\cos \theta)$, $d\Omega = -2\pi d(\cos \theta) = 2\pi k dk / k_F^2$. Moreover, $d\sigma / d\Omega = (m^2 / 4\pi^2 \hbar^4) (e^2 n_e / \varepsilon_0)^2 (|\mathbf{k} \cdot \mathbf{u}| / k^2 \varepsilon(k))^2 = (m^2 e^4 n_e^2 / 4\pi^2 \hbar^4 \varepsilon_0^2) (V \hbar \omega_k < n_k > / B) / (k^2 \varepsilon(k))^2 = (\lambda_0 k_s^4 / \rho_{\text{FV}}) (m^2 / 4\pi^2 \hbar^4) \times (V \hbar \omega_k < n_k >) / (k_s^2 \varepsilon(k))^2$. We took into account that $\lambda_0 / \rho_{\text{FV}} = E_s^2 / B$ and $E_s = e^2 n_e / \varepsilon_0 k_s^2$. Substituting in the expression for ℓ^{-1} we have $\ell^{-1} = (\lambda_0 k_s^4 / \rho_{\text{FV}}) (m^2 / 4\pi^2 \hbar^4) V^{-1} V \hbar \int \omega_k < n_k > (k^2 / 2k_F^2) (2\pi k dk / k_F^2) / (k^2 \varepsilon(k))^2 = (\lambda_0 k_s^4 m^2 / 4\pi k_F^4 \hbar^4 \rho_{\text{FV}}) \times \int dk k^3 \hbar \omega_k < n_k > / (k^2 \varepsilon(k))^2$ or, by defining $y \equiv \beta \hbar \bar{c} k$, $\ell^{-1} = (\lambda_0 m^2 k_s^4 / 4\pi \hbar^4 k_F^4 \rho_{\text{FV}}) (2^4 k_F^4 / y_0^4) \int dy y^3 \hbar \omega_k \frac{1}{k^4 \varepsilon^2(k)} \frac{1}{e^y - 1}$, where $y_0 = 2\beta \hbar \bar{c} k_F$. We have taken into account that $E_F = \hbar^2 k_F^2 / 2m$, $E_F \rho_{\text{FV}} = (3/4) n_e = (3/4) (k_F^3 / 3\pi^2) = k_F^3 / 4\pi^2$, and $k^2 \varepsilon(k) = k^2 + k_s^2 = k_s^2 [1 + (k^2 / k_s^2)]$ and we have

$$\ell^{-1} = \frac{\lambda_0 m}{8\pi \hbar} \frac{4\pi^2}{p_F} \frac{16k_B T}{y_0^4} \int_0^{y_0} \frac{dy y^4}{[1 + (2by^2/y_0^2)]^2 (e^y - 1)},$$

where $k^2 / k_s^2 = (k^2 / k_F^2) (k_F^2 / k_{\text{TF}}^2 f) = (2y^2 / y_0^2) (2k_F^2 / k_{\text{TF}}^2 f)$ and $f(k/k_F)$ is given by (D.28). We write $b \equiv 2k_F^2 / k_{\text{TF}}^2 f$. Thus

$$\rho = \frac{v_F}{\varepsilon_0 \omega_{\text{pf}}^2 \ell} = \frac{mv_F}{p_F} \frac{8\pi^2 \lambda_0}{4\pi \varepsilon_0 \hbar \omega_{\text{pf}}^2} \frac{4k_B T}{y_0^4} \int_0^{y_0} \frac{dy y^4}{[1 + (2by^2/y_0^2)]^2 (e^y - 1)},$$

which coincides with (5.59) since $mv_F \equiv p_F$.

Problem 5.15s

$$\begin{aligned} m\dot{\mathbf{v}} &= -e\mathbf{E} - \frac{e\mathbf{v} \times \mathbf{B}}{c}, \\ m\mathbf{B} \times \dot{\mathbf{v}} &= -e\mathbf{B} \times \mathbf{E} - \frac{e}{c} \mathbf{B} \times (\mathbf{v} \times \mathbf{B}), \\ \mathbf{B} \times (\mathbf{v} \times \mathbf{B}) &= vB^2 - \mathbf{B}(\mathbf{v} \cdot \mathbf{B}), \\ m\mathbf{B} \times \dot{\mathbf{v}} &= -e\mathbf{B} \times \mathbf{E} - \frac{e}{c} [vB^2 - \mathbf{B}(\mathbf{v} \cdot \mathbf{B})], \\ \frac{e}{c} B^2 \mathbf{v} &= -m\mathbf{B} \times \dot{\mathbf{v}} - e\mathbf{B} \times \mathbf{E} + \frac{e}{c} (\mathbf{v} \cdot \mathbf{B}) \mathbf{B}, \\ \mathbf{v} &= -\frac{mc}{e} \frac{1}{B^2} \mathbf{B} \times \dot{\mathbf{v}} - \frac{c}{B^2} \mathbf{B} \times \mathbf{E} + \frac{1}{B^2} (\mathbf{v} \cdot \mathbf{B}) \mathbf{B}, \\ \mathbf{v} &= -\frac{mc}{e} \frac{1}{B} \mathbf{B}_0 \times \dot{\mathbf{v}} - \frac{c}{B} \mathbf{B}_0 \times \mathbf{E} + (\mathbf{v} \cdot \mathbf{B}_0) \mathbf{B}_0, \\ \mathbf{v} &= -\frac{mc}{eB} \mathbf{B}_0 \times \dot{\mathbf{v}} + \mathbf{v}_0 + (\mathbf{v} \cdot \mathbf{B}_0) \mathbf{B}_0, \\ \mathbf{v}_\perp &= -\frac{mc}{eB} \mathbf{B}_0 \times \dot{\mathbf{v}}_\perp + \mathbf{v}_0, \mathbf{v}_\parallel = (\mathbf{v} \cdot \mathbf{B}_0) \mathbf{B}_0 = \text{Const.} \end{aligned}$$

Chapter 6

Problem 6.5s

We implement the successive transformations shown in Fig. 6.16a and at each stage we calculate the matrix elements of the Hamiltonian

$$\begin{aligned}\chi_{n-1}^1 &= \frac{1}{\sqrt{2}} (s_{n-1} + p_{x,n-1}), & \chi_n^2 &= \frac{1}{\sqrt{2}} (s_n - p_{x,n}), \\ \chi_n^1 &= \frac{1}{\sqrt{2}} (s_n + p_{x,n}), & \chi_{n+1}^2 &= \frac{1}{\sqrt{2}} (s_{n+1} - p_{x,n+1}).\end{aligned}$$

For the matrix elements of $\hat{H}$ we have

$$\begin{aligned}\langle \chi_i^1 | \hat{H} | \chi_i^1 \rangle &= \langle \chi_i^2 | \hat{H} | \chi_i^2 \rangle = \frac{\varepsilon_p + \varepsilon_s}{2}, \quad i = n-1, n, n+1, \\ \langle \chi_i^1 | \hat{H} | \chi_i^2 \rangle &= \langle \chi_i^2 | \hat{H} | \chi_i^1 \rangle = -\frac{\varepsilon_p - \varepsilon_s}{2} = -V_1, \quad i = n-1, n, n+1, \\ \langle \chi_{n-1}^1 | \hat{H} | \chi_n^1 \rangle &= \frac{1}{2} \left[\langle s_{n-1} | \hat{H} | s_n \rangle + \langle s_{n-1} | \hat{H} | p_{x,n} \rangle + \langle p_{x,n-1} | \hat{H} | s_n \rangle \right. \\ &\quad \left. + \langle p_{x,n-1} | \hat{H} | p_{x,n} \rangle \right] \\ &= \frac{\hbar^2}{2md^2} [-1.32 + 1.42 - 1.42 + 2.22] = 0.45 \frac{\hbar^2}{md^2}.\end{aligned}$$

Similarly, $\langle \chi_n^2 | \hat{H} | \chi_{n+1}^2 \rangle = \frac{\hbar^2}{2md^2} [-1.32 - 1.42 + 1.42 + 2.22] = 0.45 \frac{\hbar^2}{md^2}$,

$$\begin{aligned}\langle \chi_n^1 | \hat{H} | \chi_{n+1}^2 \rangle &= \frac{\hbar^2}{2md^2} [-1.32 - 1.42 - 1.42 - 2.22] = -3.19 \frac{\hbar^2}{md^2}, \\ \psi_{bn-1,n} &= \frac{1}{\sqrt{2}} (\chi_{n-1}^1 + \chi_n^2), \quad \psi_{bn,n+1} = \frac{1}{\sqrt{2}} (\chi_n^1 + \chi_{n+1}^2), \\ \psi_{a,n-1,n} &= \frac{1}{\sqrt{2}} (\chi_{n-1}^1 - \chi_n^2), \quad \psi_{a,n,n+1} = \frac{1}{\sqrt{2}} (\chi_n^1 - \chi_{n+1}^2), \\ H_{n,n+1}^{bb} &\equiv \langle \psi_{bn-1,n} | \hat{H} | \psi_{bn,n+1} \rangle \\ &= \frac{1}{2} \left[\langle \chi_{n-1}^1 | \hat{H} | \chi_n^1 \rangle + \langle \chi_n^2 | \hat{H} | \chi_n^1 \rangle + \langle \chi_n^2 | \hat{H} | \chi_{n+1}^2 \rangle \right] \\ &= \frac{1}{2} [0.45 \hbar^2/md^2 - V_1 + 0.45 \hbar^2/md^2] = \frac{1}{2} [0.9 \hbar^2/md^2 - V_1], \\ H_{n,n+1}^{aa} &= \frac{1}{2} [0.45 \hbar^2/md^2 + V_1 + 0.45 \hbar^2/md^2] = \frac{1}{2} [0.9 \hbar^2/md^2 + V_1], \\ H_{n,n+1}^{ab} &= \frac{1}{2} [0.45 \hbar^2/md^2 - V_1 - 0.45 \hbar^2/md^2] = V_1/2.\end{aligned}$$

Problem 6.6s

The bonding or antibonding molecular orbitals are linear combinations of χ_{nc}^1 and χ_{n+1a}^2 atomic hybrids (see Fig. 6.17):

$\psi_{bn,n+1} = c_1\chi_{nc}^1 + c_2\chi_{n+1a}^2$ with a similar expression $\psi_{an,n+1}$. Equation (1), $\hat{H}\psi_{bn,n+1} = \varepsilon\psi_{bn,n+1}$, in the basis χ_{nc}^1 and χ_{n+1a}^2 reads

$$\begin{pmatrix} \varepsilon_{hc} - \varepsilon_{b,a} & V_{2h} \\ V_{2h} & \varepsilon_{ha} - \varepsilon_{b,a} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0, \quad (4)$$

where $\varepsilon_{hc} = \varepsilon + V_{3h}$, $\varepsilon_{ha} = \varepsilon - V_{3h}$ are given by (6.81)–(6.83) and $V_{2h} = -3.19\hbar^2/md^2$. By setting the determinant equal to zero we find the eigenenergies ε_b and ε_a as given by (6.77) and (6.78). From (1) we have that $c_1/c_2 = V_{2h}/(\varepsilon_{b,a} - \varepsilon_{hc}) = V_{2h}/(\mp\sqrt{V_{2h}^2 + V_{3h}^2} - V_{3h}) = \pm(|V_{2h}|/\sqrt{V_{2h}^2 + V_{3h}^2})/(1 \pm a_p) = \pm\sqrt{1 - a_p^2}/(1 \pm a_p) = \pm[(1 - a_p^2)/(1 \pm a_p)^2]^{1/2} = [(1 \mp a_p)/(1 \pm a_p)]^{1/2}$ where the upper signs are for the bonding and the lower for the antibonding. Taking into account the requirement of normalization it follows that

$$\begin{aligned} c_1 &= \frac{1}{\sqrt{2}}(1 - a_p)^{1/2}, \quad c_2 = \frac{1}{\sqrt{2}}(1 + a_p)^{1/2}, \text{ bonding,} \\ c_1 &= \frac{1}{\sqrt{2}}(1 + a_p)^{1/2}, \quad c_2 = -\frac{1}{\sqrt{2}}(1 - a_p)^{1/2}, \text{ antibonding.} \end{aligned}$$

Problem 6.7s

Hint: Follow a similar to 6.5s step by step procedure and take into account that ψ_b and ψ_a are given by (6.79) and (6.80).

Problem 6.8s

As it was mentioned in Problem 6.3 the Hamiltonian in the basis g_{iak} is diagonal in k ; thus in the intermediate expressions we are going to omit the index k . From (6.41) we have

$$\begin{aligned} \langle g_{sc} | \hat{H} | g_{sc} \rangle &= \varepsilon_{sc}, & \langle g_{sc} | \hat{H} | g_{sa} \rangle &= V_{ss\sigma} (1 + e^{2ikd}), & \langle g_{sc} | \hat{H} | g_{pc} \rangle &= 0, \\ \langle g_{sc} | \hat{H} | g_{pa} \rangle &= V_{sp\sigma} (-1 + e^{2ikd}), & \langle g_{sa} | \hat{H} | g_{sa} \rangle &= \varepsilon_{sa}, \\ \langle g_{sa} | \hat{H} | g_{pc} \rangle &= V_{sp\sigma} (1 - e^{-2ikd}), & \langle g_{sa} | \hat{H} | g_{pa} \rangle &= 0, \\ \langle g_{pc} | \hat{H} | g_{pc} \rangle &= \varepsilon_{pc}, & \langle g_{pc} | \hat{H} | g_{pa} \rangle &= V_{pp\sigma} (1 + e^{2ikd}). \end{aligned}$$

Thus the 4×4 Hamiltonian matrix is:

$$\begin{array}{c} \begin{array}{c} sc \\ sa \\ pc \\ pa \end{array} \left| \begin{array}{cccc} & sc & sa & pc & pa \\ \begin{array}{c} sc \\ sa \\ pc \\ pa \end{array} & \begin{array}{c} \varepsilon_{sc} \\ V_{ss\sigma}(1 + e^{-2ikd}) \\ 0 \\ V_{sp\sigma}(-1 + e^{-2ikd}) \end{array} & \begin{array}{c} V_{ss\sigma}(1 + e^{2ikd}) \\ \varepsilon_{sa} \\ V_{sp\sigma}(1 - e^{2ikd}) \\ 0 \end{array} & \begin{array}{c} 0 \\ V_{sp\sigma}(1 - e^{-2ikd}) \\ \varepsilon_{ps} \\ V_{pp\sigma}(1 + e^{-2ikd}) \end{array} & \begin{array}{c} V_{sp\sigma}(-1 + e^{2ikd}) \\ 0 \\ V_{pp\sigma}(1 + e^{2ikd}) \\ \varepsilon_{pa} \end{array} \end{array} \right|.$$

For $\sin kd = 0$, i.e. $kd = 0$ or π , the above 4×4 breaks into two uncoupled 2×2 matrices, one involving the s states only and the other the p states only. These can be diagonalized immediately giving the following eigenvalues:

$$E_{v\ell} = \bar{\varepsilon}_s - \sqrt{V_{3s}^2 + 4V_{ss\sigma}^2} \quad s\text{-character},$$

$$E_{c\ell} = \bar{\varepsilon}_s + \sqrt{V_{3s}^2 + 4V_{ss\sigma}^2} \quad s\text{-character},$$

$$E_{vu} = \bar{\varepsilon}_p - \sqrt{V_{3p}^2 + 4V_{pp\sigma}^2} \quad p\text{-character},$$

$$E_{cu} = \bar{\varepsilon}_p + \sqrt{V_{3p}^2 + 4V_{pp\sigma}^2} \quad p\text{-character},$$

where

$$\begin{aligned} \bar{\varepsilon}_s &= (\varepsilon_{cs} + \varepsilon_{sa})/2, & V_{3s} &= (\varepsilon_{sc} - \varepsilon_{sa})/2, & \bar{\varepsilon}_p &= (\varepsilon_{ps} + \varepsilon_{pa})/2, \\ V_{3p} &= (\varepsilon_{pc} - \varepsilon_{pa})/2. \end{aligned}$$

The gap E_g is equal to

$$E_g = E_{c\ell} - E_{vu} = \sqrt{V_{3s}^2 + 4V_{ss\sigma}^2} + \sqrt{V_{3p}^2 + 4V_{pp\sigma}^2} - (\bar{\varepsilon}_p - \bar{\varepsilon}_s),$$

(assuming that $E_{c\ell} > E_{vu}$; if $E_{vu} > E_{c\ell}$ the gap is equal to minus the above expression). According to this analysis the band edges of the VB and the CB are obtained by the following graphical analysis (Fig. 6.19):

The resulting gap is larger than that given by (6.50).

Using the values for GaAs (from table B.3 and for $d = 2.45A$) we have

$$\begin{aligned} \bar{\varepsilon}_s &= -15.23, & V_{3s} &= 3.68, & V_{ss\sigma} &= 1.674, \\ \bar{\varepsilon}_p &= -7.325, & V_{3p} &= 1.655, & V_{pp\sigma} &= 2.815, \\ E_{v\ell} &= -20.205 \text{ eV}, & E_{c\ell} &= -10.255 \text{ eV}, & E_{vu} &= -13.1932 \text{ eV}, \\ E_{cu} &= -1.457 \text{ eV}, \\ E_g &= 2.938 \text{ eV}, \end{aligned}$$

while the approach shown in Fig. 6.17 gives

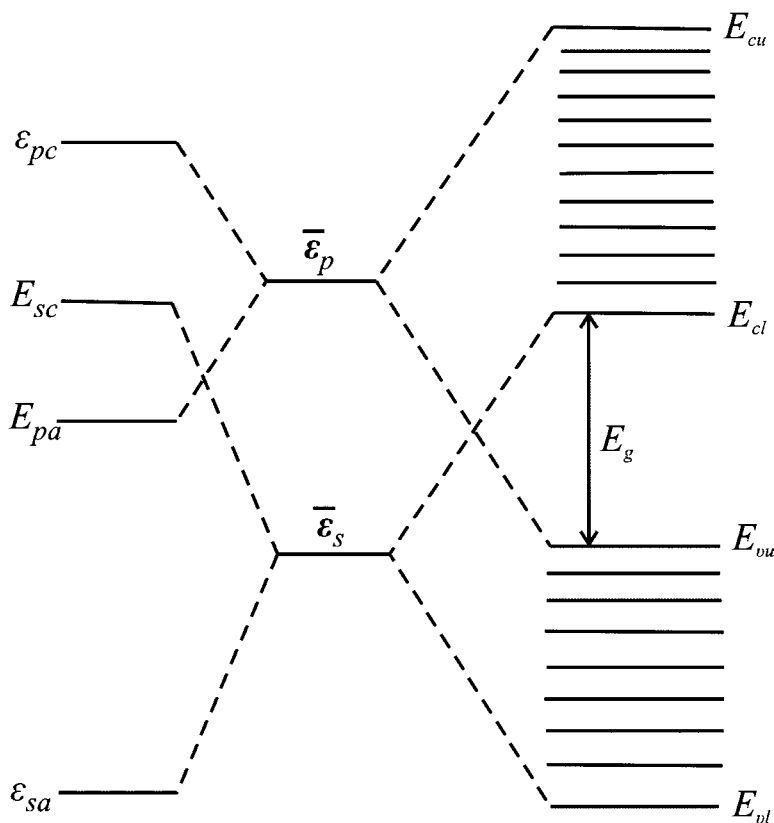


Fig. 6.19. The band edges, E_{vl} , E_{vu} , E_{cl} , E_{cu} of a one-dimensional compound semiconductor assuming that they correspond to $\sin kd = 0$; for $\sin kd = 0$ the s -states decoupled from the p -states, so that the bottoms of both the VB and the CB are of s -character, while the tops of both the VB and the CB are of p -character.

$E_{vl} \simeq -19.68$ eV, $E_{cl} \simeq -10.78$ eV, $E_{vu} \simeq -12.58$ eV, $E_{cu} \simeq -2.075$ eV, $E_g = 1.85$ eV, vs. $E_g \simeq 1.52$ eV experimentally.

In the case of an elemental “semiconductor” for which $V_{3s} = V_{3p} = 0$, we have that the coefficients $c_{sa} = c_{sc} \exp(-ikd)$ and $c_{pa} = c_{pc} \exp(-ikd)$; thus the 4×4 matrix reduces to a 2×2 matrix as follows

$$\begin{array}{cc} \begin{array}{c} sc \\ pc \end{array} & \begin{array}{c} \varepsilon_s + 2V_{ss\sigma} \cos kd \\ -2iV_{sp\sigma} \sin kd \end{array} \\ \begin{array}{c} pc \\ sc \end{array} & \begin{array}{c} \varepsilon_p + 2V_{pp\sigma} \cos kd \\ 2iV_{sp\sigma} \sin kd \end{array} \end{array}$$

Problem 6.10s

By performing the integration (since $\sum_k \rightarrow (L/2\pi) \int dk$) we obtain the following result

$$2 \sum_{k \leq k_F} E(k) = N \left[\varepsilon - \frac{2|V_2 + V_2'|}{\pi} E(\lambda) \right], \quad (2)$$

where $E(\lambda)$ is the complete elliptic integral of second kind, $E(\lambda) \equiv \int_0^{\pi/2} d\phi \sqrt{1 - \lambda^2 \sin^2 \phi}$, and $\lambda = 4V_2 V_2' / (V_2 + V_2')^2$. Assume that $V_2 = V_0 \left(\frac{a}{2} - x \right)$ and $V_2' = V_0 \left(\frac{a}{2} + x \right)$ where $V_0(y) \equiv -c/y^2$ and x is small. We call $U(x)$ the value of $2 \sum_{k \leq k_F} E(k)$ for small x and $\delta U \equiv U(0) - U(x)$. Make the appropriate expansions and show that

$$\delta U = \frac{8}{\pi} \left| V_0 \left(\frac{a}{2} \right) \right| \left[1 + \ln \left(\frac{a}{|x|} \right) \right] \frac{4x^2}{a^2}. \quad (3)$$

Equation (3) shows that the dimerization of the model given by (6.11) and (6.12) by a small amount x lowers the total electronic energy by an amount of the order $x^2 \ln(1/|x|)$. If any other energy (such as the elastic energy) contributing to the total energy changes by an amount of the order x^2 , then we can conclude that the dimerization lowers the total energy and hence, the model given by (6.11) and (6.12) with one electron per atom is unstable against lattice distortion (**Peierls instability**).

Chapter 7

Problem 7.1s

Let us calculate, e.g., the matrix element $\langle g_{os} | \hat{H} | g_{1px} \rangle$. The summation over the primitive cell vectors $\mathbf{R}$ in (6.49) involves the ones for which $\mathbf{R} + \mathbf{d}_1$ are nearest neighbors of the atom "0" located at $\mathbf{R} = 0$ (see Fig. 7.1); $\mathbf{d}_1 = (a/4)(1, 1, 1)$ is the position of the atom "1" at the primitive cell $\mathbf{R} = 0$. Out of the twelve nearest neighbors $\mathbf{R}$ of $\mathbf{R} = 0$ only the following, $(a/2)(0\bar{1}\bar{1})$, $(a/2)(\bar{1}0\bar{1})$, $(a/2)(\bar{1}\bar{1}0)$ have $|\mathbf{R} + \mathbf{d}_1| = |\mathbf{d}_1|$ and hence, are nearest neighbors of atom "0" located at $\mathbf{R} = 0$. Thus, the four nearest neighbors of atom "0" are located at $\mathbf{d}_1 = \mathbf{O} + \mathbf{d}_1$, $\mathbf{d}_2 = (a/2)(0\bar{1}\bar{1}) + \mathbf{d}_1 = (a/4)(1\bar{1}\bar{1})$, $\mathbf{d}_3 = (a/2)(\bar{1}0\bar{1}) + \mathbf{d}_1 = (a/4)(\bar{1}1\bar{1})$, and $\mathbf{d}_4 = (a/2)(\bar{1}\bar{1}0) + \mathbf{d}_1 = (a/4)(\bar{1}\bar{1}1)$. To obtain a more symmetrical expression we define $\bar{c}_{1a}$ from the relation $c_{1a} = \bar{c}_{1a} \exp(i\mathbf{k} \cdot \mathbf{d}_1)$ (see (6.42)) so that all off-diagonal matrix elements will be multiplied by $\exp(i\mathbf{k} \cdot \mathbf{d}_1)$. The matrix elements $\langle \phi_{oos} | \hat{H} | \phi_{R1px} \rangle$ are given by (F.6) and (F.8), where $\ell = 1/\sqrt{3}, 1/\sqrt{3}, -1/\sqrt{3}, -1/\sqrt{3}$ for $\mathbf{d}_1, \mathbf{d}_2, \mathbf{d}_3, \mathbf{d}_4$ respectively. Thus with these conventions we have

$$\langle g_{os} | \hat{H} | g_{1px} \rangle = E_{sp} g_1(\mathbf{k}),$$

where $E_{sp} = (1.42/\sqrt{3}) \hbar^2/md^2 = 0.82 \hbar^2/md^2$ and

$$g_1(\mathbf{k}) \equiv \exp(i\mathbf{k} \cdot \mathbf{d}_1) + \exp(i\mathbf{k} \cdot \mathbf{d}_2) - \exp(i\mathbf{k} \cdot \mathbf{d}_3) - \exp(i\mathbf{k} \cdot \mathbf{d}_4).$$

In a similar way we obtain all other matrix elements. The final result for the 8×8 matrix equation is the following:

$$\begin{vmatrix} \varepsilon_{so} - E & E_{ss}g_o & 0 & 0 & 0 & E_{sp}g_1 & E_{sp}g_2 & E_{sp}g_3 \\ E_{ss}g_o^* & \varepsilon_{s1} - E & -E_{sp}g_1^* & -E_{sp}g_2^* & -E_{sp}g_3^* & 0 & 0 & 0 \\ 0 & -E_{sp}g_1 & \varepsilon_{po} - E & 0 & 0 & E_{xx}g_o & E_{xy}g_3 & E_{xy}g_2 \\ 0 & -E_{sp}g_2 & 0 & \varepsilon_{po} - E & 0 & E_{xy}g_3 & E_{xx}g_o & E_{xy}g_1 \\ 0 & -E_{sp}g_3 & 0 & 0 & \varepsilon_{po} - E & E_{xy}g_2 & E_{xy}g_1 & E_{xx}g_o \\ E_{sp}g_1^* & 0 & E_{xx}g_o^* & E_{xy}g_3^* & E_{xy}g_2^* & \varepsilon_{p1} - E & 0 & 0 \\ E_{sp}g_2^* & 0 & E_{xy}g_3^* & E_{xx}g_o^* & E_{xy}g_1^* & 0 & \varepsilon_{p1} - E & 0 \\ E_{sp}g_3^* & 0 & E_{xy}g_2^* & E_{xy}g_1^* & E_{xx}g_o^* & 0 & 0 & \varepsilon_{p1} - E \end{vmatrix} \begin{vmatrix} c_{so} \\ \bar{c}_{s1} \\ c_{xo} \\ c_{yo} \\ c_{zo} \\ \bar{c}_{x1} \\ \bar{c}_{y1} \\ \bar{c}_{z1} \end{vmatrix} = 0,$$

where $E_{ss} \equiv V_{ss\sigma} = -1.32 \hbar^2/md^2$, $E_{xx} = \frac{1}{3}V_{pp\sigma} + \frac{2}{3}V_{pp\pi} = 0.32 \hbar^2/md^2$, and $E_{xy} = \frac{1}{3}V_{pp\sigma} - \frac{1}{3}V_{pp\pi} = 0.95 \hbar^2/md^2$; moreover,

$$\begin{aligned} g_0(\mathbf{k}) &= \exp(i\mathbf{k} \cdot \mathbf{d}_1) + \exp(i\mathbf{k} \cdot \mathbf{d}_2) + \exp(i\mathbf{k} \cdot \mathbf{d}_3) + \exp(i\mathbf{k} \cdot \mathbf{d}_4), \\ g_2(\mathbf{k}) &= \exp(i\mathbf{k} \cdot \mathbf{d}_1) - \exp(i\mathbf{k} \cdot \mathbf{d}_2) + \exp(i\mathbf{k} \cdot \mathbf{d}_3) - \exp(i\mathbf{k} \cdot \mathbf{d}_4), \\ g_3(\mathbf{k}) &= \exp(i\mathbf{k} \cdot \mathbf{d}_1) - \exp(i\mathbf{k} \cdot \mathbf{d}_2) - \exp(i\mathbf{k} \cdot \mathbf{d}_3) + \exp(i\mathbf{k} \cdot \mathbf{d}_4). \end{aligned}$$

The eigenfunctions $\psi_{\mathbf{k}}$ are of the form $\psi_{\mathbf{k}} = \sum_a c_{0a} |g_{0a\mathbf{k}}\rangle + \sum_a \bar{c}_{1a} |g_{1a\mathbf{k}}\rangle$. Notice that for $\mathbf{k} = 0$, $g_0 = 4$ and $g_1 = g_2 = g_3 = 0$, so that the 8×8 breaks into four 2×2 systems (one for s and three identical ones for the $p's$).

Problem 7.4s

We choose the atom “0” in Fig. 7.1 to be the anion and the atom “1” to be the cation. By a similar calculation as in Problem 6.6s, we find that the bonding and the antibonding molecular orbitals between atoms “0” and “1” are:

$$\begin{aligned} \psi_b^{(01)} &= \frac{1}{\sqrt{2}} \left[(1 + a_p)^{1/2} \chi_o^1 + (1 - a_p)^{1/2} \chi_1^1 \right], \\ \psi_a^{(01)} &= \frac{1}{\sqrt{2}} \left[(1 - a_p)^{1/2} \chi_o^1 - (1 + a_p)^{1/2} \chi_1^1 \right]. \end{aligned}$$

Similarly, the bonding and the antibonding orbitals between atoms “1” and “2” in Fig. 7.1 are

$$\begin{aligned} \psi_a^{(12)} &= \frac{1}{\sqrt{2}} \left[(1 - a_p)^{1/2} \chi_2^2 - (1 + a_p)^{1/2} \chi_1^2 \right], \\ \psi_b^{(12)} &= \frac{1}{\sqrt{2}} \left[(1 + a_p)^{1/2} \chi_2^2 + (1 - a_p)^{1/2} \chi_1^2 \right]. \end{aligned}$$

Let us calculate

$$\begin{aligned} H_c^{bb} &= \left\langle \psi_b^{(01)} \left| \hat{H} \right| \psi_b^{(12)} \right\rangle = \frac{1}{2} \left[(1 - a_p^2)^{1/2} \left\langle \chi_o^1 \left| \hat{H} \right| \chi_1^2 \right\rangle + (1 - a_p^2)^{1/2} \right. \\ &\quad \left. \left\langle \chi_1^1 \left| \hat{H} \right| \chi_2^2 \right\rangle + (1 - a_p) \left\langle \chi_1^1 \left| \hat{H} \right| \chi_1^2 \right\rangle \right]. \end{aligned}$$

To proceed, we have to calculate $\langle \chi_0^1 | \hat{H} | \chi_1^2 \rangle$, which by symmetry is equal to $\langle \chi_1^1 | \hat{H} | \chi_2^2 \rangle$. (The matrix element, $\langle \chi_1^1 | \hat{H} | \chi_1^2 \rangle = -V_{1c} = -(\varepsilon_p - \varepsilon_s)/4$ according to (F.65)). The matrix element $\langle \chi_0^1 | \hat{H} | \chi_1^2 \rangle$ can be obtained either by employing the analysis in s, p_x, p_y, p_z as given in (F.60) and the mirror image of (F.61) (see also Fig. 7.1) or, more conveniently, by choosing the x' axis along the χ_0^1 orbital and the y' axis in the plane defined by the three atoms “0”, “1”, “2” in Fig. 7.1. Then $\chi_0^1 = [s + \sqrt{3}p_{x'}]/2$, $\chi_1^1 = [s - \sqrt{3}p_{x'}]/2$ and $\chi_1^2 = [s + \lambda_{x'}p_{x'} + \lambda_{y'}p_{y'}]$. The orthogonality of χ_1^1 and χ_1^2 requires that $\lambda_{x'} = 1/\sqrt{3}$ and the sp^3 condition, $\lambda_{x'}^2 + \lambda_{y'}^2 = 3$, determines $\lambda_{y'} = -\sqrt{8/3}$. Hence,

$$\begin{aligned} \langle \chi_0^1 | \hat{H} | \chi_1^2 \rangle &= \frac{1}{4} \left[V_{ss\sigma} + \frac{1}{\sqrt{3}} V_{sp\sigma} + \sqrt{3} V_{ps\sigma} + V_{pp\sigma} \right] \\ &= \frac{1}{4} \left[-1.32 + \frac{1.42}{\sqrt{3}} - \sqrt{3} \times 1.42 + 2.22 \right] \frac{\hbar^2}{md^2} \\ &= -0.185 \hbar^2 / md^2. \end{aligned}$$

Thus the final result for H_c^{bb} is

$$H_c^{bb} = -\frac{1-a_p}{2} V_{1c} - \Lambda'; \quad \Lambda' = 0.185 \frac{\sqrt{1-a_p^2} \hbar^2}{md^2},$$

which coincides with (7.14). In a similar way we obtain $\hat{H}_a^{bb}$, $\hat{H}_c^{aa}$ and $\hat{H}_a^{aa}$; a_p is given by (F.30) with V_2 and V_3 replaced by V_{2h} and V_{3h} respectively.

Problem 7.6s

Notice that $v_{\mathbf{k}} = \hbar^{-1} \nabla_{\mathbf{k}} \varepsilon_{\mathbf{k}}$ and that $\varepsilon_{\mathbf{k}} v_{\mathbf{k}} = (2\hbar)^{-1} \nabla_{\mathbf{k}} \varepsilon_{\mathbf{k}}^2$. The integral of the gradient of a periodic function, $f(\mathbf{k})$, such as $\varepsilon_{\mathbf{k}}$ or $\varepsilon_{\mathbf{k}}^2$, over the BZ is zero. To prove this define

$$I(\mathbf{q}) = \int_{\text{BZ}} d^3k f(\mathbf{k} + \mathbf{q}),$$

and notice that $I(\mathbf{q})$ does not depend on $\mathbf{q}$. (To show this, change variable to $\mathbf{k}' = \mathbf{k} + \mathbf{q}$ so that $I(\mathbf{q}) = \int_{\text{pc}} d^3k' f(\mathbf{k}')$, where pc is a primitive cell; but the integral of a periodic function over a primitive cell is the same no matter how the primitive cell is chosen). Then take the gradient of $I(\mathbf{q})$:

$$\nabla_{\mathbf{k}} I(\mathbf{q}) = 0 = \int_{\text{BZ}} d^3k \nabla_{\mathbf{k}} f(\mathbf{k} + \mathbf{q}); \quad QED.$$

Chapter 8

Problem 8.7s

For Schottky defects, the energy U due to the presence of N_S defects is $U = N_S \varepsilon_V$; the entropy $S = k_B \ln \Delta\Gamma$, where $\Delta\Gamma$ is the number of ways for the N_S

defects to be placed at the N_L lattice sites:

$$\Delta\Gamma = N_L!/N_S!(N_L - N_S)! \simeq N_L^{N_L}/N_S^{N_S} (N_L - N_S)^{(N_L - N_S)}.$$

Thus the minimization condition $\partial G/\partial N_S = 0$ leads to $\varepsilon_v = -k_B T [\ln N_S - \ln (N_L - N_S)]$ ($N_S/N_L \ll 1$).

For Frenkel defects we have to combine the $N_L!/N_F!(N_L - N_F)!$ ways of placing the N_F vacancies in the N_L lattice sites with the $N_I!/N_F!(N_I - N_F)!$ ways of placing the N_F atoms in the N_I interstitial sites. From this point on the procedure is to minimize the Gibbs free energy $G = U - TS = N_F \varepsilon_F - k_B T \ln \Delta\Gamma$, taking into account that $N_F/N_L \ll 1$ and $N_F/N_I \ll 1$.

Problem 8.8s

The bound state eigenenergy does not belong to the spectrum of the unperturbed Hamiltonian. This implies that the operator $\varepsilon_b - \hat{H}_0$ never becomes zero and that the only solution of $\hat{H}_0 |\chi\rangle = \varepsilon_b |\chi\rangle$ is the trivial one, $|\chi\rangle = 0$. Thus the only possibility, if any, to have a non-zero $|\psi\rangle$ in (B.59) for $E = \varepsilon_b$ and $|\chi\rangle = 0$ is for the operator

$$\left[1 - \hat{G}_0(E) \hat{H}_1\right]^{-1},$$

to blow up; given the form of $\hat{H}_1$, the only non-zero matrix elements of this operator are the ones between any $\langle n|$ and the $|0\rangle$ orbital. Expanding the operator in a power series and taking the matrix element $\langle n|, |0\rangle$ we obtain

$$\left\langle n \left| \left[1 - \hat{G}_0(E) \hat{H}_1\right]^{-1} \right| 0 \right\rangle = \delta_{n0} - \varepsilon G_{n0} \frac{1}{1 + \varepsilon G_{00}},$$

where

$$G_{n0}(E) = \left\langle n \left| \hat{G}_0(E) \right| 0 \right\rangle = \left\langle n \left| \frac{1}{E - \hat{H}_0} \right| 0 \right\rangle = \sum_{\mathbf{k}} \frac{\langle n | \mathbf{k} \rangle \langle \mathbf{k} | 0 \rangle}{E - E(\mathbf{k})},$$

and $\hat{H}_0 |\mathbf{k}\rangle = E(\mathbf{k}) |\mathbf{k}\rangle$, i.e. $|\mathbf{k}\rangle$ are the eigenstates and $E(\mathbf{k})$ are the eigenenergies of $\hat{H}_0$. The sum over $\mathbf{k}$ can be simplified by introducing the DOS, $\rho(E') = \sum_{\mathbf{k}} \delta(E' - E(\mathbf{k}))$, as follows

$$\begin{aligned} G_{n0}(E) &= \int dE' \sum_{\mathbf{k}} \delta(E' - E(\mathbf{k})) \frac{\langle n | \mathbf{k} \rangle \langle \mathbf{k} | 0 \rangle}{E - E(\mathbf{k})} \\ &= \int dE' \frac{1}{E - E'} \sum_{\mathbf{k}} \delta(E' - E(\mathbf{k})) \times \langle n | \mathbf{k} \rangle \langle \mathbf{k} | 0 \rangle. \end{aligned}$$

By choosing $\langle n| = \langle 0|$ we have

$$G_{00}(E) = \int \frac{dE'}{E - E'} \frac{\rho(E')}{V}, \text{ since } \langle 0 | \mathbf{k} \rangle \langle \mathbf{k} | 0 \rangle = 1/V.$$

Hence, the bound eigenenergy ε_b is given as solution of the equation $1 + \varepsilon G_{00}(E) = 0$, or equivalently

$$\frac{1}{\varepsilon} = -\frac{1}{V} \int_{E_l}^{E_u} \frac{dE' \rho(E')}{E - E'} = -\int_{E_l}^{E_u} \frac{dE' \rho_0(E')}{E - E'}; \quad \rho_0(E') = \frac{1}{V} \rho(E'),$$

where E_l is the lower and E_u is the upper band edge.

Show that $G_{00}(E)$ is negative with negative slope for $E < E_l$; moreover, as E approaches E_l from below, $G_{00}(E)$ blows up as $-(E_l - E)^{-1/2}$ when $\rho_0(E') \rightarrow (E' - E_l)^{-1/2}$, or as $\ln(E_l - E)$ if $\rho_0(E)$ goes to a constant as $E' \rightarrow E_l$; finally $G_{00}(E)$ goes to a negative constant as $E' \rightarrow E_l^-$, if $\rho_0(E') \rightarrow (E' - E_l)^a$ with $a > 0$.

Chapter 9

Problem 9.1s

The phase of the incoming wave at the point $\mathbf{R}$ relative to that of the origin is $\phi_{\mathbf{R}i} - \phi_{oi} = \mathbf{k}_i \cdot \mathbf{R}$. The phase of the scattered wave at the point $\mathbf{R}$ is delayed relative to that at the origin by $\phi_{\mathbf{R}f} - \phi_{of} = -\mathbf{k}_f \cdot \mathbf{R}$ (the minus sign because of the delay). Hence, the scattered wave by a scatterer at $\mathbf{R}$ has a phase difference $\Delta\phi$ relative to that in the origin given by

$$\Delta\phi = \phi_{\mathbf{R}i} - \phi_{oi} + \phi_{\mathbf{R}f} - \phi_{of} = \mathbf{k}_i \cdot \mathbf{R} - \mathbf{k}_f \cdot \mathbf{R} = \mathbf{k} \cdot \mathbf{R}.$$

Problem 9.2s

If we choose to work with the *cubic unit* cell of the *bcc* lattice (instead of the primitive cell), the vectors of the direct lattice are $a(n_1\mathbf{i} + n_2\mathbf{j} + n_3\mathbf{k})$ and that of the reciprocal are $(2\pi/a)(m_1\mathbf{i} + m_2\mathbf{j} + m_3\mathbf{k})$. There are two atoms per cubic unit cell, one at the origin and the other at $\mathbf{r} = (a/2)(\mathbf{i} + \mathbf{j} + \mathbf{k})$. Hence, the structure factor of the cubic unit cell is

$$S_G = g[1 + \exp(-i\mathbf{G} \cdot \mathbf{r})] = g[1 + \exp(-i\pi(m_1 + m_2 + m_3))],$$

where g is the atomic form factor. Notice that if, $m_1 + m_2 + m_3$ is odd, $S_G = 0$. Thus only $\mathbf{G}'$'s such that $m_1 + m_2 + m_3$ is even contribute to S_G giving $2g$.

If we choose to work with the primitive cell of the *bcc* we have

$$\begin{aligned} \mathbf{R}_n &= (a/2)[(-n_1 + n_2 + n_3)\mathbf{i} + (n_1 - n_2 + n_3)\mathbf{j} + (n_1 + n_2 - n_3)\mathbf{k}], \\ \mathbf{G}_m &= \frac{2\pi}{a}[(m_2 + m_3)\mathbf{i} + (m_3 + m_1)\mathbf{j} + (m_1 + m_2)\mathbf{k}]. \end{aligned}$$

In this case all $\mathbf{G}'$'s contribute, and $S_G = g$; however, the sum of their Cartesian component is $2(m_1 + m_2 + m_3)$, i.e. always even. The cubic unit cell will give $2g$ since there are two primitive cells per cubic cell. Thus both approaches give the same result. The reader may work out the **fcc** case with four primitive cells per cubic unit cell.

Problem 9.3s

The distance between two points lying in two consecutive direct lattice planes along the direction of the basic vector $\mathbf{a}_1$ is $|\mathbf{a}_1|$; then the distance d_p between these two planes is $\mathbf{a}_1 \cdot \mathbf{n}$ where $\mathbf{n}$ is a vector of magnitude one normal to both planes. But $\mathbf{n} = \mathbf{G}/|\mathbf{G}|$ where $\mathbf{G}(m_1, m_2, m_3)$ is a vector of the reciprocal lattice normal to the plane with Miller indices, m_1, m_2, m_3 . Hence, the distance $d_p = \mathbf{a}_1 \cdot \mathbf{G}/|\mathbf{G}| = 2\pi m_1/|\mathbf{G}|$, or $|\mathbf{G}| = 2\pi m_1/d_p$ QED.

Problem 9.5s

In Fig. 9.10 below we plot the phonon dispersion $\pm\hbar\omega(q)$ vs. q in the repeated zone scheme (continuous curves) and the parabolas $\varepsilon_f - \varepsilon_i = (\hbar^2/2m)(k_i \pm q)^2 - \varepsilon_i$ for the neutron (dashed curves). The intersection of solid and the dashed curves, gives the values of q which satisfy both (9.26) and (9.27).

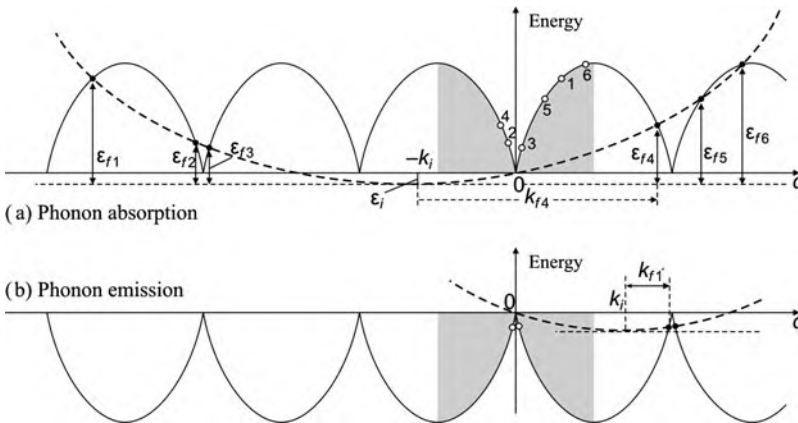


Fig. 9.10. Phonon dispersion, $\hbar\omega$ vs q , in the repeated zone scheme (continuous lines) and the neutron parabolas $\varepsilon_f - \varepsilon_i$ vs $(k_i \pm q)^2$ (dashed lines). The intersections of the continuous lines with the dashed lines provide the energies and the wavenumbers for absorbed and emitted phonons

Problem 9.7s and 9.9s

Let $|\lambda\rangle$ be a normalized eigenfunction of the hermitean non negative operator $a_Q^\dagger a_Q : a_Q^\dagger a_Q |\lambda\rangle = \lambda |\lambda\rangle$, where λ is the corresponding eigenvalue ($\lambda \geq 0$). Consider the state $a_{Q'} |\lambda\rangle$ and act on it by $a_Q^\dagger a_Q : a_Q^\dagger a_Q a_{Q'} |\lambda\rangle = (a_Q a_Q^\dagger a_Q - \delta_{QQ'} a_Q) |\lambda\rangle = a_{Q'} \lambda |\lambda\rangle - \delta_{QQ'} a_Q |\lambda\rangle = \lambda a_{Q'} |\lambda\rangle - \delta_{QQ'} a_Q |\lambda\rangle = (\lambda - \delta_{QQ'}) a_{Q'} |\lambda\rangle$. Thus the state $a_Q |\lambda\rangle$ is also an eigenstate of $a_Q^\dagger a_Q$ with an eigenvalue $\lambda - 1$; moreover, the state $a_Q^n |\lambda\rangle$ is also an eigenstate of $a_Q^\dagger a_Q$ with eigenvalue $\lambda - n$ where n is any natural number. Since the eigenvalues of $a_Q^\dagger a_Q$ are non negative, it follows that these eigenvalues are $n = 0, 1, 2, \dots$, because, otherwise, $a_Q^\dagger a_Q$ would have negative eigenvalues.

We found that $a_Q |n\rangle = \chi_n |n-1\rangle$, where $|n-1\rangle$ is normalized and χ_n is the normalization factor. We have $\langle n | a_Q^+ a_Q | n \rangle = n = \chi_n^2 \langle n-1 | n-1 \rangle = \chi_n^2$. Hence

$$a_Q |n\rangle = \sqrt{n} |n-1\rangle.$$

Similarly we can show that $a_Q^+ |n\rangle = \chi'_n |n+1\rangle$ and that $\chi'_n = \sqrt{n+1}$.

Problem 9.12s

We assume central forces and cubic symmetry. Let $\mathcal{V}(R)$ be the potential energy between an atom at the origin and one located at the lattice point $\mathbf{R}$. The change Δ in the total potential energy due to displacements $\mathbf{u}(\mathbf{R})$ is

$$\Delta = \frac{1}{2} \sum_{\mathbf{R}} (\partial^2 V / \partial R^2) (\delta R)^2,$$

where $\delta R^2 = [\mathbf{R} \cdot (\mathbf{u}(\mathbf{R}) - \mathbf{u}(0)) / R]^2 = \left\{ R_x^2 (u_x(\mathbf{R}) - u_x(0))^2 + R_y^2 (u_y(\mathbf{R}) - u_y(0))^2 + R_x R_y (u_x(\mathbf{R}) - u_x(0)) (u_y(\mathbf{R}) - u_y(0)) + R_y R_x (u_y(\mathbf{R}) - u_y(0)) (u_x(\mathbf{R}) - u_x(0)) \right\} / R^2$ assuming displacements in the x, y plane. It follows that the spring constants $\kappa_{ij}(\mathbf{R}) = -D_{ij}(\mathbf{R})$ are proportional to $R_i R_j$: $D_{ij}(\mathbf{R}) = -A R_i R_j$. Substituting in (9.63) we have

$$\begin{aligned} c_{12} \equiv c_{xxyy} &= \frac{-1}{8V_{\text{pc}}} \sum_{\mathbf{R}} [R_x D_{xy} R_y + R_x D_{xy} R_y + R_x D_{xy} R_y + R_x D_{xy} R_y] \\ &= \frac{A}{2V_{\text{pc}}} \sum_{\mathbf{R}} R_x^2 R_y^2. \end{aligned}$$

Similarly

$$\begin{aligned} c_{44} \equiv c_{xyxy} &= -\frac{1}{8V_{\text{pc}}} \sum_{\mathbf{R}} [R_x D_{yy} R_x + R_y D_{xy} R_x + R_x D_{yx} R_y + R_y D_{xx} R_y] \\ &= \frac{A}{8V_{\text{pc}}} \sum_{\mathbf{R}} [R_x^2 R_y^2 + R_y^2 R_x^2 + R_x^2 R_y^2 + R_y^2 R_x^2] = \frac{A}{2V_{\text{pc}}} \sum_{\mathbf{R}} R_x^2 R_y^2 = c_{12}. \end{aligned}$$

(For a more general treatment of Cauchy's relations see the book by Born and Huang [AW64], p. 136).

Problem 9.13s

The force, $\mathbf{F}_i$ exercised on the atom 0 at the center by the spring i ($i = 1, \dots, 8$) is the product of the unit vector $\mathbf{n}_i = \cos \theta_i \mathbf{i} + \sin \theta_i \mathbf{j}$ in the direction of the spring i , times the elongation of the spring i along the direction $\mathbf{n}_i$, $\mathbf{n}_i \cdot (\mathbf{u}_i - \mathbf{u}_0)$, times the spring constant:

$\mathbf{F}_i = \kappa_i \mathbf{n}_i \cdot (\mathbf{u}_i - \mathbf{u}_0) \mathbf{n}_i = \kappa_i [\cos \theta_i (u_{ix} - u_{0x}) + \sin \theta_i (u_{iy} - u_{0y})] [\cos \theta_i \mathbf{i} + \sin \theta_i \mathbf{j}]$; $\kappa_i = \kappa$, if i odd, $\kappa_i = \kappa'$, if i even.

Newton's equation for the ℓ component ($\ell = x, y$) of the displacement $\mathbf{u}_0$ is

$$\begin{aligned} -m\omega^2 u_{0x} = & \kappa(u_{1x} - u_{0x}) + \frac{1}{2}\kappa'(u_{2x} - u_{0x} + u_{2y} - u_{0y}) \\ & + \frac{1}{2}\kappa'(u_{4x} - u_{0x} - u_{4y} + u_{0y}) + \kappa(u_{5x} - u_{0x}) \\ & + \frac{1}{2}\kappa'(u_{6x} - u_{0x} + u_{6y} - u_{0y}) + \frac{1}{2}\kappa'(u_{8x} - u_{0x} - u_{8y} + u_{0y}), \end{aligned} \quad (1)$$

where $\cos^2 \theta_i = 1/2$ and $\cos \theta_i \cdot \sin \theta_i = \pm 1/2$, for even i ; there is an equation similar to (1) for the u_{0y} component.

Employing Bloch theorem, $\mathbf{u}_i = \mathbf{u}_0 \exp(i\mathbf{k} \cdot \mathbf{R}_i)$, and the following relations:

$$\begin{aligned} \mathbf{k} \cdot \mathbf{R}_1 = k_x a, \quad \mathbf{k} \cdot \mathbf{R}_2 = k_x a + k_y a, \quad \mathbf{k} \cdot \mathbf{R}_3 = k_y a, \quad \mathbf{k} \cdot \mathbf{R}_4 = -k_x a + k_y a, \\ \mathbf{k} \cdot \mathbf{R}_5 = -k_x a, \quad \mathbf{k} \cdot \mathbf{R}_6 = -k_x a - k_y a, \quad \mathbf{k} \cdot \mathbf{R}_7 = -k_y a, \\ \text{and } \mathbf{k} \cdot \mathbf{R}_8 = k_x a - k_y a, \end{aligned} \quad (2)$$

we obtain from (1), by setting $\omega_0^2 = \kappa/m$ and $\omega_0'^2 = \kappa'/m$:

$$\begin{aligned} [\omega^2 - 2\omega_0^2(1 - \cos k_x a) - \omega_0'^2(2 - \cos(k_x a + k_y a) - \cos(k_x a - k_y a))] u_{0x} \\ + \omega_0'^2 [\cos(k_x a + k_y a) - \cos(k_x a - k_y a)] u_{0y} = 0. \end{aligned} \quad (3)$$

Similarly, for the y -component we have

$$\begin{aligned} \omega_0'^2 [\cos(k_y a + k_x a) - \cos(k_y a - k_x a)] u_{0x} \\ + [\omega^2 - 2\omega_0^2(1 - \cos k_y a) - \omega_0'^2(2 - \cos(k_y a + k_x a) - \cos(k_y a - k_x a))] u_{0y} = 0. \end{aligned} \quad (4)$$

Setting the determinant of (3) and (4) equal to zero we obtain a quadratic equation for ω^2 , the solutions of which give the two eigenfrequencies. Plot with the help of the computer the eigenfrequencies vs. $\mathbf{k}$ as $\mathbf{k}$ follows the line segments, ΓX , $X M$, $M \Gamma$. Plot also the contours $\omega = \omega_1(\mathbf{k})$ and $\omega = \omega_2(\mathbf{k})$ for various values of ω . Notice that, for $\mathbf{k}$ along ΓX , (3) and (4) decouple and the solutions are either pure longitudinal or pure transverse. Along ΓM also the solutions are pure LA or pure TA. The sound velocities for $\mathbf{k}$ along ΓX or along ΓM are:

$c_l = a\sqrt{\omega_0^2 + \omega_0'^2}$, $c_t = a\omega_0'$ and $c_l = a\sqrt{\frac{1}{2}\omega_0^2 + 2\omega_0'^2}$, $c_t = a\omega_0/\sqrt{2}$ respectively.

Problem 9.16s

We have shown that $2W = \langle (\mathbf{k} \cdot \mathbf{u})^2 \rangle = \langle k^2 u^2 \cos^2 \theta \rangle = \frac{1}{3} k^2 \langle u^2 \rangle$; we took into account that $\mathbf{k}$ is constant and that the average of $\cos^2 \theta$ over all solid

angles is $1/3$. But twice the potential energy $\frac{1}{2}\kappa\langle u^2 \rangle$ is equal to the total vibrational energy ε per atom. Hence, $2W = \frac{1}{3}k^2\langle u^2 \rangle = \frac{1}{3}k^2\varepsilon/\kappa$; but $\omega_D^2 = c_1\kappa/M$, where c_1 is a numerical constant of the order of one and M is the mass of each atom. Thus

$$2W = \frac{c_1}{3} \frac{1}{\omega_D^2 M} k^2 \varepsilon. \quad (1)$$

For low temperatures $T \ll \Theta_D$, $\varepsilon = (9/8)\hbar\omega_D$, while for $T \gtrsim \Theta_D$, $\varepsilon = 3k_B T$. Hence

$$2W = \frac{3c_1}{8} \frac{\hbar^2 k^2 / M}{\hbar\omega_D}, \quad T \ll \Theta_D, \quad (2)$$

$$2W = c_1 \frac{k^2 k_B T}{\omega_D^2 M} = c_1 \frac{\hbar^2 k^2 / M}{\hbar\omega_D} \frac{T}{\Theta_D}, \quad T \ll \Theta_D. \quad (3)$$

The exact asymptotic expressions for the Debye model are obtained by setting $c_1 = 2$ in (2) and $c_1 = 3$ in (3).

Chapter 10

Problem 10.2s

We change the integration to summation over the $\mathbf{k}'$ s of the 1st BZ, according to (B.19); then we use the identity $(x + is)^{-1} \rightarrow P(x^{-1}) - i\pi\delta(x)$, as $s \rightarrow 0^+$. Thus, we end up with $\rho_n(E) = \sum_{\mathbf{k}} \delta(E - E_n(\mathbf{k}))$, which is valid by the definition of $\rho_n(E)$.

Problem 10.4s

The full answer can be found in the book by E. N. Economou [DSL153], pp.422–425.

Problem 10.5s

According to (10.42) m_c^* is proportional to $|\partial A(E, k_z)/\partial E|$ where A is the area enclosed by the curve resulting from the intersection of the constant energy surface $E = \frac{1}{2} \sum_{ij} \gamma_{ij} q_i q_j + \varepsilon_0$ and the plane $q_z = 0$, where $\mathbf{q} = \mathbf{k} - \mathbf{k}_0$; the tensor γ_{ij} is related to the mass tensor as follows: $\gamma_{ij} = \hbar^2 (M^{-1})_{ij}$. The equation of the closed curve, $\frac{1}{2} \gamma_{xx} q_x^2 + \frac{1}{2} \gamma_{yy} q_y^2 + \gamma_{xy} q_x q_y = E - \varepsilon_0$, can be brought to a diagonal form $\frac{1}{2} \tilde{\gamma}_{xx} \tilde{q}_x^2 + \frac{1}{2} \tilde{\gamma}_{yy} \tilde{q}_y^2 = E - \varepsilon_0 + c$ by a rotation plus translation transformation; c is a constant. This is the equation of an ellipse with semiaxes $a^2 = 2|E - \varepsilon_0 + c|/\tilde{\gamma}_{xx}$ and $b^2 = 2|E - \varepsilon_0 + c|/\tilde{\gamma}_{yy}$; its enclosed area is $A = \pi ab = 2\pi|E - \varepsilon_0 + c|/\sqrt{\tilde{\gamma}_{xx}\tilde{\gamma}_{yy}}$ and $|\partial A/\partial E| = 2\pi/\sqrt{\tilde{\gamma}_{xx}\tilde{\gamma}_{yy}}$. The rotation preserves the determinant so that $\tilde{\gamma}_{xx}\tilde{\gamma}_{yy} = \gamma_{xx}\gamma_{yy} - \gamma_{xy}^2$; but,

because $\gamma M = \hbar^2$, we have that $\gamma_{xx}\gamma_{yy} - \gamma_{xy}^2 = \hbar^4 M_{zz} / \det |M_{ij}|$. hence, $m_c^* = (\hbar^2/2\pi) |\partial A / \partial E| = |\det(M)/M_{zz}|^{1/2}$.

Chapter 11

Problem 11.3s

See the book by S. Flügge [Q26], problem 81, pp. 210–213.

Problem 11.5s

Equation (11.75), by employing the identity $\nabla' \cdot (f_1(\mathbf{r}') \nabla' f_2(\mathbf{r}')) = f_1(\mathbf{r}') \nabla'^2 f_2(\mathbf{r}') + \nabla' f_1(\mathbf{r}') \cdot \nabla' f_2(\mathbf{r}')$ and the equations (11.43) and (11.16), turns out to be identical to (11.47). From (11.75) we have by employing Gauss theorem

$$\int d\mathbf{S}' G_o(\mathbf{r} - \mathbf{r}') \cdot \nabla' \psi(\mathbf{r}') = \int d\mathbf{S}' \psi(\mathbf{r}') \cdot \nabla' G_o(\mathbf{r} - \mathbf{r}'), \quad (1)$$

where $d\mathbf{S}'$ is the infinitesimal element of the area of the sphere $|\mathbf{r}'| = r_0$ pointing along the direction $\mathbf{r}'$. Setting: $\mathbf{r} = \rho, \theta, \phi$, $\mathbf{r}' = \rho', \theta', \phi'$, and $\rho = \rho' = r_0$, we have $d\mathbf{S}' \cdot \nabla' \psi(\mathbf{r}') = r_0^2 d\Omega' (\partial \psi(\mathbf{r}') / \partial \rho')$ and $d\mathbf{S}' \cdot \nabla' G_o(\mathbf{r} - \mathbf{r}') = r_0^2 d\Omega' (\partial G(\mathbf{r} - \mathbf{r}') / \partial \rho')$; substituting in (1), (11.49) follows (with the renaming $\rho', \theta', \phi', d\Omega' \leftrightarrow \rho, \theta, \phi, d\Omega$).

Problem 11.9s

The interaction energy, $U_{ie} = \int V_i(\mathbf{r}) n(\mathbf{r}) d^3r$, in view of (11.77) and (11.78) can be written as follows

$$U_{ie} = \frac{1}{V} \sum_{\mathbf{q}, \mathbf{k}} V_{i\mathbf{q}} n_{\mathbf{k}} \int e^{i(\mathbf{q}+\mathbf{k}) \cdot \mathbf{r}} d^3r = \sum_{\mathbf{q}} V_{i\mathbf{q}} n_{-\mathbf{q}} = -\frac{1}{e} \sum_{\mathbf{q}} V_{i\mathbf{q}} \rho_{-\mathbf{q}}, \quad (1)$$

since the integral is equal to $V \delta_{-\mathbf{q}, \mathbf{k}}$. The ionic potential $V_i(\mathbf{r})$ can be written as follows: $V_i(\mathbf{r}) = (-e/4\pi\epsilon_0) \int d^3r' \rho_i(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'|$. Writing both $\rho_i(\mathbf{r}')$ and $|\mathbf{r} - \mathbf{r}'|^{-1}$ in terms of their Fourier transforms, $\rho_i(\mathbf{r}') = \frac{1}{\sqrt{V}} \sum_{\mathbf{q}} \rho_{i\mathbf{q}} \exp(i\mathbf{q} \cdot \mathbf{r}')$

and $|\mathbf{r} - \mathbf{r}'|^{-1} = \frac{1}{V} \sum_{\mathbf{k}} \frac{4\pi}{k^2} \exp(i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}'))$, we obtain

$$V_i(\mathbf{r}) = -\frac{4\pi e}{4\pi\epsilon_0 \sqrt{V}} \sum_{\mathbf{q}} (\rho_{i\mathbf{q}} / q^2) e^{i\mathbf{q} \cdot \mathbf{r}}. \quad (2)$$

Comparing (11.77) and (2), we find that $V_{i\mathbf{q}} = -4\pi e \rho_{i\mathbf{q}} / 4\pi\epsilon_0 q^2$; substituting this expression for $V_{i\mathbf{q}}$ in (11.78), (11.79) follows.

Chapter 12

Problem 12.5s

The potential energy $V_i(d')$, which is the quantity in brackets in (12.23), can be written as follows by taking into account (12.21), (12.18), and the identity

$$d'^{-1} \equiv (2/\pi d') \int_0^{\infty} dk (\sin kd')/k$$

$$V_i(d) = -\frac{2e^2\zeta^2}{4\pi\epsilon_0\pi d'} \int_0^{\infty} dk \sin kd' \left[\frac{(\cos^2 kr_c)\tilde{f}(k) - 1}{k} \right]. \quad (1)$$

In arriving at (1) we have set $1 - \varepsilon^{-1} \equiv \tilde{f}$ and we have used the empty-core pseudopotential given by (11.4). The integrand in (1) is an even function; so we can extend the integration from $-\infty$ to $+\infty$ by dividing by two. Next we write: $\sin kd' = [\exp(ikd') - \exp(-ikd')]/2i$; in the integral over $\exp(-ikd')$ we change variables from k to $-k$, and this integral becomes identical to the one involving $\exp(ikd')$. Thus the end result is

$$V_i(d') = -\frac{e^2\zeta^2}{4\pi\epsilon_0 i\pi d'} \int_{-\infty}^{\infty} dk e^{ikd'} \left[\frac{\cos^2 kr_c \tilde{f}(k) - 1}{k} \right]. \quad (2)$$

If we choose the Thomas–Fermi expression for $\varepsilon(k)$ we have that $\tilde{f}(k) = k_{\text{TF}}^2/(k^2 + k_{\text{TF}}^2)$; then the integral in (2) can be calculated by closing the integration path with an infinite semicircle in the upper complex plane (which gives no contribution for $d' > 2r_c$) and by employing the residue theorem at the pole $k = ik_{\text{TF}}$ (the $k = 0$ is not a pole because $\cos^2 kr_c \tilde{f}(k) = 1 + O(k^2)$ as $k \rightarrow 0$). The residue is $-\frac{1}{2} \exp(-k_{\text{TF}}d') \cosh^2 k_{\text{TF}}r_c$ and, thus, (12.25) is obtained.

In the case where the RPA dielectric function is used we perform first two successive integrations by parts in (1) by setting $\sin kd' = -(1/d')d(\cos kd')/dk$ and $\cos kd' = (1/d')d(\sin kd')/dk$, so that the RPA singularity at $k = 2k_{\text{F}}$ would give rise to two poles at $k = \pm 2k_{\text{F}}$; then we do the same transformations which took us from (1) to (2). We have at the end the following result:

$$V_i(d') = \frac{1}{4\pi\epsilon_0} \frac{e^2\zeta^2}{i\pi d'^3} \int_{-\infty}^{\infty} dk e^{ikd'} \frac{d^2}{dk^2} \left[\frac{\cos^2 kr_c \tilde{f}(k) - 1}{k} \right]. \quad (3)$$

The quantity $\tilde{f} \equiv 1 - \varepsilon^{-1}$, given the expression $\varepsilon = 1 + (k_{\text{TF}}/k^2)f$, becomes $\tilde{f} = \frac{k_{\text{TF}}^2 f}{k^2 + k_{\text{TF}}^2 f}$, where f is given by (D.28). The most singular part of the integrand in (3), for real k , is due to the second derivative of f . Thus, for

$k^2 \simeq (2k_F)^2$, we have

$$\frac{d^2}{dk^2} \left[\frac{\cos^2 kr_c \tilde{f}(k) - 1}{k} \right] \simeq \frac{\cos^2 2k_F r_c}{2k_F} \frac{1}{\varepsilon^2(2k_F)} \frac{1}{\pi a_B k_F} \frac{1}{2(2k_F)} \left[\frac{1}{k - 2k_F} + \frac{1}{k + 2k_F} \right]. \quad (4)$$

In arriving at (4) we use the relation, $k_{TF}^2 = 4k_F/\pi a_B$. Substituting (4) in (3) and performing the integration by the residue theorem we find

$$V_1(d') = \frac{e^2 \zeta^2}{4\pi \varepsilon_0} \frac{\cos 2k_F d'}{d'^3} \frac{\cos^2 2k_F r_c}{(2k_F)^2} \frac{1}{\varepsilon^2(2k_F)} \frac{1}{\pi a_B k_F}. \quad (5)$$

Replacing $\cos^2 2k_F r_c$ from the relation, $\tilde{v}_{iA}(2k_F) = -4\pi\zeta e^2 n_a \cos 2k_F r_c / 4\pi\varepsilon_0 (2k_F)^2$, taking into account that $n_a = k_F^3/3\pi^2\zeta$ and $\tilde{v} = v_i/\varepsilon$, we obtain finally (12.24).

Chapter 13

Problem 13.2ts

To solve the system

$$\begin{vmatrix} E - E^{(0)} & V & \cdots & V \\ V & E - E^{(0)} & \cdots & V \\ \vdots & \vdots & \ddots & \vdots \\ V & V & \cdots & E - E^{(0)} \end{vmatrix} \begin{vmatrix} c_1 \\ c_2 \\ \vdots \\ c_N \end{vmatrix} = 0, \quad (1)$$

we try solutions of the form $c_n = c_o \exp(i\phi n)$ with $c_{N+1} = c_1$, so that $\phi = (2\pi/N)\ell$, $\ell = 1, 2, \dots, N$. The solution corresponding to $\ell = N$ is $c_1 = c_2 = \dots = c_N$ with eigenenergy $E = E^{(0)} - (N-1)V$. For all other solutions we have

$$V e^{i\phi} + V e^{2i\phi} + \dots + (E - E^{(0)}) e^{i n_0 \phi} + \dots + V e^{i N \phi} = 0. \quad (2)$$

We add and subtract the quantity $V \exp(i\phi n_0)$ so that (2) becomes

$$(E - E^{(0)} - V) e^{i\phi n_0} + V \sum_{n=1}^N e^{i\phi n}. \quad (3)$$

But the sum is equal to $\exp(i\phi) [e^{iN\phi} - 1] / [e^{i\phi} - 1] = 0$. Thus the other $N-1$ eigensolutions are all degenerate corresponding to the eigenenergy

$$E = E^{(0)} + V.$$

Problem 13.6ts

Let x' be the axis joining the misaligned atoms 0 and 1. The axis x' makes an angle θ with the original axis x joining the atoms 0 and 1 when they were aligned. The hybrid orbital $\chi_0^1 = \frac{1}{2}(|s\rangle_o + \sqrt{3}|p_x\rangle_o)$ for atom 0 is written in the new axes x' and y' $\chi_0^1 = \frac{1}{2}[|s\rangle_o + \sqrt{3}\cos\theta|p_{x'}\rangle_o - \sqrt{3}\sin\theta|p_{y'}\rangle_o]$. Similarly the hybrid for atom 1 is $\chi_1^1 = \frac{1}{2}[|s\rangle_1 - \sqrt{3}\cos\theta|p_{x'}\rangle_1 + \sqrt{3}\sin\theta|p_{y'}\rangle_1]$. Thus the matrix element $\langle\chi_0^1|\hat{H}|\chi_1^1\rangle$ is equal to

$$\frac{1}{4} [V_{ss\sigma} - 2\sqrt{3}\cos\theta V_{sp\sigma} - 3\cos^2\theta V_{pp\sigma} - 3\sin^2\theta V_{pp\pi}], \quad (4)$$

vs.

$$\frac{1}{4} [V_{ss\sigma} - 2\sqrt{3}V_{sp\sigma} - 3V_{pp\sigma}], \quad \text{for } V_{2h}. \quad (5)$$

Taking into account that for small θ , $\cos\theta \simeq 1 - \theta^2/2$, $\sin^2\theta = 1 - \cos^2\theta = \theta^2$, we have for the difference $(5) - (4) = \frac{\theta^2}{4} [-\sqrt{3}V_{sp\sigma} - 3V_{pp\sigma} + 3V_{pp\pi}] = -2.75 \frac{\hbar^2}{md^2} \theta^2$. Thus $\frac{(5)-(4)}{V_{2h}} = \frac{2.75}{3.22} \theta^2 = 0.85 \theta^2$.

Problem 13.7ts

The energy per bond Δ divided by the volume per bond $V_0 = a^3/16$ is related to the bulk modulus B as follows $\Delta/V_0 = \frac{1}{2}B(\delta V/V_0)^2$ but $\delta V/V_0 = 3\delta d/d_0$ so that $\Delta/V_0 = \frac{9}{2}B(\delta d/d_0)^2$ or $\Delta = \frac{1}{2}\frac{9Ba^3}{16}(\delta d/d_0)^2$. Comparing with (13.26) we obtain (13.27). For a derivation of (13.28) see Harrison [SS76], p. 195, and for a derivation of (13.29) see Harrison [SS76], p. 197–200.

Chapter 14

Problem 14.1ts

The zero point energy per atom must depend on $\hbar$ (due to its quantum nature), on the mass m_a (since it is due to vibrations of atoms), and on σ and ε , which are the two parameters characterizing the interaction energy. The mass must enter as a factor $m_a^{-1/2}$ because of the vibrational character of the phenomenon. Out of the three quantities $\hbar$, σ , ε the only combination to produce mass is the following: $\hbar^2/\varepsilon\sigma^2$. Hence, $U_i^{(0)}/N_a = c_1\varepsilon\sqrt{\hbar^2/\varepsilon\sigma^2 m_a} = c_1(\hbar/\sigma)\sqrt{\varepsilon/m_a}$.

Problem 14.2s

The Debye temperature Θ_D is given by (14.10) and the zero point motion by (14.11). We need the value of f which depends on the ratio $x = \mu_s/B$ (see

(4.67)). For $x = 0.32, 0.445$, and 0.49 , $f = 0.636, 0.745$, and 0.78 respectively. We expect the smaller values of f to be associated with the lighter noble gas atoms and the larger ones with the heavier. We chose f as shown in the table below:

	f	Θ_D , theory	Θ_D , exp	$U_i^{(0)}/N_a$ theory (meV)	U_c/N_a , theory (meV)	U_c/N_a exp (meV)
Ne	0.6	68	75	6.6	20.4	20
Ar	0.7	83	92	8.0	81	80
Kr	0.75	66	72	6.4	114.6	116
Xe	0.8	62	64	6	166	170

Problem 14.5s

In Fig. 14.4, we plot schematically the phase diagram in the P, T plane.

For noble gases the difference between B.P. and F.P. (under normal pressure) is very small (between 2.5 K and 4 K). Hence, taking into account the freezing temperatures and Fig. 14.4, we expect the triple point temperatures to be approximately 24.5 K, 83.8 K, 115.8 K and 161.4 K, for Ne, Ar, Kr, and Xe respectively (experimental values 24.5561, 83.8058, 115.8, 161.4); the triple point pressure is expected to be lower than the normal pressure of 100 kPa (experimental values 50 kPa, 68.95 kPa, 72.92 kPa, 81.59 kPa for Ne,

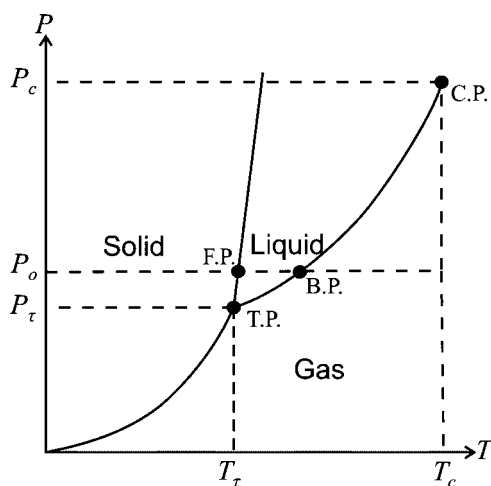


Fig. 14.4. Schematic phase diagram for a typical substance. T.P. is the triple point where the three phases (solid, liquid, gas) coexist. C.P. is the critical point where the liquid/gas coexistence line terminates. The solid/liquid coexistence curve is almost vertical. The freezing point (F.P.) and the boiling point (B.P.) under normal pressure are also shown.

Ar, Kr, and Xe respectively). Can you obtain the slope of the liquid/gas coexistence line as to estimate how much below the normal pressure the triple point pressure is?

Chapter 15

Problem 15.2s

We classify the 17 orbitals (or combination of orbitals) into columns of similarly behaving ones under rotation around the z -axis as shown below (see also Fig. 15.12)

$$\begin{array}{cccccc}
 d \{ & d_{3z^2-r^2} & d_{zx} & d_{zy} & d_{xy} & d_{x^2-y^2} \\
 p \left\{ \begin{array}{l} p_{3z} \\ \frac{1}{\sqrt{2}}(p_{1z} + p_{2z}) \end{array} \right. & p_{1x} & p_{1y} & & & \\
 & p_{2x} & p_{2y} & & \frac{1}{\sqrt{2}}(p_{1z} - p_{2z}) & \\
 & p_{3x} & p_{3y} & & & \\
 s \left\{ \begin{array}{l} s_3 \\ \frac{1}{\sqrt{2}}(s_1 + s_2) \end{array} \right. & & & & \frac{1}{\sqrt{2}}(s_1 - s_2) &
 \end{array} \quad (1)$$

The advantage of this classification is that any matrix element of the Hamiltonian between orbitals belonging to different columns is zero. Notice also that the combinations $(1/\sqrt{2})(s_1 \pm s_2)$ and $(1/\sqrt{2})(p_{1z} \pm p_{2z})$, obey Bloch's theorem in spite of 1 and 2 being non Bravais lattice points; the reason is that $\exp[i\mathbf{k} \cdot (\mathbf{R} + \mathbf{d}_1)] = \exp[i\mathbf{k} \cdot (\mathbf{R} + \mathbf{d}_2)] = \exp(i\mathbf{k} \cdot \mathbf{R})$ as a result of our choice for $\mathbf{k}$ to be along the z -direction.

Let us proceed with the calculation of a few representative matrix elements of the form $\sum_{\mathbf{R}} \exp(i\mathbf{k} \cdot \mathbf{R}_n) \langle 0, a | \hat{H} | \mathbf{R}_n, \beta \rangle$. As an example, consider the case where $|\alpha\rangle = d_{3z^2-r^2}$ and $|\beta\rangle = (s_1 + s_2)/\sqrt{2}$. The only non-zero matrix elements $\langle 0, \alpha | \hat{H} | \mathbf{R}_n, \beta \rangle$ in this case are for $\mathbf{R}_n = 0$ and for $\mathbf{R}_n = -a(\mathbf{x}_0 + \mathbf{y}_0)$ (the last one corresponds to $(s_{1'} + s_{2'})/\sqrt{2}$, where 1' and 2' are symmetric of 1 and 2 with respect to the origin. If we call V_{sd} the matrix element, $\langle s | \hat{H} | d_{3z^2-r^2} \rangle$, we have

$$\begin{aligned}
 \sum_{\mathbf{R}} \exp(i\mathbf{k} \cdot \mathbf{R}_n) \langle 0, d_{3z^2-r^2} | \hat{H} | \mathbf{R}_n, (s_1 + s_2)/\sqrt{2} \rangle &= (2/\sqrt{2})[V_{sd} + V_{sd}] \\
 &= (4/\sqrt{2})V_{sd}.
 \end{aligned}$$

Next we must express V_{sd} in terms of the first matrix element shown in Fig. 15.9. This can be achieved by the so called Slater-Koster relations¹ which are the analogs of F.7 to F.10 for d orbitals; these relations express matrix

¹ J.C. Slater and G.F. Koster, Phys. Rev. **94**, 1498 (1954). The Slater-Koster relations are reproduced in the book by Harrison [SS76], p. 481 and the book by Papaconstantopoulos [SS81].

elements of the form $\langle \alpha | \hat{H} | \beta \rangle$ involving at least one d orbital in terms of those in Fig. 15.9 and the direction cosines ℓ, m, n of the vector going from the center of $|\alpha\rangle$ to the center of $|\beta\rangle$. In the present case $V_{sd} = -\frac{1}{2}V_{sd\sigma} = (3.16/2)\hbar^2 r_d^{3/2}/md^{7/2} = 0.0479$. Thus $(4/\sqrt{2})V_{sd} = 0.136$ a.u. = 3.69 eV. ($r_d = 1.08$ Å for Ti and $d_{TiO} = 1.95$ Å).

As another example consider the case $|\alpha\rangle = d_{3z^2-r^2}$ and $|\beta\rangle = p_{3z}$. Then $\sum_{\mathbf{R}} \langle 0, d_{3z^2-r^2} | \hat{H} | \mathbf{R}, p_{3z} \rangle = V_{dp}^+ + V_{dp}^- e^{-i\mathbf{k}\cdot\mathbf{R}} = e^{-i\mathbf{k}d} (V_{dp}^+ e^{i\mathbf{k}d} + V_{dp}^- e^{-i\mathbf{k}d}) = e^{-i\mathbf{k}d} V_{dp}^+ (e^{i\mathbf{k}d} - e^{-i\mathbf{k}d}) = -e^{-i\mathbf{k}d} 2iV_{pd\sigma} \sin kd$ where $\mathbf{k} = 0, 0, k$, $\mathbf{R} = -a(0, 0, 1)$, $kd = ka/2$, $d = d_{Ti-O}$. We can get rid of the factor $\exp(-i\mathbf{k}d)$ by redefining the corresponding coefficient, c_{3p_z} . Continuing this way we obtain the 5×5 Hamiltonian for each $\mathbf{k} = (0, 0, k)$ corresponding to the first column in (1)

	$d_{3z^2-r^2}$	p_{3z}	$\frac{1}{\sqrt{2}}(p_{1z} + p_{2z})$	s_3	$\frac{1}{\sqrt{2}}(s_1 + s_2)$
$d_{3z^2-r^2}$	ε_d	$-2iV_{pd\sigma} \sin kd$	0	$2V_{pd\sigma} \cos kd$	$-\sqrt{2}V_{sd\sigma}$
p_{3z}	$2iV_{pd\sigma} \sin kd$	ε_p	$2\sqrt{2}E_{x,x} \cos kd$	0	0
$\frac{1}{\sqrt{2}}(p_{1z} + p_{2z})$	0	$2\sqrt{2}E_{x,x} \cos kd$	ε_p	0	0
s_3	$2V_{pd\sigma} \cos kd$	0	0	ε_s	0
$\frac{1}{\sqrt{2}}(s_1 + s_2)$	$-\sqrt{2}V_{sd\sigma}$	0	0	0	ε_s

), (2)

where $E_{x,x} = (V_{pp\sigma} + V_{pp\pi})/2$, taken as 0.153 eV. (These atoms are second nearest neighbors).

The 4×4 Hamiltonian corresponding to the second column of (1) is (the third column is the same)

	d_{zx}	p_{1x}	p_{2x}	p_{3x}
d_{zx}	ε_d	0	0	$-2iV_{pd\pi} \sin kd$
p_{1x}	0	ε_p	$4E_{x,x}$	$4E_{x,x} \cos kd$
p_{2x}	0	$4E_{x,x}$	ε_p	0
p_{3x}	$2iV_{pd\pi} \sin kd$	$4E_{x,x} \cos kd$	0	ε_p

). (3)

Finally the 3×3 Hamiltonian matrix corresponding to the last column in (1) is

	$d_{x^2-y^2}$	$\frac{1}{\sqrt{2}}(p_{1z} - p_{2z})$	$\frac{1}{\sqrt{2}}(s_1 - s_2)$
$d_{x^2-y^2}$	ε_d	0	$\sqrt{6}V_{sd\sigma}$
$\frac{1}{\sqrt{2}}(p_{1z} - p_{2z})$	0	ε_p	0
$\frac{1}{\sqrt{2}}(s_1 - s_2)$	$\sqrt{6}V_{sd\sigma}$	0	ε_s

). (4)

The matrix (4) is independent of k and can be diagonalized analytically yielding

$$E_1 = \varepsilon_p$$

$$E_{2,3} = \frac{1}{2}(\varepsilon_s + \varepsilon_d) \pm \sqrt{\frac{1}{4}(\varepsilon_s - \varepsilon_d)^2 + 6V_{sd\sigma}^2}.$$

The one element fourth column gives, obviously

$$E_4 = \varepsilon_d.$$

The 4×4 shown in (3) can be diagonalized analytically at $k = 0$ and at $k = \pi/a$ yielding

$$E_{5,6}(0) = \varepsilon_d, \quad E_{5,6}(\pi/a) = \frac{1}{2}(\varepsilon_d + \varepsilon_p) + \left[\frac{1}{4}(\varepsilon_d - \varepsilon_p)^2 + 4V_{pd\pi}^2 \right]^{1/2},$$

$$E_{7,8}(0) = \varepsilon_p, \quad E_{7,8}(\pi/a) = \frac{1}{2}(\varepsilon_d + \varepsilon_p) - \left[\frac{1}{4}(\varepsilon_d - \varepsilon_p)^2 + 4V_{pd\pi}^2 \right]^{1/2},$$

$$E_{9,10}(0) = \varepsilon_p + 4\sqrt{2}E_{x,x}, \quad E_{9,10}(\pi/a) = \varepsilon_p + 4E_{x,x},$$

$$E_{11,12}(0) = \varepsilon_p - 4\sqrt{2}E_{x,x}, \quad E_{11,12}(\pi/a) = \varepsilon_p - 4E_{x,x}.$$

Finally the 5×5 shown in (2) yields at $k = 0$

$$E_{13}(0) = \varepsilon_s,$$

$$E_{14}(0) = \varepsilon_p + 4\sqrt{2}E_{x,x},$$

$$E_{15}(0) = \varepsilon_p - 4\sqrt{2}E_{x,x},$$

$$E_{16}(0) = \frac{1}{2}(\varepsilon_d + \varepsilon_s) + \left[\frac{1}{4}(\varepsilon_d - \varepsilon_s)^2 + 6V_{sd\sigma}^2 \right]^{1/2},$$

$$E_{17}(0) = \frac{1}{2}(\varepsilon_d + \varepsilon_s) - \left[\frac{1}{4}(\varepsilon_d - \varepsilon_s)^2 + 6V_{sd\sigma}^2 \right]^{1/2}.$$

The reader may attempt to diagonalize the 5×5 Hamiltonian matrix also for $k = \pi/a$.

Chapter 16

Problem 16.1ts

The system $\mathbf{x}_K, \mathbf{y}_K, \mathbf{K}$ is an orthogonal one. Hence, $\mathbf{K} = |\mathbf{K}| \mathbf{K}_0 = |\mathbf{K}| (\mathbf{x}_K \times \mathbf{y}_K)$. Similarly, $\mathbf{K}' = |\mathbf{K}'| (\mathbf{x}_{K'} \times \mathbf{y}_{K'})$. $\mathbf{K}' \times \mathbf{H}_{K'} = |\mathbf{K}'| (\mathbf{x}_{K'} \times \mathbf{y}_{K'}) \times (H_{K'x'} \mathbf{x}_{K'} + H_{K'y'} \mathbf{y}_{K'}) = |\mathbf{K}'| (H_{K'x'} \mathbf{y}_{K'} - H_{K'y'} \mathbf{x}_{K'})$. By multiplying the last expression by $\mathbf{K} \times$ we have.

$$|\mathbf{K}| |\mathbf{K}'| (\mathbf{x}_K \times \mathbf{y}_K) \times (H_{K'x'} \mathbf{y}_{K'} - H_{K'y'} \mathbf{x}_{K'})$$

$$|\mathbf{K}| |\mathbf{K}'| [\mathbf{y}_K (\mathbf{x}_K \cdot \mathbf{y}_{K'}) H_{K'x'} - \mathbf{x}_K (\mathbf{y}_K \cdot \mathbf{y}_{K'}) H_{K'x'} \quad (1)$$

$$+ \mathbf{x}_K (\mathbf{y}_K \cdot \mathbf{x}_{K'}) H_{K'y'} - \mathbf{y}_K (\mathbf{x}_K \cdot \mathbf{x}_{K'}) H_{K'y'}].$$

Substituting (1) in (16.15) and equating the $\mathbf{x}_K$ coefficients on both sides, we have

$$\sum_{K'} a_{K-K'} |\mathbf{K}| |\mathbf{K}'| [(\mathbf{y}_K \cdot \mathbf{y}_{K'}) H_{K'x'} - (\mathbf{y}_K \cdot \mathbf{x}_{K'}) H_{K'y'}] = \frac{\omega^2}{c^2} H_{Kx}. \quad (2)$$

Similarly, by equating the $\mathbf{y}_K$ coefficients, we obtain

$$\sum_{K'} a_{K-K'} |\mathbf{K}| |\mathbf{K}'| [-(\mathbf{x}_K \cdot \mathbf{y}_{K'}) H_{K'x'} + (\mathbf{x}_K \cdot \mathbf{x}_{K'}) H_{K'y'}] = \frac{\omega^2}{c^2} H_{Ky}. \quad (3)$$

Equations (2) and (3) can be written in the compact form (16.18) with $M_{\mathbf{K}\mathbf{K}'}$ given by (16.19).

Problem 16.2ts

$$E_K = \frac{1}{2} \rho_0 S r \dot{r}^2 = \frac{1}{2} \rho_0 S r \omega^2 \delta r^2, E_P = \frac{1}{2} \delta P S \delta r, \delta P = \frac{P_i}{V_i} \delta V_i, \delta V_i = 4\pi r^2 \delta r,$$

$$E_P = \frac{1}{2} \frac{P_i}{V_i} 4\pi r^2 \delta r S \delta r = \frac{1}{2} \frac{B_i}{\rho_i} \frac{\rho_i}{\frac{4\pi}{3} r^3} 4\pi r^2 S \delta r^2 = \frac{1}{2} c_i^2 3\rho_i \frac{1}{r} S \delta r^2.$$

Setting $E_K = E_P$, we obtain $\rho_0 r \omega^2 = c_i^2 3\rho_i \frac{1}{r}$, or $\frac{\omega^2 r^2}{c_i^2} = \frac{3\rho_i}{\rho_0}$.

Problem 16.5ts

From (16.33), we have $u = \frac{c^2}{4\pi\omega} \frac{k}{v} (1+x) \frac{E_0^2}{\mu} = \frac{c^2}{4\pi\omega} \frac{k}{v} (1+x) \frac{H_0^2}{\varepsilon}$;
 $\omega = v \cdot k = c \cdot k/n$,

$$x = (\omega/n)/(\partial\omega/\partial n) \text{ and } n^2(1+x) = \frac{1}{2} \left[\left(\varepsilon\mu + \omega\mu \frac{\partial\varepsilon}{\partial\omega} \right) + \left(\varepsilon\mu + \omega\varepsilon \frac{\partial\mu}{\partial\omega} \right) \right],$$

$$u = \frac{1}{4\pi} n^2 (1+x) \frac{E_0^2}{\mu} = \frac{n^2}{4\pi} (1+x) \frac{H_0^2}{\varepsilon} = \frac{1}{8\pi} \left[\left(\varepsilon\mu + \omega\mu \frac{\partial\varepsilon}{\partial\omega} \right) \frac{E_0^2}{\mu} \right. \\ \left. + \left(\varepsilon\mu + \omega\varepsilon \frac{\partial\mu}{\partial\omega} \right) \frac{H_0^2}{\varepsilon} \right]$$

$$= \frac{1}{8\pi} \left[\varepsilon E_0^2 + \omega \frac{\partial\varepsilon}{\partial\omega} E_0^2 + \mu H_0^2 + \omega \frac{\partial\mu}{\partial\omega} H_0^2 \right] = \frac{1}{8\pi} \left[\frac{\partial(\omega\varepsilon)}{\partial\omega} E_0^2 + \frac{\partial(\omega\mu)}{\partial\omega} H_0^2 \right].$$

Chapter 17

Problem 17.6ts

The power P produced by a photovoltaic is $P = (FF) I_L V_0$. The voltage V_0 is a fraction of E_g/e : $V_0 = a_1 E_g/e$, where, usually, $a_1 \simeq 2/3$. The current I_L is proportional to j_L given by (17.81). Hence

$$P = (FF)a_1(E_g/e)a_2 \frac{e}{\hbar} \int_{E_g/\hbar}^{\infty} d\omega \frac{I(\omega)}{\omega},$$

where $a_2 < 1$ and $I(\omega) = A\omega^3/(e^{\beta\hbar\omega} - 1)$ with A a known universal constant. Thus

$$P = (FF)a_1a_2 \frac{AE_g}{\hbar^4\beta^3} \int_{\beta E_g}^{\infty} \frac{dx x^2}{e^x - 1}, \text{ and}$$

$$P_t = \frac{A}{(\beta\hbar)^4} \int_0^{\infty} \frac{dx x^3}{e^x - 1}, \text{ so that}$$

$$\eta = (FF)a_1a_2(E_g\beta) \frac{I_1}{I_0}; \quad I_1 = \int_{\beta E_g}^{\infty} dx x^2 (e^x - 1)^{-1}, \text{ and}$$

$I_0 = \int_0^{\infty} dx x^3 (e^x - 1)^{-1} = \pi^4/15$. To maximize η with respect to E_g is equivalent to maximize

$$\Gamma = y \int_y^{\infty} dx x^2 (e^x - 1)^{-1}, \text{ where } y = \beta E_g :$$

$d\Gamma/dy = 0 \Rightarrow \int_y^{\infty} \frac{dx x^2}{e^x - 1} = \frac{y^3}{e^y - 1}$. By plotting both sides we found the solution to be $y = 2.166$. Hence, $E_g = (5800/11600)2.166 \text{ eV} = 1.083 \text{ eV}$. For this value of y , $\eta = (FF)a_1a_2 \times 2.166 \times 1.316/(\pi^4/15) = (FF)a_1a_2 \times 0.44 \lesssim 22\%$. This upper limit of about 22% is not unrealistic for optimal E_g , although the values of the latter are higher than our crude estimate of 1.08 eV and vary between 1.2 and 1.6 eV depending, among other factors, on the shape of the solar spectrum at the surface of the Earth.

Problem 17.1s

From each point of a diamond lattice, located at the sides $\mathbf{R}_n$ of the **fcc** lattice, four bonds emerge in the directions (111) , $(\bar{1}\bar{1}1)$, $(1\bar{1}\bar{1})$ and $(\bar{1}\bar{1}\bar{1})$. Hence, a plane normal to the direction (111) will cut a minimum of one bond per lattice point of the 2-D hexagonal lattice shown in Fig. 17.8. Hence, the minimum number of bonds cut by (111) planes per unit area is $1/(\sqrt{3}a^2/4) = 4/\sqrt{3}a^2$ and the corresponding energy cost for creating such a surface is $(E_c/2)(4/\sqrt{3}a^2) = 2E_c/\sqrt{3}a^2 = \sqrt{3}E_c/8d^2$ per unit area, where E_c is the cohesive energy per atom.

For the direction (100) two bonds, the (111) and the ($\bar{1}\bar{1}\bar{1}$) have positive dot product with the vector (100), while the other two, the ($\bar{1}\bar{1}1$) and the ($1\bar{1}\bar{1}$) have negative. Hence, two bonds are on the one side of the lattice plane (100) and the other two on the other side. It follows that the minimum number of bonds that the (100) plane will cut, will be two per lattice point of the square lattice shown in Fig. 17.8. Hence, the bonds cut per unit area is $2/(a^2/2) = 4/a^2$ and the surface energy (per unit area) is $2E_c/a^2 = 3E_c/8d^2$. Thus the ratio of the two surface energies $E_{100}/E_{111} = \sqrt{3}$.

For the direction (1,1,0) the dot products with the vectors (111), ($\bar{1}\bar{1}1$), ($1\bar{1}\bar{1}$) and ($\bar{1}1\bar{1}$) are 2, -2, 0, 0, which means that two bonds are on the lattice plane (110) and the other two are on each side of this plane. The fact that two diamond lattice points, the $\mathbf{d}_1 = (\bar{1}\bar{1}\bar{1})(a/4)$ and $\mathbf{d}_2 = (\bar{1}1\bar{1})(a/4)$, are on the (110) **fcc** plane without belonging to the **fcc** 2D rectangular lattice² shown in Fig. 17.8, shows that the diamond (110) 2D lattice results from the rectangular **fcc** lattice by inserting a two atom basis with one atom located at the lower left corner of the rectangular lattice shown in Fig. 17.8 and the other located at the point $-(a/4)\mathbf{x}_0 + (a\sqrt{2}/4)\mathbf{y}_0$ relative to the rectangular lattice. For each of the two atoms in the basis we have to cut one bond, so that the minimum number of bonds cut for the (110) surface of the diamond lattice per unit area is $2/(\sqrt{2}a^2/2) = 2\sqrt{2}/a^2$. Hence, the surface energy per unit area is $\sqrt{2}E_c/a^2 = 3\sqrt{2}E_c/16d^2$. The final result is $E_{100} : E_{110} : E_{111} = 2 : \sqrt{2} : (2/\sqrt{3})$.

Problem 17.2s

Let the surface and the volume of a regular octahedron of edge length a be S and V , where

$$\begin{aligned} S &= 2\sqrt{3}a^2, \\ V &= \frac{1}{3}\sqrt{2}a^3. \end{aligned}$$

Truncated octahedron: The volume V_1 of each of the six pyramids cut off the octahedron is

$$V_1 = \frac{1}{6}\sqrt{2}b^3 \Rightarrow V_t = V(a) - 6V_1 = \frac{1}{3}\sqrt{2}a^3 - \sqrt{2}b^3.$$

The truncated octahedron surface is decreased by $6 \times \sqrt{3}b^2$ but is increased by $6b^2$. Thus

$$S_t = \underbrace{2\sqrt{3}a^2 - 6\sqrt{3}b^2}_{E_{111}} + \underbrace{6b^2}_{E_{100}}.$$

The surface energy for the truncated octahedron is $E_t = 2\sqrt{3}E_{111}(a^2 - 3b^2) + 6b^2E_{100}$.

² Their difference $\mathbf{d}_1 - \mathbf{d}_2 = (1, 1, 0)(a/2)$ belongs to this 2-D rectangular lattice.

We must minimize E_t with respect to b *under* constant volume:

$$\begin{aligned}
 V_t = \text{const} &\Rightarrow dV_t/db = 0. \\
 dV_t/db = 0 &\Rightarrow \sqrt{2}a^2(da/db) = 3\sqrt{2}b^2 \Rightarrow da/db = 3b^2/a^2. \text{ Thus} \\
 dE_t/db = 0 &\Rightarrow 2\sqrt{3}E_{111} (2a(3b^2/a^2) - 6b) + 12bE_{100} = 0, \\
 2\sqrt{3}E_{111} \left(6\frac{b}{a} - 6\right) + 12E_{100} &= 0, \quad \frac{b}{a} = 1 - \frac{E_{100}}{\sqrt{3}E_{111}}. \quad (1)
 \end{aligned}$$

In arriving at the last equation, it was implicitly assumed that $2b \leq a$ (otherwise our formulas for the volume and the surface of truncated octahedron are invalid). This inequality combined with (1) implies that $E_{100} \geq \sqrt{3}E_{111}/2$; actually, as it was argued in problem 17.1s, it is expected that $E_{100} \simeq \sqrt{3}E_{111}$. If, $E_{100} \geq \sqrt{3}E_{111}$, then $b = 0$ and the regular octahedron would have the lower surface energy; if $E_{100} = (\sqrt{3} - x)E_{111}$ with x positive and small, then $b/a = x/\sqrt{3}$, the surface energy of a truncated octahedron would be $2\sqrt{3}E_{111}a^2 \left(1 - \frac{x^3}{\sqrt{3}}\right)$, while the surface energy of a regular octahedron *of equal volume with the truncated one* would be $2\sqrt{3}E_{111}a^2 \left(1 - \frac{x^3}{\sqrt{3}}\right)^{2/3}$, i.e., higher than that of the truncated octahedron.

Chapter 18

Problem 18.9ts

We write $x \equiv (\varepsilon_n - \Sigma)g_0$ and we have $\varepsilon_n(1-x)^{-1} = \varepsilon_n(1+x+x^2+x^3+\dots) = \varepsilon_n + \varepsilon_n^2g_0 - g_0\varepsilon_n\Sigma + \varepsilon_n^3g_0^2 - 2\varepsilon_n^2g_0^2\Sigma + g_0^2\varepsilon_n\Sigma^2 + \varepsilon_n g_0^3(\varepsilon_n^3 - 3\varepsilon_n^2\Sigma + 3\varepsilon_n\Sigma^2 - \Sigma^3) + \mathcal{O}(w^6)$. The odd powers of ε_n would give zero contributions to the integral (18.74). Keeping terms up to 4th order in w and performing the integrations shown in (18.74) we have

$$\Sigma = w^2g_0 - 2w^2g_0^2\Sigma + \mu_4g_0^3 + \mathcal{O}(w^6) = w^2g_0 - (2w^4 - \mu_4)g_0^3 + \mathcal{O}(w^6).$$

Problem 18.11ts

Figure 18.13 shows that, for $D \leq 2$, β is negative. Hence, dG/dL is negative and, as a result, as $L \rightarrow \infty$, $G \rightarrow 0$. In this case, strictly speaking a truly metallic behavior is not possible. On the other hand for $D > 2$ and $G > G_c$ a truly metallic behavior is realized. A metallic behavior is definitely possible for $D = 2$ in the presence of magnetic forces.

Problem 18.12ts

Taking into account that $\beta = (L/Q)(dQ/dL)$ and that $Q = \hbar G/e^2 = (\hbar/e^2)\sigma L^{D-2}$ and substituting in (18.102) we end up with the following simple

differential equation

$$\frac{d\sigma}{dL} = -\frac{\Gamma_D}{L^{D-1}}, \Gamma_D = A_D e^2/\hbar,$$

which gives

$$\begin{aligned}\sigma &= \sigma_0 + \frac{\Gamma_D}{D-2} L^{2-D}, \quad D \neq 2, \\ \sigma &= \sigma_0 - \Gamma_2 \ln \frac{L}{L_e}, \quad D = 2.\end{aligned}$$

Problem 18.1s

To prove the relation, $s = -k_B[p \ln p + (1-p) \ln(1-p)]$, where $p = p_{AB} + p_{BA}$ and $1-p = p_{AA} + p_{BB}$, we have to show first that the probability p of a bond to be AB or BA is independent of what is happening in a nearest neighbor bond. This is indeed the case, if $x = 0.5$. To show this, consider three consecutive sites 1, 2, 3 and check whether the probability for the bond 2, 3 to be AB or BA depends on what is happening in the bond 1, 2. If the latter is AA , BB , AB or BA the probability for the bond 2, 3 to be either AB or BA is respectively $p_{B/A} = p$, $p_{A/B} = p$, $p_{A/B} = p$, $p_{B/A} = p$. Having established that the bonds are statistically independent we can use (C.30) with P_I taking two values: p and $1-p$. To obtain the equilibrium value of p we minimize the free energy $f \equiv \langle \varepsilon \rangle - Ts = \frac{1}{2}[(1-p)(U_{AA} + U_{BB})/N] + \frac{1}{2}[p(U_{AB} + U_{BA})/N] - Ts$. Thus $\partial f / \partial p = u + k_B T [\ln p - \ln(1-p)] = 0 \Rightarrow p = (e^{\beta u} + 1)^{-1}$; $\beta = 1/k_B T$.

Problem 18.4s

We have to calculate the integral, $g_0(E) = \frac{2}{\pi B^2} \int_{-B}^B \frac{dE' (B^2 - E'^2)^{1/2}}{E - E'}$. Change variables to $E' = B \sin \theta \Rightarrow dE' = B \cos \theta d\theta$, $(B^2 - E'^2)^{1/2} = B(1 - \sin^2 \theta)^{1/2} = B \cos \theta$; $E \equiv Bz$. Thus $g_0(E) = \frac{2}{\pi B} \int_{-\pi/2}^{\pi/2} \frac{d\theta \cos^2 \theta}{z - \sin \theta} = \frac{1}{\pi B} \int_{-\pi}^{\pi} \frac{d\theta \cos^2 \theta}{z - \sin \theta}$. Setting $w = \exp(i\theta)$ we have $dw = iwd\theta$ and $g_0(E) = \frac{1}{2\pi B} \int_{c_0} \frac{dw(w+w^{-1})^2}{2iw(z - \frac{1}{2i}(w-w^{-1}))} = \frac{1}{2\pi B} \int_{c_0} \frac{dw(w+w^{-1})^2}{2izw-w^2+1}$, where the contour c_0 of integration is along the unit circle in the complex w plane, as shown in Fig. 18.16 below. However, in order to apply the residue theorem, we have to avoid the singularity at $w = 0$ by following the contour $c_0 + c_1 + c_2 + c_3$, i.e., the contour $c_0 + c_2$ (since the contributions of c_1 and c_3 cancel each other) (Fig. 18.16). Hence,

$$g_0 = \frac{-1}{2\pi B} \int_{c_0+c_2} \frac{dw(w+w^{-1})^2}{(w-w_1)(w-w_2)} - \frac{1}{2\pi B} \int_{c_2} d\omega (w+w^{-1})^2 (1-2izw + \mathcal{O}(w^2)), \quad (1)$$

where w_1, w_2 are the roots of $w^2 - 2izw - 1 = 0$, $w_{1,2} = iz \pm \sqrt{1-z^2}$ with $|w_1| < 1$. The first term in the *rhs* of (1) by residue theorem and in

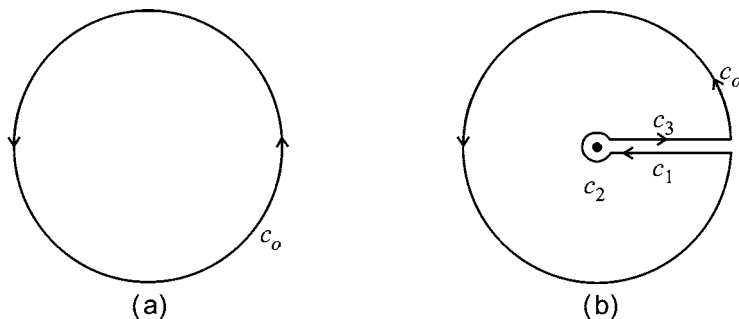


Fig. 18.16. The contour of integration (a) encloses the singular point $w = 0$, while that in (b) does not

view of $w_1 w_2 = -1$ gives $-(2\pi i/2\pi B)(w_1 - w_2) = -(2/B)i\sqrt{1 - z^2}$. In the second term the only non-zero contribution, as the radius of c_2 tends to zero, comes from the product $(-2izw)w^{-2} = -2izw^{-1}$ in the integrand. Setting $w = \rho \exp(i\theta)$, $dw = iwd\theta$ we obtain $-\frac{2z}{2\pi B} \int_{\pi}^{-\pi} d\theta = 2z/B$. Thus, finally $g_0 = \frac{2}{B}(z - i\sqrt{1 - z^2}) = -\frac{2i}{B}w_1 = \frac{2}{B} \frac{1}{z + i\sqrt{1 - z^2}} = \frac{2}{E + i\sqrt{B^2 - E^2}}$.

Chapter 19

Problem 19.1ts

From (14.12), $\ln \sigma = \ln 4.64 - 0.6 \ln(IP) = \ln 4.64 - 0.6 \ln(3/27.2) = 2.857 \Rightarrow \sigma = 17.418 \text{ a.u.} = 9.21 \text{ \AA}$; $d = 1.09\sigma = 10.043 \text{ vs. } 10.013 \text{ \AA}$ experimentally; $a = \sqrt{2}d = 14.203 \text{ \AA}$. $\tilde{a} = 4(3.4125/0.527)^2/(3/27.2) = 1509 \text{ a.u.} = 223.4 \text{ \AA}^3$; $\varepsilon = 0.4\tilde{a}^2(IP)/\sigma^6 = 0.4(223.4)^2 3/(9.2138)^6 = 0.0979 \text{ eV}$. $E'_i/N = -8.61\varepsilon = 0.8424 \text{ eV/molecule}$. $\Lambda = \hbar/\sigma\sqrt{m_a\varepsilon} = 8.35 \times 10^{-4}$; $U_i^{(0)}/N = 37.46 f\Lambda\varepsilon = 37.46 \times 0.6 \times 8.35 \times 10^{-4} \times 0.979 \text{ eV} = 1.83 \text{ meV}$. $U_c/N = (E'_i/N) - (U_i^{(0)}/N) = 0.8427 \text{ eV} - 1.83 \text{ meV} \simeq 0.84 \text{ eV}$, vs. 0.4 eV experimentally.

Problem 19.2ts

$U_c/M_3 C_{60} \simeq |3(\text{IP})_{\text{M}} - 3(\text{EA})_{\text{F}} - (3e^2\alpha/4\pi\varepsilon_0 d')|$, where $d' = (2d'_{\text{tetr.}} + d'_{\text{oct.}})/3 = [(2\sqrt{3}a/4) + (a/2)]/3 = 6.46 \text{ \AA} = 12.2 \text{ a.u.}$. $U_c/M_3 C_{60} \simeq 6.46 \text{ eV}$.

Problem 19.8ts

Because the wave functions $\Psi_{3/2}(r)$ and $\Psi_{1/2}(r)$ are even in x, y and z , the matrix elements $\left\langle \Psi_\ell(\mathbf{r}) \left| \frac{\partial}{\partial x_i} \frac{\partial}{\partial x_j} \right| \Psi_m(\mathbf{r}) \right\rangle = 0$ for $i \neq j$, where $i, j = 1, 2, 3$ and $l, m = \frac{3}{2}, \frac{1}{2}$. Hence,

$$\langle \Psi_\ell(\mathbf{r}) | S | \Psi_m(\mathbf{r}) \rangle = 0; \quad l, m = \frac{3}{2}, \frac{1}{2}. \quad (19.39)$$

For the same reason the corresponding matrix element of the imaginary of R is zero; furthermore, because of symmetry,

$$\langle \Psi_\ell(\mathbf{r}) | R | \Psi_\ell(\mathbf{r}) \rangle = 0, \quad l, m = \frac{3}{2}, \frac{1}{2}. \quad (19.40)$$

Thus the only matrix element which is non-zero is the following

$$\tilde{R} \equiv \langle \Psi_{1/2}(\mathbf{r}) | R | \Psi_{3/2}(\mathbf{r}) \rangle = -\frac{\sqrt{3}\hbar^2}{2m} \gamma_2 \langle \Psi_{1/2}(\mathbf{r}) | (k_x^2 - k_y^2) | \Psi_{3/2}(\mathbf{r}) \rangle. \quad (19.41)$$

Problem 19.1s

The eigenfunctions of a particle moving within a spherical potential well of radius a with infinite walls are of the form $A j_l(kr) Y_{lm}(\theta, \varphi)$, with ka coinciding with the roots ρ_{nl} of the spherical Bessel functions $j_l: k_{nl}a = \rho_{nl}$; the ordering of $k_{nl}a$ is the same as that of the corresponding eigenenergies $\varepsilon_{nl} = \hbar^2 k_{nl}^2 / 2m$. The results for $k_{nl}a$ are (see [D4]): 3.14, 4.49, 5.76, 6.28, 6.98, 7.72, 8.18, 9.09, 9.35, 9.42 for 1s, 1p, 1d, 2s, 1f, 2p, 1g, 2d, 1h, 3s respectively. This ordering coincides with the one given in Section 19.2 with the single exception of the 3s being lower than 1h.

Problem 19.2s

The k_y coordinate of the point P' (which is equal to $\mathbf{\Gamma}P + \mathbf{G}$, where P is the point at which the gap closes in graphene) is $\pm 1/3$ in units of $2\pi/\sqrt{3}d$. The allowed values of k_y for the zig-zag case are ℓ'/n (in units of $2\pi/\sqrt{3}d$). Hence, the minimum value of $\delta k_y = \min \left| \frac{1}{3} - \frac{\ell'}{n} \right| \left(\frac{2\pi}{\sqrt{3}d} \right)$. For $n = 4$, $\delta k_y = (1/12)(2\pi/\sqrt{3}d)$; for $n = 7$, $\delta k_y = (1/21)(2\pi/\sqrt{3}d)$. The gap according to (11.68) is estimated to be $E_g \simeq 3|Vd|\delta k_y = 3 \times 0.63 \times (\hbar^2/md^2)(2\pi/\sqrt{3})(1/12) = 2.15 \text{ eV}$ for $n = 4$ and $E_g = 1.23 \text{ eV}$ for $n = 7$. Actually for $n = 7$ the gap is 0.2 eV, which shows that the rolling up reduces significantly the matrix elements of the Hamiltonian. This is to be expected, since, among other reasons, the rolling up multiplies the nearest neighbor matrix element $V_{pp\pi}$ by $\cos \theta$, where $\theta = 2\pi/n$.

Chapter 20

Problem 20.2ts

See the book by Landau and Lifshitz [E15], pp. 147–150.

Problem 20.2s

Setting $H = 0$ and the derivatives $\partial\tilde{g}/\partial L_i = 0$, $i = x, y$, $\partial\tilde{g}/\partial L_z = 0$ we obtain

$$\begin{aligned} L_i(2a + 4bL^2 + b') &= 0, \quad i = x, y, \\ L_z(2a + 4bL^2) &= 0. \end{aligned}$$

If $b' > 0$, the easy axis will be in the z -direction, $L_i = 0$ ($i = x, y$) and

$$L = (-a/2b)^{1/2} = (a_1/2b)^{1/2}(T_N - T)^{1/2}.$$

If $b' < 0$, then $L_z = 0$ and $2a + 4bL^2 + B = 0$ or $L = (a_1/2b)^{1/2}(T_N - T)^{1/2}$, where $a_1 T_N = a_1 T'_N - B/2$, and $a = a_1(T - T'_N)$. Combining the general thermodynamic relation (20.38) with the derivatives of $\tilde{g}$ with respect to H_i , $i = x, y, z$, we obtain

$$\begin{aligned} -\mu_0(\mathbf{H} + \mathbf{M}) &= 2\mu_0 D(\mathbf{H} \cdot \mathbf{L})\mathbf{L} + 2\mu_0 D' L^2 \mathbf{H} \\ &\quad - \mu_0 \chi_p \mathbf{H} - \mu_0 \gamma (H_x \mathbf{i} + H_y \mathbf{j}) - \mu_0 \mathbf{H}. \end{aligned}$$

Dropping $-\mu_0 \mathbf{H}$ from both sides and dividing by $-\mu_0$ we end up with (20.39). For $T > T_N$, for which $\mathbf{L} = 0$, we obtain (20.40) from (20.39) by dividing by H_x, H_y, H_z . To arrive at (20.41) and (20.42) we assume $B > 0$, so that $L_z \neq 0$, $L_x = L_y = 0$ and we use (20.37). If $B < 0$, then $(\mathbf{H} \cdot \mathbf{L}) \cdot \mathbf{L} = (H_x L_x + H_y L_y)(L_x \mathbf{i} + L_y \mathbf{j})$.

Problem 20.5s

See the book by Landau and Lifshitz [E15], p. 141–143.

Chapter 21**Problem 21.1s**

To the Hamiltonian $\hat{H}$, we add the proton–proton repulsion $\hat{H}_{pp} = e^2/4\pi\epsilon_0 r$ so that $\hat{H}_t = \hat{H} + \hat{H}_{pp} = \hat{H}_1 + \hat{H}_2 + \hat{H}_{ee} + \hat{H}_{1B} + \hat{H}_{2A} + \hat{H}_{pp} = \hat{H}_1 + \hat{H}_2 + \Delta\hat{H}$. The presence of $\hat{H}_{pp}$ does not change the value of J , since $\langle \Psi | \hat{H}_{pp} | \Psi \rangle$ is the same for $\Psi = \Psi_s$ or $\Psi = \Psi_t$. Thus

$$2J = \frac{D' + E'}{1 + \ell^2} - \frac{D' - E'}{1 - \ell^2}, \quad (1)$$

where $D' = 2E_H + \Delta D$, $E' = 2E_H \ell^2 + \Delta E$; ΔD is as in (21.8) with $\Delta\hat{H}$ replacing $\hat{H}$, and ΔE is as in (21.9) with $\Delta\hat{H}$ replacing $\hat{H}$. Substituting D' , E' in (1), we obtain

$$2J = \frac{\Delta D + \Delta E}{1 + \ell^2} - \frac{\Delta D - \Delta E}{1 - \ell^2}. \quad (2)$$

All the quantities entering (2) are of the order $\exp(-2r/a_B)$ for large r so that $2J = (\Delta D + \Delta E)(1 - \ell^2) - (\Delta D - \Delta E)(1 + \ell^2) = 2\Delta E + O(\exp(-4r/a_B))$, which coincides with (21.11), (21.12).

Problem 21.5s

We will present the general method of canonical transformation for handling situations where $\hat{H} = \hat{H}_0 + \hat{H}_1$ and $\hat{H}_1$ is a small perturbation to the Hamiltonian $\hat{H}_0$. The transformation to a new equivalent Hamiltonian $\hat{\hat{H}}$ will be implemented by a unitary transformation $\exp(-\hat{S})$ such that $\hat{\hat{H}}$ will not include terms of first order in $\hat{H}_1$.

$$\hat{\hat{H}} = e^{-\hat{S}} \hat{H} e^{\hat{S}}. \quad (1)$$

By expanding $\exp(-\hat{S})$ and $\exp(\hat{S})$ in power series, we have $\hat{\hat{H}} = \hat{H} + [\hat{H}, \hat{S}] + \frac{1}{2} [[\hat{H}, \hat{S}], \hat{S}] + \dots = \hat{H}_0 + \hat{H}_1 + [\hat{H}_0, \hat{S}] + [\hat{H}_1, \hat{S}] + \dots$. If we chose $\hat{S}$ so that $\hat{H}_1 + [\hat{H}_0, \hat{S}] = 0$ we have

$$\hat{H}_1 = -\hat{H}_0 \hat{S} + \hat{S} \hat{H}_0, \quad (2)$$

$$\hat{S} = \hat{H}_0^{-1} \hat{S} \hat{H}_0 - \hat{H}_0^{-1} \hat{H}_1, \quad (3)$$

$$\hat{\hat{H}} = \hat{H}_0 + \frac{1}{2} [\hat{H}_1, \hat{S}] + O(\hat{H}_1^3). \quad (4)$$

For the Hubbard case and for $U \gg |V_2|$ we have $\hat{H}_0 = U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$ and $\hat{H}_1 = V_2 \sum_i \Sigma'_j \Sigma_\sigma |i\sigma\rangle \langle j\sigma|$. Let us symbolize by $\Psi_n, \Psi_m, \dots$ the states (not eigenstates) of the Hubbard Hamiltonian where every site is singly occupied. For such states

$$\hat{H}_0 \Psi_n = \hat{H}_0 \Psi_m = \dots = 0. \quad (5)$$

From (2), (4) and (5) we have

$$\langle \Psi_m | \hat{\hat{H}} | \Psi_n \rangle = \langle \Psi_m | \hat{S} \hat{H}_0 \hat{S} | \Psi_n \rangle, \quad (6)$$

or, by introducing a complete set Φ_i of eigenstates of H_0 ,

$$\langle \Psi_m | \hat{\hat{H}} | \Psi_n \rangle = \sum_i \langle \Psi_m | \hat{S} \hat{H}_0 | \Phi_i \rangle \langle \Phi_i | \hat{S} | \Psi_n \rangle. \quad (7)$$

$$\langle \Phi_i | \hat{S} | \Psi_n \rangle = -E_i^{-1} \langle \Phi_i | \hat{H}_1 | \Psi_n \rangle, \text{ because of (3) and (5),}$$

$$\langle \Psi_m | \hat{S} \hat{H}_0 | \Phi_i \rangle = \langle \Psi_m | \hat{H}_1 | \Phi_i \rangle, \text{ because of (2) and (5).}$$

The only eigenfunctions Φ_i for which $\langle \Psi_m | \hat{H}_1 | \Phi_i \rangle \langle \Phi_i | \hat{H}_1 | \Psi_n \rangle$ is non-zero are the ones where Φ_i has a site doubly occupied and a nearest neighbor

empty (because $\hat{H}_1$ can only take one electron from one site and transfer it to a nearest neighbor site). For all those states, Φ_i , $E_i = U$. Hence

$$\begin{aligned} \langle \Psi_m | \hat{H} | \Psi_n \rangle &= -\frac{1}{U} \langle \Psi_m | \hat{H}_1^2 | \Psi_n \rangle \\ &= \langle \Psi_m | \frac{2V_2^2}{U} \Sigma'_{ij} (\hat{s}_i - \hat{s}_{j+} + \hat{s}_{iz} \hat{s}_{jz}) | \Psi_n \rangle - \frac{N_a Z}{2} \frac{V_2^2}{U}. \end{aligned} \quad (8)$$

It is not so difficult to justify physically that the expression in the last line is indeed equivalent to the rhs of the previous line: If the nearest neighbor pair ij has parallel spins, $\langle \Psi_m | \hat{s}_i - \hat{s}_{j+} | \Psi_n \rangle = 0$, $\langle \Psi_m | (2V_2^2/U) (\hat{s}_{iz} \hat{s}_{jz} + \hat{s}_{jz} \hat{s}_{iz}) | \Psi_n \rangle = V_2^2/U$; thus the last line in (8) is zero and so $\langle \Psi_m | \hat{H}_1^2 | \Psi_n \rangle$ is. If the pair ij has antiparallel spins there are two possibilities: (a) $|\Psi_n\rangle$, $|\Psi_m\rangle$ correspond to no spin flip, in which case $\langle \hat{s}_i - \hat{s}_{j+} + \hat{s}_{j-} \hat{s}_{i+} \rangle = 0$ and $\langle \hat{s}_{iz} \hat{s}_{jz} + \hat{s}_{jz} \hat{s}_{iz} \rangle = -\delta_{nm}/2$ so that the total energy per pair is $-2V_2^2/U$ in agreement with the results $-\langle \Psi_m | \hat{H}_1^2 | \Psi_n \rangle / U$. The factor of 2 in the latter comes because there are two intermediate states corresponding to double occupation of either in i or in j . Finally, if ij are antiparallel and there is spin flip, $|\Psi_m\rangle \neq |\Psi_n\rangle$ and $\langle \Psi_m | \hat{s}_i - \hat{s}_{j+} + \hat{s}_{j-} \hat{s}_{i+} | \Psi_n \rangle$ would be one and the strength of the spin flip would be $2V_2^2/U$. The same result will be obtained from $-\langle \Psi_m | \hat{H}_1^2 | \Psi_n \rangle / U$ (The factor of two because of the two intermediate states and an extra factor -1 because of the antisymmetry of the electronic wave function). Taking into account (21.74) and (8) we have:

$$\hat{H} = \frac{2V_2^2}{U} \sum_{i \neq j} \hat{s}_i \cdot \hat{s}_j - \frac{N_a Z}{2} \frac{V_2^2}{U}; \quad |V_2|/U \rightarrow 0.$$

in agreement with (21.63).

Problem 21.7s

From the definition of $\hat{S}_{i\pm}$, (21.70), and the commutation relations (21.69), eqns. (21.71) and (21.72) follow in a straightforward way. Thus, if $\hat{S}_z |S_z\rangle = S_z |S_z\rangle$, we have (dropping the index i)

$$\hat{S}_z \hat{S}_{\pm} |S_z\rangle = (\hat{S}_{\pm} \hat{S}_z \pm \hat{S}_{\pm}) |S_z\rangle = (S_z \pm 1) \hat{S}_{\pm} |S_z\rangle; \quad (1)$$

Equation (1) means that $\hat{S}_{\pm} |S_z\rangle$ are eigenstates of $\hat{S}_z$ with eigenvalues, $\hat{S}_z \pm 1$:

$$\hat{S}_{\pm} |S_z\rangle = A_{\pm}(S, S_z) |S_z \pm 1\rangle.$$

Taking into account that the inner product of $\hat{S}_{\pm} |S_z\rangle$ with itself is equal to $\langle S_z | \hat{S}_{\mp} \hat{S}_{\pm} | S_z \rangle$, we have that $[A_{\pm}(S_z)]^2 = A_{\mp}(S_z \pm 1) A_{\pm}(S_z)$ or $A_{\pm}(S_z) = A_{\mp}(S_z \pm 1)$ (assuming reality of $A_{\pm}$). Furthermore, $\hat{S}_{\pm} \hat{S}_{\mp} = \hat{S}_x^2 + \hat{S}_y^2 \pm \hat{S}_z$; hence, $\hat{S}^2 = \hat{S}_{\pm} \hat{S}_{\mp} + \hat{S}_z^2 \mp \hat{S}_z$. Acting on $|S_z\rangle$ by $\hat{S}^2$ we have $S(S+1) |S_z\rangle = ([A_{\mp}(S_z)]^2 + S_z^2 \mp S_z) |S_z\rangle$, or $[A_{\mp}(S_z)]^2 = S(S+1) \pm S_z - S_z^2 = (S \pm S_z)(S+1 \mp S_z)$, which coincides with (21.73).

Chapter 22

Problem 22.1ts

Outside the superconductor $\mathbf{B}(\mathbf{r}) = \mu_0 \mathbf{H}(\mathbf{r})$; hence, since there is no external current density, $\nabla \times \mathbf{H} = 0 \Rightarrow \nabla \times \mathbf{B} = 0$. This last equation is valid in the interior of the superconductor as well, since $\mathbf{B}(\mathbf{r}) = 0$ there. Hence, $\mathbf{B}(\mathbf{r})$ can be written as

$$\mathbf{B} = -\nabla\phi, \quad (1)$$

which combined with the equation $\nabla \cdot \mathbf{B} = 0$ yields

$$\nabla^2\phi = 0. \quad (2)$$

The continuity of $\mathbf{B}_\perp$ at the surface in combination with $\mathbf{B} = 0$ in the interior of the superconductor implies that

$$\frac{\partial\phi}{\partial n} = 0. \quad (3)$$

At infinity, $r \rightarrow \infty$

$$\mathbf{B}(\mathbf{r}) \rightarrow \mathbf{B}_0. \quad (4)$$

Equations (1)–(4) uniquely determine $\mathbf{B}(\mathbf{r})$. The surface current density $\mathbf{g}(\mathbf{r}_s)$ at the points $\mathbf{r}_s$ of the surface is given by (see (A.11)) and keep in mind that $\mathbf{M} = \mathbf{H} = \mathbf{B}/\mu_0$

$$\mathbf{g}(\mathbf{r}_s) = \frac{1}{\mu_0} \mathbf{n} \times \mathbf{B}(\mathbf{r}_s). \quad (5)$$

For a spherical superconductor, the most general solution of ϕ_{ind} which vanishes as $r \rightarrow \infty$ is the sum $\sum_{\ell=1}^{\infty} c_\ell Y_\ell(\theta) r^{-\ell-1}$. Only the $\ell = 1$ spherical harmonic has a $\cos\theta$ dependence identical to that of the $\phi_0 = -B_0 r \cos\theta$ as to satisfy (3). Hence

$$\phi(\mathbf{r}) = -\left(B_0 r + \frac{c_1}{r^2}\right) \cos\theta, \quad (6)$$

where, because of (3), $c_1 = \frac{1}{2} B_0 a^3$. From (1), we have

$$\begin{aligned} \mathbf{B}(\mathbf{r}) &= \mathbf{B}_0 - B_0 \left[\boldsymbol{\theta}_0 \frac{a^3}{2r^3} \sin\theta + \mathbf{r}_o \frac{a^3}{r^3} \cos\theta \right] \\ &= B_0 \left[\mathbf{r}_0 \left(1 - \frac{a^3}{r^3} \right) \cos\theta - \boldsymbol{\theta}_o \left(1 + \frac{a^3}{2r^3} \right) \sin\theta \right], \end{aligned}$$

and, according to (5), the surface current density is

$$\mathbf{g}(r = a, \theta, \phi) = -\frac{3}{2} \frac{B_0}{\mu_0} \sin\theta \boldsymbol{\phi}_o. \quad (7)$$

We can calculate the magnetic moment $\mathbf{m}_t$ induced by the surface charge density using (A.7)

$$\begin{aligned}\mathbf{m}_t &= \frac{1}{2} \int \mathbf{r} \times \mathbf{g} \, dS = -\frac{3}{4} \frac{B_0}{\mu_0} \int dS \sin \theta \, \mathbf{r} \times \mathbf{r}_0 = +\frac{3}{4} \frac{B_0 a}{\mu_0} \\ &\int a^2 d\phi \, d\theta \sin \theta \sin \theta \, \mathbf{\theta}_0 = \frac{3}{4} \frac{B_0 a^3}{\mu_0} 2\pi \int d\theta \sin^2 \theta \, \mathbf{\theta}_0 = -\frac{3\pi}{2} \frac{B_0 a^3}{\mu_0} \\ &\int d\theta \sin^2 \theta \sin \theta \, \mathbf{z}_0 = -2\pi \mathbf{H}_0 a^3 = -\frac{3}{2} V \mathbf{H}_0.\end{aligned}\quad (8)$$

which could have been obtained from the very beginning by using the general formula

$$\mathbf{m}_t = -\frac{V \mathbf{H}_0}{1 - n^{(z)}}, \quad (9)$$

where $n^{(z)}$ is the depolarization coefficient along the axis z (Notice that in general for the principal axes $n^{(x)} + n^{(y)} + n^{(z)} = 1$ and for a sphere $n^{(x)} = n^{(y)} = n^{(z)} = 1/3$).

Problem 22.2s

Differentiating (22.11) with respect to the temperature under constant pressure and omitting the small term $\partial V_{s0}/\partial T$ we have the entropy difference

$$S_N - S_S = -\mu_0 V_{s0} H_c \partial H_c / \partial T, \quad T \leq T_c, \quad (1)$$

which shows that for $T < T_c$, $S_N > S_S$, since $\partial H_c / \partial T$ is negative; at $T = T_c$, $S_N = S_S$, since $H_c = 0$ there. Differentiating once more with respect to T and then multiplying by T we obtain the difference in the specific heats

$$C_S - C_N = \mu_0 V_{s0} T \left(\frac{\partial H_c}{\partial T} \right)^2 + \mu_0 V_{s0} T H_c \frac{\partial^2 H_c}{\partial T^2}, \quad T \leq T_c. \quad (2)$$

At $T = T_c$, $H_c = 0$ and $(\partial H_c / \partial T)^2 = 4H_c^2(0)/T_c^2$ according to (22.1). Actually the BCS theory (to be presented in the next chapter) shows that $(\partial H_c / \partial T)^2 = 3.02H_c^2(0)/T_c^2$. Hence, using this improved value, we have

$$C_S - C_N = 3.02\mu_0 V_{s0} H_c^2(0)/T_c = 3.02\rho_F \Delta^2/T_c = 9.41\rho_F k_B^2 T_c = 1.43C_N.$$

To arrive at the last result we employed the BCS relation $2\Delta(0) = 3.53k_B T_c$ (see (23.28) in the next chapter) and the relation $C_N = (2\pi^2/3)\rho_F k_F^2 T_c \simeq 6.58\rho_F k_F^2 T_c$.

Problem 22.5s

Since $\mathbf{A}(\mathbf{r}')$ is essentially constant over length scales much larger than ξ_P we can take it out of the integral. Moreover, if θ is the angle between $\mathbf{R}$ and $\mathbf{A}$,

we will have $\mathbf{R} \cdot \mathbf{A} = R A \cos \theta$. Hence, $\mathbf{R}(\mathbf{R} \cdot \mathbf{A}) = R^2 \cos^2 \theta \mathbf{A} + \mathbf{R}_\perp A R \cos \theta$. Notice that the component $\mathbf{R}_\perp$ (normal to $\mathbf{A}$) of $\mathbf{R}$ will be integrated to zero because of rotational symmetry around $\mathbf{A}$. We change integration variables from $\mathbf{r}'$ to $\mathbf{R} = \mathbf{r} - \mathbf{r}'$ and we have

$$\begin{aligned} j &= -\frac{3}{4\pi\xi_o} \frac{e^2 n_s}{mc} \mathbf{A} 2\pi \int_{-1}^1 d(\cos \theta) \cos^2 \theta \int_0^\infty dR e^{-R/\xi_P} \\ &= -(2\pi) \frac{3}{4\pi\xi_o} \frac{e^2 n_s}{mc} \mathbf{A} \frac{2}{3} \xi_P = -\frac{e^2 n_s}{mc} \frac{\xi_P}{\xi_o} \mathbf{A}, \end{aligned}$$

which coincides with (22.17), if $\xi_P = \xi_o$.

Chapter 23

Problem 23.1ts

We have the following relations:

$\mathbf{P} = \hbar \mathbf{K}$, $\mathbf{p} = \hbar \mathbf{k}$, $\mathbf{k}_1 = \frac{1}{2} \mathbf{K} + \mathbf{k}$, $\mathbf{k}_2 = \frac{1}{2} \mathbf{K} - \mathbf{k}$; $E = (\hbar^2 K^2/4m) + (\hbar^2 k^2/m)$; $k_1^2 = \frac{1}{4} K^2 + k^2 + K k \cos \theta$, $k_2^2 = \frac{1}{4} K^2 + k^2 - K k \cos \theta$. Since both k_1^2 and k_2^2 are equal to or larger than k_F^2 we have the inequalities:

$$-t_1 \leq \cos \theta \leq t_1 \equiv \left(\frac{1}{4} K^2 + k^2 - k_F^2 \right) / K k.$$

t_1 can be written as follows: $t_1 = \sqrt{m}(E - 2E_F)/P[E - (P^2/4m)]^{1/2}$. Of course, $|\cos \theta|$ must be smaller than or equal to one. Thus,

$$-t \leq \cos \theta < t; \quad t = \min[1, t_1]. \quad (1)$$

Inequalities (1) imply both $k_1 \geq k_F$, $k_2 \geq k_F$ as well as the obvious fact that $\cos \theta$ cannot be larger than 1. According to (23.10) and (1) we have

$$\begin{aligned} \rho_0(E) &= \frac{2\pi}{(2\pi)^3} \int_{-t}^t d(\cos \theta) \int_0^\infty dk k^2 \delta(E - (\hbar^2 K^2/4m) - (\hbar^2 k^2/m)) \\ \text{or } \rho_0(E) &= \frac{t}{(2\pi)^2} \left(\frac{m}{\hbar^2} \right)^{3/2} \left[E - \frac{\hbar^2 K^2}{4m} \right]^{1/2}, \quad E \geq \max \left[2E_F, \frac{P^2}{4m} \right]. \quad (2) \end{aligned}$$

When $P = \hbar K = 0$, $t = 1$ according to (23.12), and $\rho_0(2E_F) = \frac{1}{2} \rho_{FV}$. On the other hand, if $P \neq 0$ with $2E_F > P^2/4m$, then $t \rightarrow 0$, as $E \rightarrow 2E_F$ and

$$\rho_0(E) \rightarrow \frac{m^2}{(2\pi)^2 \hbar^3} \frac{E - 2E_F}{P}, \quad E \rightarrow 2E_F.$$

Problem 23.8ts

Because $\tanh \frac{x}{2} = 1 - 2(e^x + 1)^{-1}$, (23.58) can be written as follows

$$\frac{1}{\lambda} = \int_0^{\hbar\omega_D} \frac{d\varepsilon}{(\varepsilon^2 + \Delta^2)^{1/2}} - \int_0^{\hbar\omega_D} \frac{d\varepsilon}{(\varepsilon^2 + \Delta^2)^{1/2}} \frac{2}{\exp(\beta\sqrt{\varepsilon^2 + \Delta^2}) + 1}. \quad (1)$$

We notice that the second integral vanishes for $T \rightarrow 0$, $\beta \rightarrow \infty$. Hence

$$\frac{1}{\lambda} = \int_0^{\hbar\omega_D} \frac{d\varepsilon}{(\varepsilon^2 + \Delta_0^2)^{1/2}}, \quad T = 0. \quad (2)$$

Subtracting (1) from (2) and taking into account that the integral in (2) (and the similar one in (1)) is $\ln \frac{\hbar\omega_D + \sqrt{(\hbar\omega_D)^2 + \Delta_0^2}}{\Delta_0}$, we have (by changing variables to $y = \beta\varepsilon$)

$$\ln \frac{\Delta}{\Delta_0} = - \int_0^{\beta\hbar\omega_D} \frac{dy}{(y^2 + \gamma^2)^{1/2}} \frac{2}{e^{\sqrt{y^2 + \gamma^2}} + 1}, \quad \gamma = \beta\Delta, \quad \text{and} \quad \beta\hbar\omega_D \gg 1. \quad (3)$$

Equation (3) shows that Δ/Δ_0 is a function only of $\gamma = \Delta/k_B T$ (since $\beta\hbar\omega_D$ will be replaced by ∞). This function can be approximated by $\Delta/\Delta_0 = \tanh[T_c\Delta/T\Delta_0]$ (recall that $\Delta_0/T_c = 1.7639k_B$). Taking into account that $\tanh x = x - \frac{1}{3}x^3 + \dots$ ($x \rightarrow 0$) we have

$$\frac{\Delta^2}{\Delta_0^2} = 3 \left(\frac{\beta}{\beta_c} - 1 \right) \left(\frac{\beta_c}{\beta} \right)^3 = 3 \left(\frac{T}{T_c} \right)^3 \left(\frac{T_c}{T} - 1 \right), \quad T \rightarrow T_c^-. \quad (4)$$

In the solution of problem 22.2s instead of 3 we have used the more accurate value of 3.02.

Problem 23.9ts

According to (4) of the solution of problem 23.8ts, we have that $\partial\Delta^2/\partial\beta = 3.02\Delta_0^2/\beta_c = 3.02\Delta_0^2 k_B T_c$ in the limit $T \rightarrow T_c$. In the same limit $T \rightarrow T_c^-$, (23.59) becomes

$$C_V = -\frac{2\rho_F}{T} \int_{-\infty}^{\infty} d\varepsilon \left[\varepsilon^2 + \frac{3.02}{2} \Delta_0^2 \right] \frac{\partial}{\partial \varepsilon} \left(\frac{1}{e^{\beta\varepsilon} + 1} \right),$$

or, by introducing $x = \beta\varepsilon$ and $\gamma_0 = \beta_c\Delta_0$,

$$\begin{aligned}
 C_V &= -2\rho_F k_B^2 T \int_{-\infty}^{\infty} dx \left[x^2 + \frac{3.02}{2} \gamma_0^2 \right] \frac{d}{dx} \left(\frac{1}{e^x + 1} \right) \\
 &= 8\rho_F k_B^2 T \int_0^{\infty} dx x \frac{1}{e^x + 1} + 3.02\rho_F \frac{\Delta_0^2}{T} \\
 &= 8\rho_F k_B^2 T \frac{\pi^2}{12} + 3.02\rho_F \frac{(1.7639)^2 k_B^2 T_c^2}{T}, \quad T \rightarrow T_c \\
 &= 15.98\rho_F k_B^2 T_c,
 \end{aligned}$$

vs. $(2\pi^2/3)\rho_F k_B^2 T$ for the electronic contribution to the specific heat for the normal state. Thus

$$\left. \frac{C_{Vs} - C_{VN}}{C_{VN}} \right|_{T=T_c^-} = \frac{3.02 \times (1.7639)^2}{(2\pi^2/3)} = 1.43.$$

Problem 23.1s

Schrödinger's equation becomes

$$\left(\frac{\hbar^2 k^2}{2\mu} - E \right) c_{\mathbf{k}} + \frac{1}{V} \sum_{\mathbf{k}'} V_{\mathbf{k}-\mathbf{k}'} c_{\mathbf{k}'} = 0, \quad \mu = m/2,$$

which, taking into account the forms of $c_{\mathbf{k}}$ and $V_{\mathbf{k}-\mathbf{k}'}$, becomes

$$(2\varepsilon - E)a(\varepsilon) = \lambda \int_{E_F}^{E_F + \hbar\omega_D} d\varepsilon' a(\varepsilon'). \quad (1)$$

Call Δ' the integral in (1) so that $a(\varepsilon) = \lambda\Delta'/(2\varepsilon - E)$ and

$$\Delta' \equiv \int_{E_F}^{E_F + \hbar\omega_D} d\varepsilon' a(\varepsilon') = \lambda\Delta' \int_{E_F}^{E_F + \hbar\omega_D} d\varepsilon' \frac{1}{2\varepsilon' - E}$$

or

$$\frac{1}{\lambda} = \frac{1}{2} \ln \left| \frac{2E_F + 2\hbar\omega_D - E}{2E_F - E} \right| \simeq \frac{1}{2} \ln \left| \frac{2\hbar\omega_D}{2E_F - E} \right|,$$

or

$$|2E_F - E| = 2\hbar\omega_D \exp \left(-\frac{2}{\lambda} \right).$$

Problem 23.2s

By implementing the change in variables we have

$$-I = \frac{1}{2} \rho_{\text{VF}} \int_{-\beta \hbar \omega_{\text{D}}}^{\beta \hbar \omega_{\text{D}}} dx \frac{2 \tanh(x/2)}{\beta (2x/\beta)} = \rho_{\text{VF}} \int_0^{\beta \hbar \omega_{\text{D}}} dx \frac{\tanh(x/2)}{x}.$$

Integrating by parts we obtain

$$-I = \rho_{\text{VF}} (\ln \beta \hbar \omega_{\text{D}}) \tanh \frac{\beta \hbar \omega_{\text{D}}}{2} - \rho_{\text{VF}} \int_0^{\beta \hbar \omega_{\text{D}}} dx \ln x \frac{d}{dx} \tanh \left(\frac{x}{2} \right).$$

In the last integral we replace $\beta \hbar \omega_{\text{D}}$ (which is much larger than 1) by ∞ (the resulting error is of the order of $\ln \beta \hbar \omega_{\text{D}} \exp(-\beta \hbar \omega_{\text{D}})$). The integral $\int_0^{\infty} dx \ln x d[\tanh(x/2)]/dx$ is equal to $-\ln(2e^{\gamma}/\pi)$ (See [D5], p. 580, 4.371.3)
Thus

$$I = -\rho_{\text{VF}} \ln \left(\frac{2e^{\gamma}}{\pi} \beta \hbar \omega_{\text{D}} \right) + \mathcal{O}(\ln \beta \hbar \omega_{\text{D}} e^{-\beta \hbar \omega_{\text{D}}}).$$

General Reading

Data

- D1. H.L. Anderson, *A physicist's Desk Reference*, (American Institute of Physics, New York, 1989. (2nd edition, 1990)
- D2. R.C. Weast, *Handbook of Chemistry and Physics*, 61st edn. (CRC Press, Boca Raton, Florida, 1980) (D. R. Lide, editor, 89th edition, 2008)
- D3. O. Madelung (ed.), *Semiconductors-Basic Data*, 2nd edn. (Springer-Verlag, Berlin, 1996) (3rd edition, 2004)
- D4. M. Abramowitz, I.A. Stegun (eds.), *Handbook of Mathematical Functions* (Dover, New York, 1974)
- D5. I.S. Gradshteyn, I.M. Ryzhik, *Table of Integrals, Series, and Products*, 6th edn. (Academic, New York, 2000)
- D6. A.R. Cortan, In *Encyclopedia of Applied Physics*, vol. 5, ed. by Trigg, (VCH, New York, 1996). (Last¹ ed. 1997, 2008 computer file)
- D7. J. Mathews, R.L. Walker, *Mathematical Method of Physics*, 2nd edn. (Addison-Wesley, USA, Reading, MA, 1970). (Addison-Wesley 2nd ed., 1994)
- D8. P.M. Morse, H. Feshbach, *Methods of Theoretical Physics*, Vol. 1 and 2, (McGraw-Hill, New York, 1953). (Last ed. 1999)
- D9. D.E. Gray, (ed.), *American Institute of Physics Handbook*, (McGraw-Hill, New York, 1957). (Last ed. 1972)

Mechanics

- Me10. L.D. Landau, E.M. Lifshitz, *Mechanics, Volume 1, Course of Theoretical Physics* 3rd edn. (Butter-Heinemann, Great Britain, 2007)
- Me11. H. Goldstein, C.P. Poole, J.L. Safko, *Classical Mechanics*, 3rd edn. (Addison-Wesley, USA, 2001). (Last ed. 2002)
- Me12. K.R. Symon, *Mechanics*, 3rd edn. (Addison-Wesley, USA, 1971). (Last ed. 1980)
- Me13. L.D. Landau, E.M. Lifshitz, *Fluid Mechanics*, vol. 6, (Pergamon Press, London, 1959). (repr. with corrections, Butterworth-Heinemann, London, 2nd edition, 1997)

¹ At the time of this writing.

Electromagnetism

- E14. D.J. Griffiths, *Introduction to Electrodynamics*, 2nd edn. (Prentice Hall, 1996). (Benjamin, 3rd edition, 2008)
- E15. L.Landau, E.M. Lifshitz, *Electrodynamics of Continuous*, 2nd edn. (Pergamon Press, Oxford, 1984)
- E16. J.A. Stratton, *Electromagnetic Theory*, (McGraw Hill, New York, 1941). (Last ed. Wiley, New York, 2007)
- E17. J.D. Jackson, *Classical Electrodynamics*, 3rd edn. (J. Wiley, New York, 1998). (3rd ed., 1999)
- E18. M. Born, E. Wolf. *Principles of Optics*, 7th edn. (Cambridge University Press, Cambridge, expanded, 1999). (repr. with corrections, 2002)
- E19. W.R. Smythe, *Static and Dynamic Electricity*, (McGraw-Hill, New York, 1968). (Last ed. Hemisphere Pub. Corp., 1989)
- E20. C.F. Bohren, Donald, R. Huffman, *Absorption and Scattering of Light by small Particles*, (J. Wiley-Science Paperback. Wiley-Interscience, New York, 1998). (repr., 2004)
- E21. S.C. Maxwell, *A treatise on Electricity and magnetism (1873)*, (Dover, New York, 1945)
- E22. C.A. Balanis, *Advanced Engineering Electromagnetics*, (Wiley, New, York, 1989)

Quantum Mechanics

- Q23. R. Eisberg, R. Resnick, *Quantum Physics of Atoms, Molecules, Solids, Nuclei and Particles*, (J. Wiley, New York, 1974). (2nd International ed. 2000)
- Q24. J.J. Sakurai, *Modern Quantum Mechanics*, (Addison-Wesley, Reading, MA, London, 1994). (rev. ed., 2008)
- Q25. L.D. Landau, E.M. Lifshitz, *Quantum Mechanics*, 3rd edn. (Pergamon Press, Oxford, 1977). (Butterworth-Heinemann, Great Britain, 3rd rev. and enl. ed., 2003)
- Q26. S. Flügge, *Practical Quantum Mechanics*, (Springer, Heidelberg, 1974). (Last ed. 1999)
- Q27. L.I. Schiff, *Quantum Mechanics*, 2nd edn. (McGraw-Hill, New York, 1955). (3rd edition, 1968)
- Q28. E. Merzbacher, *Quantum Mechanics*, 3rd edn. (J. Wiley, New York, 1998). (Last ed. 2004).
- Q29. H.A. Bethe, *Intermediate Quantum Mechanics*, (Benjamin, New York, 1964). (Addison-Wesley, 3rd ed., 1997)
- Q30. C. Cohen-Tannoudji, B. Diu, F. Laloë, *Quantum Mechanics*, Vol. 1 and 2. (J. Wiley, 1977). (Last ed. 2006)
- Q31. D.J. Griffiths, *Introduction to Quantum Mechanics*, 2nd edn. (Prentice Hall, 2004). (Last ed. 2005)
- Q32. A. Messiah, *Quantum Mechanics, two Volumes*, (Dover Publications, New York, 1999)
- Q33. P.A.M. Dirac, *The principle of Quantum Mechanics*, (Oxford University Press, Oxford, 1967). (4th edition, 1982)
- Q34. R. Shankar, *Principles of Quantum Mechanics*, 2nd edn. (Springer, USA, 1994). (2nd ed., corr., 2008)

Statistical and Thermal Physics

- ST35. L.D. Landau, E.M. Lifshitz, *Statistical Physics*, Part I. 3rd edn. (Pergamon Press, Oxford, 1980). (Butterworth-Heinemann, Great Britain, 3rd edition, rev and enl. ed., 2000)
- ST36. M.W. Zemansky, R.H. Dittman, *Heat and Thermodynamics*, 6th edn. (McGraw-Hill, New York, 1981). (7th edition, 1997)
- ST37. F. Reif, *Fundamentals of Statistical and Thermal Physics*, (McGraw-Hill, New York, 1965). (International ed., 1987)
- ST38. C.J. Thompson, *Mathematical Statistical Mechanics*, (Macmillan, London, 1972). (Last ed. Princeton University Press, 1979)
- ST39. C. Kittel, H. Kroemer, *Thermal Physics*, 2nd edn. (W. H. Freeman, San Francisco, 1980). (Last ed. 2003)
- ST40. R.K. Pathria, *Statistical Mechanics*, (Pergamon Press, Oxford, 1972). (Butterworth-Heinemann, Boston, 2nd edition 2008)
- ST41. K. Huang, *Statistical Mechanics*, (J. Wiley, New York, 2nd edition, 1987)
- ST42. L.E. Reichl, *A modern Course in Statistical Physics*, (Texas University Press, Austin, 1980). (Wiley-Interscience, New York, 2nd edition, 2004)
- ST43. D. Chandler, *Introduction to Modern Statistical Mechanics*, (Oxford University Press, Oxford, 1987) and Solutions Manual

Many Body Theory

- MB44. L.P. Kadanoff, G. Baym, *Quantum Statistical Mechanics*, (Benjamin, New York, 1962). (Last ed. Westview Press, 1994)
- MB45. A.L. Fetter, J.D. Walecka, *Quantum Theory of Many-Particle Systems*, (McGraw-Hill, New York, 1971). (Last ed. Dover, USA, 2003)
- MB46. G.D. Mahan. *Many-Particle Physics*, 2nd edn. (Plenum, London, 1990). (Springer, Berlin, 3rd edition, 2007)
- MB47. A.A. Abrikosov, L.P. Gor'kov, I. Ye. Dzyaloshinskii, *Quantum Field Theoretical Methods in Statistical Physics*, 2nd edn. (Pergamon Press, Oxford, 1965)
- MB48. E.M. Lifshitz, L. P. Pitaevskii, in *Landau and Lifshitz Course of Theoretical Physics*, Part 2, vol. 9, (Pergamon Press, Oxford, 1980)
- MB49. Ch. P. Enz. *A course on Many-Body Theory Applied to Solid-State Physics*. (World Scientific, Singapore, 1992). (repr., 1998)
- MB50. W.E. Parry, *The Many-Body Problem*, (Oxford, 1973)
- MB51. D. Pines, *The many Body problem*, (Benjamin, New York, 1962). (Last ed. Addison-Wesley, 1997)
- MB52. S. Rao, *Field Theories in Condensed Matter Physics*, (Institute of Physics Publishing, U.K., 2002)
- MB53. P.M. Chaikin, T.C. Lubensky, *Principles of Condensed Matter Physics*, (Cambridge University Press, Cambridge, 1995) (Last ed. 1999)
- MB54. C. Domb, M.S. Green, (eds.), *Phase Transitions and Critical Phenomena*, vol. 4, (Academic Press, London, 1974) (Last ed. 2001)
- MB55. S. Doniach, E.H. Sondheimer, *Green's Functions for Solid State Physicists*, (Imperial College Press, London, 1988), Reedition. (Last ed. 1999)

- MB56. E.H. Lieb, D.C. Mattis, *Mathematical Physics in One Dimension*, (Academic, New York, 1966)
- MB57. G. Rickayzen, *Green's Functions and Condensed Matter*, (Academic Press, London, 1980). (Last ed. 1984)
- MB58. Ph. Nozieres, *Theory of Interacting Fermi Systems*, (Benjamin, New York, 1964). (Last ed. Westview Press, 1997)
- MB59. E. Dagotto, *Correlated Electrons in High-Temperature Superconductors*, *Reviews of Modern Physics*, vol. 66, (American Institute of Physics, 1994)

Acoustic and Elastic Wave

- AW60. L.D. Landau, E.M. Lifshitz, *Theory of Elasticity*, vol. 7, (Addison-Wesley, Oxford, 1959). (3rd ed., rev. and enl. by E.M. Lifshitz, A.M. Kosevich, and L.P. Pitaevskii, reprint. 2002)
- AW61. T.G. Leighton, *The Acoustic Bubble*, (Academic Press, San Diego, 1994). (Last ed. 1997)
- AW62. G.K. Horton, A.A. Maradudin, *Dynamical properties of Solids*, Vol. 1 and 2. (North Holland, 1995)
- AW63. P. Markoš, C.M. Soukoulis, *Wave Propagation*, (Princeton University Press, Princeton, 2008)
- AW64. M. Born, K. Huang, *Dynamical Theory of Crystal Lattices*, (Oxford University Press, London, 1968). (Last ed. Oxford Classic Texts in the Physical Sciences, USA, 1998)

Chemistry

- C65. M. Karplus, R.N. Porter, *Atoms and Molecules*, (W.A. Benjamin, 1970). p. 287
- C66. J. McMurry. *Organic Chemistry*, 4th edn. (Brooks/Cole, 1996). (Thomson, 7th ed., 2008)
- C67. J.E. Brady. *General Chemistry*, 5th edn. (J. Wiley, New York, 1990)

Materials

- M68. R.A.L. Jones, *Soft Condensed Matter*, (Oxford Master Series in Condensed Matter Physics). (Oxford University Press, New York, 2002). (repr., 2007)
- M69. I.W. Hamley, *Introduction to Soft Matter: Polymers, Colloids, Amphiphiles and Liquid Crystals*, (Wiley, New York, 2000). (rev., 2007)
- M70. G. Strobl, *The Physics of Polymers*, 2nd edn. (Springer-Verlag, Berlin, 1997). (3rd rev. and exp. edition, 2007)
- M71. P.G. de Gennes, J. Prost, *The Physics of Liquid Crystals*, 2nd edn. (Clarendon Press, Oxford, 1993). (repr., 2007)
- M72. I.W. Hamley, *Introduction to Soft Matter: Synthetic and Biological Self-Assembling Materials*. (Wiley, New York, 2007). Revised edition
- M73. M.T. Dove, *Structure and Dynamics-An Atomic View of Materials* (Oxford Master Series in Condensed Matter Physics), (Oxford University Press, USA, 2003)

Solid State Books (general)

- SS74. C. Kittel, *Introduction to Solid State Physics*, 8th edn. (J. Wiley, London, 2005)
- SS75. N.W. Ashcroft, N.D. Mermin, *Solid State Physics*, (Holt, Rinehart and Winton, London, 1976). (Brooks/Cole, college ed., 2005)
- SS76. W.A. Harrison, *Electronic Structure and the Properties of Solids*, ed by. W. H. Freeman, (San Francisco, 1980). (Last ed. Dover, USA, 1989)
- SS77. G. Burns, *Solid State Physics*, (Academic Press, London, 1985). (Last ed. 1990)
- SS78. R.H. Bube. *Electrons in Solids*, 3rd edn. (Academic Press, New York, 1992)
- SS79. H. Ibach, H. Luth, *Solid State Physics: An introduction to Theory and Experiment*, (Springer-Verlag, Berlin, 1991). (3rd upd. and enlar. ed., 2003)
- SS80. B.K. Tanner, *Introduction to the Physics of Electrons in Solids*, (Cambridge University Press, Cambridge, 1995)
- SS81. D.A. Papaconstantopoulos, *Handbook of the Band Structure of Elemental Solids*, (Plenum Press, London, 1986)
- SS82. M.P. Marder, *Condensed Matter Physics*, (J. Wiley-Interscience, New York, 2000)
- SS83. E. Kaxiras, *Atomic and Electronic Structure of Solids*, (Cambridge University Press, Cambridge, 2003)
- SS84. W.A. Harrison, *Elementary Electronic Structure*, (World Scientific, Singapore, 1999). (Revised edition, 2005)
- SS85. J. Callaway, *Quantum Theory of the Solid State*, 2nd edn. (Academic Press, Boston, 1991)
- SS86. J.C. Blakemore, *Solid State Physics*, 2nd edn. (Cambridge University Press, Cambridge, 1985). (Last ed. 1987)
- SS87. J.R. Christman, *Fundamentals of Solid State Physics*, (J. Wiley, New York, 1988)
- SS88. R. Dalven, *Introduction to Applied Solid State Physics*, 2nd edn. (Plenum Press, London, 1990)
- SS89. J.D. Patterson, B. Bailey, *Solid State Physics, Introduction to the Theory*, 2nd edn. (Springer, Berlin, 2007)
- SS90. J.R. Hooks, H.E. Hall, *Solid State Physics*, 2nd edn. (J. Wiley, New York, 2007)
- SS91. L. Brillouin, *Wave Propagation in Periodic Structures*, 2nd edn. (Dover, U.S.A., 1953). (Last ed. 2003)
- SS92. L. M. Sanders. *Advanced Condensed Matter Physics*. (Cambridge University. Press, Cambridge, 2009).
- SS93. M.A. Omar, *Elementary Solid State Physics*, (Addison-Wesley, London, 1975). (rev., repr., ed., 1993)
- SS94. H.M. Rosenberg, *The Solid State*, (Oxford University Press, Oxford, 1988). (repr., with corr., 1992)
- SS95. B.K. Tanner, *Introduction to the Physics of Electrons in Solids*, (Cambridge University Press, Cambridge, 1995). (Last ed. 2000)
- SS96. J.M. Ziman. *Principles of the theory of Solid*, (Cambridge University Press, Cambridge, 1964). (2nd edition, 1979)
- SS97. Ph.L. Taylor, Ol. Heinonen, *A Quantum Approach to Condensed Matter Physics*, (Cambridge University Press, Cambridge, 2002). (repr. with corr., 2004)

- SS98. W. Jones, N.H. March, *Theoretical Solid State Physics*, vol. 2, (J. Wiley, New York, 1973). (Dover, USA, 1985)
- SS99. C. Kittel, *Quantum Theory of Solids*, (J. Wiley, London, 1963). (2nd edition, 1987, Revised edition)
- SS100. J.M. Ziman, *Electrons and Phonons*, (Clarendon Press, Oxford, 1960). ((Oxford Classical Texts in the Physical Sciences). Oxford University Press, Oxford, 2001)
- SS101. R.E. Peierls, *Quantum Theory of Solids*, (Oxford University Press, Oxford, 1955). (Last ed. (Oxford Classical Texts in the Physical Sciences), 2001)
- SS102. F. Seitz, *Modern Theory of Solids*, (McGraw-Hill, 1940). (Dover, USA, 1987)
- SS103. G.H. Wannier, *Elements of Solid State Theory*, (Cambridge University Press, Cambridge, 1954). (Last ed. 1970)
- SS104. A.A. Abrikosov, *Fundamentals of the Theory of Metals*, (North-Holland, Amsterdam, 1988)
- SS105. A.H. Wilson, *Theory of metals*, 2nd edn. (Cambridge University Press, Cambridge, 1959). (Last ed. 1965)
- SS106. N.F. Mott, H. Jones, *Theory of the Properties of Metals and Alloys*, (Dove, Oxford, 1936). (Last ed. 1958)
- SS107. W.A. Harrison, *Pseudopotentials in the Theory of Metals*, (Benjamin, New York, 1966)
- SS108. B. Alder, S. Fernbach, M. Rotenberg, (eds.), *Methods in Computational Physics*, vol. 8 (Energy Bands of Solids). (Academic Press, New York, 1968).
- SS109. V. Heine, D. Weaire, in *Solid State Physics*, vol. 24, ed. by H. Ehrenreich, F. Seitz, and D. Turnbull, (Academic Press, New York, 1970)
- SS110. D.W. Snoke, *Solid State Physics: Essential Concepts*. Dorling Kinderley (India) Pvt Ltd, paperback, 2009.
- SS111. P. Phillips, *Advanced Solid State Physics*, (Westview Press, 2002). (Last ed. 2003)
- SS112. J. Singleton, *Band Theory and Electronic Properties of Solids* (Oxford Master Series in Condensed Matter Physics). (Oxford University Press, USA, 2001)
- SS113. M. Fox, *Optical Properties of Solids*, (Oxford Master Series in Condensed Matter Physics). (Oxford University Press, USA, 2002). (repr. with corr., 2006)
- SS114. H. Ehrenreich, *Solid State Physics, Advances in Research and Applications*, V. 37, 93. (Academic Press, 1982)
- SS115. F.C. Phillips, *An Introduction to Crystallography*, 4th edn. (Wiley, New York, 1971). (Last ed. Longman, 1977)
- SS116. W.G. Wyckoff, *Crystal Structures, Krieger, International tables for x-ray crystallography*, vol. 4, 2nd edn. (Kynoch Press, Birmingham, 1981)
- SS117. J.P. Hirth, J. Lothe, *Theory of Dislocations*, 2nd edn. (Krieger and Malabar, 1992)
- SS118. R. Dalven, *Introduction to Applied Solid State Physics*, 2nd edn. (Plenum Press, New York, 1990)

Semiconductors

- Se119. P.Y. Yu, M. Cardona, *Fundamentals of Semiconductors*, 3rd edn. (Springer, Berlin, 2005)
- Se120. B. R. Nag, *Electron Transport in Compound Semiconductors*, vol. 11 of *Solid State Sci.*, (Springer, Berlin, 1980)
- Se121. S. M. Sze, *Physics of Semiconductor Devices*, 2nd edn. (Wiley, New York, 1981). (Wiley-Interscience, Hoboken, 3rd ed., 2007)

Photonic and Phononic Crystals

- PC122. J.D. Joannopoulos, R.D. Meade, J.N. Winn. *Photonic Crystals: Molding the Flow of Light*, (Princeton University Press, Princeton, 1995). (2nd edition, 2008)
- PC123. K. Sakoda, *Optical Properties of Photonic Crystals*, vol.80, Springer Series in Optical Sciences, (Springer-Verlag, Berlin, 2001). (2nd edition, 2005)
- PC124. C.M. Soukoulis, (ed.), *Photonic Crystals and Light Localization in the 21st Century*, (Kluwer Academic Press Publishers, Dordrecht, 2001)
- PC125. C.M. Soukoulis, *Photonic Band Gaps and Localization*, (NATO Advanced Study Institute Series). (Plenum, New York, 1993)
- PC126. C.M. Soukoulis, (ed.), *Photonic Band Gap Materials*, vol. 315, (NATO Advanced Study Institute Series), (Kluwer, Dordrecht, 1996)
- PC127. P. Sheng, *Introduction to Wave Scattering, Localization and Mesoscopic Phenomena*, (Academic, San Diego, 1995). ((Springer Series in Material Sciences). Springer, Berlin, 2nd edition, 2006)
- PC128. M.S. Kushawaha, *International Journal of Modern Physics*, **B10**, 977 (1996)
- PC129. St. A.Meier. *Plasmonics: Fundamentals and Applications*, (Springer-Verlag, Heidelberg, 2007)
- PC130. J.M. Lourtioz, et al.. *Photonic Crystals*, (Springer-Verlag, Berlin, 2005)

Disordered and Mesoscopic Systems

- DS131. N.E. Cusack, *The Physics of Structurally Disordered Matter*, (Adam Hilger, Bristol, 1987). (repr., 1988)
- DS132. R.E. Street, *Hydrogenated Amorphous Silicon*, (Cambridge University Press, Cambridge, 1991). (Last ed. 2005)
- DS133. N.F. Mott, E.A. Davis, *Electronic Processes in Non-Crystalline Materials*, (Oxford University Press, Oxford, 1979)
- DS134. E.M. Lifshitz, S.A. Gredeskul, L.A. Pastur, *Introduction to the Theory of Disordered Systems*, (Wiley, New York, 1988)
- DS135. S. Datta, *Electronic Transport in Mesoscopic Systems*, (Cambridge University Press, Cambridge, 1995). (Last ed. 1997)
- DS136. P. Sheng, *Introduction to Wave Scattering, Localization and Mesoscopic Phenomena*, (Academic Press, San Diego, 1995). (Springer, Berlin, 2006)

- DS137. Y. Imry, *Introduction to Mesoscopic Physics*, 2nd edn. (Oxford University Press, Oxford, 2002). (Last ed. 2009)
- DS138. J.M. Ziman, *Models of Disorder*, (Cambridge University Press, London, 1979). (Last ed. 1982)
- DS139. H. Kamimura, H. Aoki, *The Physics of Interacting Electrons in Disordered Systems*, (Clarendon Press, Oxford, 1989). (Oxford University Press, USA, 1990)
- DS140. D. Stauffer, *Introduction to Percolation Theory*, (Taylor and Francis, London, 1987). (rev. 2nd ed., 1998)
- DS141. M.F. Thorpe, in *Excitations in Disordered Systems*, vol. B78, ed. by M.F. Thorpe, (NATO Advanced Study Institute Series). (Plenum, New York, 1981). (Last ed. 1982)
- DS142. P. Phariseau, B.L. Györfy, L. Scheire (eds.), *Electrons in Disordered Metals and at Metallic Surfaces*, (NATO Science Series). (Plenum, New York, 1979)
- DS143. R.J. Elliot, in *Excitations in Disordered Systems*, vol. B78, ed. by M.F. Thorpe, (NATO Advanced Study Institute Series). (Plenum, New York, 1981). (Last ed. 1982)
- DS144. A. Gonis, *Green Functions for Ordered and Disordered Systems*, Vol. 4 Studies in Mathematical Physics (North-Holland, Amsterdam, 1992)
- DS145. F. Yonezawa, (ed.), *Fundamental Physics of Amorphous Semiconductors*, Vol. 25 of Springer Ser. *Solid-State Sci.* (Springer, Berlin, 1980). (Last ed. 1981).
- DS146. W.A. Phillips, (ed.), *Amorphous Solids*, Vol. 24 of Topics in Current Physics. (Springer, Berlin, 1980). (Last ed. 1981)
- DS147. R.J. Elliot, J.A. Krumhansl, and P.L. Leath, *Review of Modern Physics*, **46**, 465 (1974)
- DS148. H. Fritzsche, (ed.), *Transport, Correlation and Structural Defects*, Vol. 3 of Advances in Disordered Semiconductors. (World Scientific, Singapore, 1990). (Last ed. 1991)
- DS149. S.R. Elliot, *Physics of Amorphous Materials*. Longman, 2nd edn. (Essex, 1990)
- DS150. R.O. Pohl, X. Liu, E.J. Thompson, *Rev. Mod. Phys.*, **74**(4), 991 (2002)
- DS151. J.N. Sherwood, (ed.), *The Plastically Crystalline State (Orientationally-Disordered Crystals)*. (J. Wiley, New York, 1987). (Last ed. 1979)
- DS152. D. Delitz, T.R. Kirkpatrick, *Reviews of Modern Physics*, **66**, 261 (1994)

Disorder and Localization

- DSL153. E.N. Economou., *Green's Functions in Quantum Physics*, 3rd edn. (Springer-Verlag, Berlin, 2006)
- DSL154. B. Kramer, A. MacKinnon, *Rep.Prog. Phys.*, **56**, 1469, (1993)
- DSL155. B. Kramer, G. Schön, (eds.), *Phys.*, A167, 1990
- DSL156. E. Abrahams, S. Kravchenko, M.P. Sarachik, *Reviews of Modern Physics*, **73**, 251 (2001)
- DSL157. C.M. Soukoulis, E.N. Economou, *Waves in Random Media*, **9**, (1999)
- DSL158. M. Schreiber (ed.), *Localization. Ann. Physics* Vol. 8, and 8, Special Issue, 1999
- DSL159. T. Brandes, S. Kettmann, (eds.), *Anderson Localization and its Ramifications*, (Springer, Heidelberg, 2003)

- DSL160. P. Sheng, *Scattering and Localization of Classical Waves in Random Media*, (World Scientific, Singapore, 1990)
- DSL161. P.A. Mello, N. Kumar, *Quantum Transport in Mesoscopic Systems: Complexity and Statistical Fluctuations*, (Oxford University Press, Oxford, 2005)

Mott Localization

- ML162. P.P. Edwards, C.N.R. Rao, *Metal-Insulator Transitions*, (Taylor and Francis, London, Revis. 1995)
- ML163. D. Belitz, T.R. Kirkpatrick, *The Anderson-Mott Transition*, vol. 66. (Reviews of Modern Physics, 1994)
- ML164. N.F. Mott, *Metal-Insulator Transitions*, (Taylor and Francis, London, 1974). (1990)

Quantum Hall Effect

- QHE165. M. Janssen, *Introduction to the Theory of the Integer Quantum Hall Effect*, (VCH, Weinheim, 1994)

Finite Systems

- FS166. S.V. Rotkin, S. Subramoney (eds.) *Applied Physics of Carbon Nanotubes*, (Springer-Verlag, Berlin, 2005)
- FS167. K. Nakamura, T. Harayama, *Quantum Chaos and Quantum Dots*, (Oxford University Press, Oxford, 2006)

Magnetism

- Ma168. D.C. Mattis, *The Theory of magnetism made Simple*, (World Scientific, Singapore, 2006). (Last ed. 2008)
- Ma169. D.C. Mattis, *The Theory of Magnetism*, Vol. 1 and 2, (Springer, Berlin, 1988)
- Ma170. A. Auerbach, *Interacting Electrons and Quantum Magnetism*, (Springer, Berlin, 1994). (Last ed. 1998)
- Ma171. A. Montorsi, *The Hubbard Model*, (World Scientific, Singapore, 1992)
- Ma172. G.T. Rado, H. Suhl, *Magnetism*, vol. 2B, (Academic Press, London, 1966). (Last ed. 1973)
- Ma173. C. Herring, *Exchange Interactions among Itinerant Electrons*, vol. 4, (Academic Press, London, 1966)
- Ma174. S. Maekawa, (ed.), *Concepts in Spin Electronics*, (Science Publications). (Oxford University Press, New York, 2006)
- Ma175. S. Blundell, *Magnetism in Condensed Matter*, (Oxford Master Series in Condensed Matter Physics). (Oxford University Press, New York, 2001). (repr., 2003)

- Ma176. C. Domb, M.S. Green, (eds.), *Phase Transition and Critical Phenomena*, vol. 3, (Academic Pres, London, 1974)
- Ma177. D.D. Awschalom, R.A. Buhrman, J.M. Daughton, S. von Molnár, and M.L. Roukes, (eds.), *Spin Electronics*, (Kluwer Academic, Dordrecht, 2003)
- Ma178. J. Stöhr, H.C. Siegmann, *Magnetism from Fundamentals to Nanoscale Dynamics*, (Springer, Berlin, 2003). (Last ed. 2006)

Superconductivity

- Su179. M. Tinkham, *Introduction to Superconductivity*, (Mc-Graw-Hill, New York, 1996). (Dover, USA, 2nd edition, 2004)
- Su180. J.R. Schrieffer, *Theory of Superconductivity*, (Addison-Wesley, Redwood City, 1983). (Perseus Books, Revised edition, 1999)
- Su181. G. Rickayzen, *Theory of Superconductivity*, (Interscience, New York, 1965)
- Su182. R.D. Parks, (ed.), *Superconductivity*, Vol. 1, and 2, (M. Dekker, New York, 1969)
- Su183. D.R. Tilley, J. Tilley, *Superfluidity and Superconductivity*, (A. Hilger, Bristol, 1990). (Last ed. Institute of Physics Pub., 1994)
- Su184. Th. P. Sheahen, *Introduction to High-Temperature Superconductivity*, (Plenum, New York, 1994). (Last ed. Kluwer Academic Press, 2002)
- Su185. M. Cyrot, D. Pavuna, *Introduction to Superconductivity and High- T_c Materials*, (World Scientific, Singapore, 1992). (Last ed. 1995)
- Su186. C.N. Rao, *Chemistry of High Temperature Superconductors*, (World Scientific, Singapore, 1991). (Last ed. 1992)
- Su187. J.C. Gallop, *SQUIDS, The Josephson Effects, and Superconducting Electronics*. (A. Hilger, Bristol, 1991)
- Su188. P.B. Littlewood, G. Varelogiannis, (eds.), *Anomalous Complex Superconductors*, (Elsevier Science, North-Holland, 1999)
- Su189. J.F. Annett, *Superconductivity, Superfluids, and Condensates*, (Oxford MasterSeries in Condensed Matter Physics). (Oxford University Press, USA, 2004). (repr. with corr., 2007)
- Su190. L. Pitaevskii, S. Stringari, *Bose-Einstein Condensation*, (Clarendon Press, Oxford, 2003)
- Su191. J.G. Bednorz, K.A. Müller, *Rev. Mod. Phys.* **60**, 585 (1988)

Mathematics

- Mat192. B.B. Mandelbrot, *The Fractal Geometry of Nature*. (W. H. Freeman and Co, New York, 1982). (Last ed. updated and augmented, 1983)
- Mat193. K. Falconer, *Fractal Geometry: Mathematical Foundations and Applications*, 2nd edn. (J. Willey, England, 2003)

Synchrotron Radiation

- SR194. E. Isaacs, Ph. Platzman, *Physics Today*, 40 (1996)

References

Chapter 2

- 2.1. J.T. Waber, D.T. Cromer, J. Chem. Phys. **42**, 4116 (1965)

Chapter 5

- 5.1. B.P. Johnson, R.W. Christy, Phys. Rev. B **6**, 4370 (1972)
5.2. H. Ehrenreich, M.H. Cohen, Phys. Rev. **115**, 786 (1959)

Chapter 6

- 6.1. L. Shi, D.A. Papaconstantopoulos, Phys. Rev. B **70**, 205101 (2004)

Chapter 7

- 7.1. J.R. Chelikowsky, M.L. Cohen, Phys. Rev. B **14**, 556 (1976)

Chapter 8

- 8.1. P. Hohenberg, W. Kohn, Phys. Rev. B **136**, 864 (1964)
8.2. W. Kohn, L.J. Sham, Phys. Rev. A **140**, 1133 (1965)
8.3. J.P. Perdew, A. Zunger, Phys. Rev. B **23**, 5048 (1981).
8.4. M.C. Payne, M.P. Teter, D.C. Allan, T.A. Arias, J.D. Joannopoulos, Rev. Modern Phys. **64**, 1045 (1992)
8.5. R. Car, M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985)
8.6. M.E. Eberhart, Sci. Am. **281**, 66 (1999)
8.7. M. Marder, J. Fineberg, Phys. Today **49**, 24 (1996)

- 8.8. F.F. Abraham, J. Broughton, N. Bernstein, E. Kaxiras, *Comput. Phys.* **12**, 538 (1998)
- 8.9. J.R. Rice, G.E. Beltz J., *Phys. Solids* **42**, 333 (1994)
- 8.10. S.G. Roberts, *Mater. Sci. Eng. A* **234–236**, 52 (1997)
- 8.11. V.V. Bulatov, E. Kaxiras, *Phys. Rev. Lett.* **78**, 4221 (1997)
- 8.12. J. Bardeen, L.N. Cooper, J.R. Schrieffer, *Phys. Rev.* **108**, 1175 (1957)
- 8.13. P.G. Drazin, R.S. Johnson, *Solitons: An Introduction* (Cambridge University Press, Cambridge, reprinted with corrections 1996)
- 8.14. L.F. Mollenauer, J.P. Gordon, *Solitons in Optical Fibers* (Elsevier Academic Press, Amsterdam, 2006)
- 8.15. Yu.S. Kivshar, G.P. Agrawal, *Optical Solitons: From Fibers to Photonic Crystals* (Elsevier Science, The Netherlands, 2003)
- 8.16. A.J. Sievers, S. Takeno, *Phys. Rev. Lett.* **61**, 970 (1988)
- 8.17. S. Flach, A.V. Gorbach, *Phys. Reports* **467**, 1 (2008); and references therein

Chapter 9

- 9.1. N.D. Mermin, *J. Math. Phys.* **7**, 1038 (1966)

Chapter 12

- 12.1. N.W. Ashcroft, *J. Phys.* **C 1**, 232 (1968)
- 12.2. R.A. Cowley, A.D.B. Woods, G. Dolling, *Phys. Rev.* **150**, 487 (1966)

Chapter 13

- 13.1. M.H. Cohen, E.N. Economou, C.M. Soukoulis, *Phys. Rev. B* **30**, 4463 (1984)
- 13.2. F.D.M. Haldane, *Phys. Rev. Lett.* **61**, 2015 (1988)
- 13.3. K. Nomura, A.H. MacDonald, *Phys. Rev. Lett.* **96**, 256602 (2006)
- 13.4. S.V. Morozov, K.S. Novoselov, M.I. Katsnelson, F. Schedin, L.A. Ponomarenko, D. Jiang, A.K. Geim, *Phys. Rev. Lett.* **97**, 016801 (2006)
- 13.5. K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov, *Science* **306**, 666 (2004)
- 13.6. S.V. Morozov, K.S. Novoselov, M.I. Katsnelson, F. Schedin, D.C. Elias, J.A. Jaszczak, A.K. Geim, *Phys. Rev. Lett.* **100**, 016602 (2008)
- 13.7. F. Miao, S. Wijeratne, Y. Zhang, U.C. Coskun, W. Bao, C.N. Lau, *Science* **317**, 1530 (2007)
- 13.8. R.R. Nair, P. Blake, A.N. Grigorenko, K.S. Novoselov, T.J. Booth, T. Stauber, N.M.R. Peres, A.K. Geim, *Science* **320**, 1308 (2008)
- 13.9. A.K. Geim, K.S. Novoselov, *Nat. Mater.* **6**, 13 (2007)
- 13.10. C. Lee, X.D. Wei, J.W. Kysar, J. Hone, *Science* **321**, 385 (2008)
- 13.11. G.P. Collins, *Scientific Am* **291**, 74 (August 2004)

Chapter 14

- 14.1. S. T. Pantelides, Phys. Rev. B **11**, 5082 (1975)
- 14.2. L. Pauling, Proc. R. Soc. London A**114**, 181 (1927)
- 14.3. S. S. Jaswal, T. P. Sharma J. Phys. Chem. Solids **34**, 509 (1973)
- 14.4. J. Tesson, A. Kahn, W. Shockley Phys. Rev. **92**, 890 (1953)

Chapter 15

- 15.1. V.L. Moruzzi, A.R. Williams, J.F. Janak, Phys. Rev. B **15**, 2854 (1977)
- 15.2. J. Friedel, in *The Physics of Metals*, ed. by J.M. Ziman (Cambridge University Press, New York, 1969)
- 15.3. L.F. Mattheiss, Phys. Rev. B **6**, 4718 (1972)
- 15.4. W.Y. Ching, Y. Xu, G.L. Zhao, K.W. Wong, F. Zandiehnam, Phys. Rev. Lett. **59**, 1333 (1987)
- 15.5. W. Pickett, R.E. Cohen, H. Krakauer, Phys. Rev. B **42**, 8764 (1990)
- 15.5. W.A. Harrison, Phys. Rev. B **38**, 270 (1988)
- 15.7. J.C. Slater, G.F. Koster, Phys. Rev. **94**, 1498 (1954)

Chapter 16

- 16.1. E. Yablonovitch, Inhibited spontaneous emission in solid-state physics and electronics, Phys. Rev. Lett. **58**, 2059 (1987)
- 16.2. S. John, Strong localization of photons in certain disordered dielectric superlattices, Phys. Rev. Lett. **58**, 2486 (1987)
- 16.3. C.M. Soukoulis, E.N. Economou, G.S. Grest, M.H. Cohen, Existence of Anderson localization of classical waves in a random two-component medium, Phys. Rev. Lett. **62**, 575 (1989)
- 16.4. E.N. Economou, A.D. Zedetsis, Classical wave propagation in periodic structures, Phys. Rev. B **40**, 1334 (1989)
- 16.5. E. Yablonovitch, T.J. Gmitter, Photonic band structure: The face-centered-cubic case, Phys. Rev. Lett. **63**, 1950 (1989)
- 16.6. K.M. Ho, C.T. Chan, C.M. Soukoulis, Existence of a photonic gap in periodic dielectric structures, Phys. Rev. Lett. **65**, 3152 (1990)
- 16.7. K.L. Leung, Y.F. Liu, Full vector wave calculation of photonic band structures in face-centered-cubic dielectric media, Phys. Rev. Lett. **65**, 2646 (1990)
- 16.8. Z. Zhang, S. Satpathy, Electromagnetic wave propagation in periodic structures: Bloch wave solution of Maxwell's equations, Phys. Rev. Lett. **65**, 2650 (1990)
- 16.9. R.D. Meade, K.D. Brommer, A.M. Rappe, J.D. Joannopoulos, Electromagnetic Bloch waves at the surface of a photonic crystal, Phys. Rev. B **44**, 10961 (1991)
- 16.10. S. John, J. Wang, Quantum electrodynamics near a photonic band gap: Photon bound states and dressed atoms, Phys. Rev. Lett. **64**, 2418 (1990)

- 16.11. E. Yablonovitch, T.J. Gmitter, K.M. Leung, Photonic band structure: The face-centered-cubic case employing nonspherical atoms, *Phys. Rev. Lett.* **67**, 2295 (1991)
- 16.12. K.M. Ho, C.T. Chan, C.M. Soukoulis, R. Biswas, M.M. Sigalas, Photonic band-gaps in 3-dimensions-new layer by layer periodic structures, *Sol State Commun* **89**, 413 (1994)
- 16.13. E. Ozbay, A. Abeyta, G. Tuttle, M. Tringides, R. Biswas, C.T. Chan, C.M. Soukoulis, K.M. Ho, Measurement of a three-dimensional photonic band gap in a crystal structure made of dielectric rods, *Phys. Rev. B* **50**, 1945 (1994) and *Appl. Phys. Lett.* **64**, 2059 (1994)
- 16.14. G. Feiertag, W. Ehrfeld, H. Freimuth, H. Kolbe, H. Lehr, M. Schmidt, M.M. Sigalas, C.M. Soukoulis, G. Kiriakidis, T. Pedersen, J. Kuhl, W. Koenig, in [PC126], p. 63; *Appl. Phys. Lett.* **71**, 1441 (1997)
- 16.15. J.G. Fleming, S.Y. Lin., Three-dimensional photonic crystal with a stop band from 1.35 to 1.95 microns, *Opt. Lett.* **24**, 49 (1999)
- 16.16. E. Judith, G.J. Wijnhoven, L.W. Vos, Preparation of photonic crystals made of air spheres in titania, *Science* **281**, 802 (1998)
- 16.17. G. Subramania, K. Constant, R. Biswas, M.M. Sigalas, K.M. Ho, Optical photonic crystals fabricated from colloidal systems, *Appl. Phys. Lett.* **74**, 3933 (1999)
- 16.18. T.F. Krauss, R.M. De La Rue, Photonic crystals in the optical regime – past, present and future, *Progr. Quant. Electron.* **23**, 51 (1999)
- 16.19. S. Noda, K. Tomoda, N. Yamamoto, A. Chutinan, Full three-dimensional photonic bandgap crystals at near-infrared wavelengths, *Science* **289**, 604 (2000)
- 16.20. J. Schilling, R.B. Wehrspohn, A. Birner, F. Muller, R. Hillebrand, U. Gosele, S.W. Leonard, J.P. Mondia, F. Genereux, H.M. van Driel, P. Kramper, V. Sandoghdar, K. Busch, A model system for two-dimensional and three-dimensional photonic crystals: macroporous silicon, *J. Pure Appl. Opt.* **3**, S121 (2001)
- 16.21. V. Yu Miklyaev, D.C. Meisel, A. Blanco, G. von Freymann, K. Busch, W. Koch, C. Enkrich, M. Deubel, M. Wegener, Three-dimensional face-centered-cubic photonic crystal templates by laser holography: fabrication, optical characterization, and band-structure calculations, *Appl. Phys. Lett.* **82**, 1284 (2003)
- 16.22. M. Deubel, G. von Freymann, M. Wegener, S. Pereira, K. Busch, C.M. Soukoulis, Direct laser writing of three-dimensional photonic-crystal templates for telecommunications, *Nat. Mater.* **3**, 444 (2004)
- 16.23. G. Subramania, Y.J. Lee, I. Brener, T.S. Luk, P.G. Clem, Nanolithographically fabricated titanium dioxide based visible frequency three dimensional gap photonic crystal, *Opt. Exp.* **15**, 13049 (2007)
- 16.24. J.C. Knight, J. Broeng, T.A. Birks, P. St. Russel, Photonic band cap guidance in optical fibers, *Science* **282**, 1476 (1998)
- 16.25. R.F. Cregan, B.J. Mangan, J.C. Knight, T.A. Birks, P. St. J. Russell, P.J. Roberts, D.C. Allan, Single-mode photonic band gap guidance of light in air, *Science* **285**, 1537 (1999)
- 16.26. J. Broeng, S.E. Barkou, T. Sondergaard, A. Bjarklev, Analysis of air-guiding photonic bandgap fibers, *Opt. Lett.* **25**, 96 (2000)

- 16.27. S.Y. Lin, E. Chow, J. Bur, S.G. Johnson, J.D. Joannopoulos, Low-loss, wide-angle Y splitter at similar to 1.6-micron wavelengths built with a two-dimensional photonic, *Opt. Lett.* **40**, 1400 (2002)
- 16.28. T.F. Krauss, Planar photonic crystal waveguide devices for integrated optics, *Phys. Stat. Solid. A* **197**, 688 (2003)
- 16.29. E.R. Brown, C.D. Parker, E. Yablonovitch, Radiation properties of a planar antenna on a photonic-crystal substrate, *J. Opt. Soc. Am. B* **10**, 404 (1993)
- 16.30. R. Biswas, S.D. Cheng, E. Ozbay, S. McCalmont, W. Leung, G. Tuttle, K. M. Ho, in [PC126], p. 377
- 16.31. E. Ozbay, G. Tuttle, M. Sigalas, C.M. Soukoulis, K.M. Ho, Defect structures in a layer-by-layer photonic band-gap crystal, *Phys. Rev. B* **51**, 13961 (1995)
- 16.32. J. Ge, Y. Hu, Y. Yin, Highly tunable superparamagnetic colloidal photonic crystals, *Angew. Chem. Int. Ed.* **46**, 7428 (2007)
- 16.33. Z. Wang, Y.D. Chong, J.D. Joannopoulos, M. Soljacic, Reflection-free one-way edge modes in a gyromagnetic photonic crystal, *Phys. Rev. Lett.* **100**, 013905 (2008)
- 16.34. Z. Yu, G. Veronis, Z. Wang, Sh. Fan, One-way electromagnetic waveguide formed at the interface between a plasmonic metal under a static magnetic field and a photonic crystal, *Phys. Rev. Lett.* **100**, 023902 (2008)
- 16.35. M. Sigalas, M.S. Kushwaha, E.N. Economou, M. Kafesaki, I.E. Psarobas, W. Steuer, Classical vibrational modes in phononic lattices: theory and experiment, *Z. Kristallographie* **220**, 765 (2005)
- 16.36. M. Kafesaki, E.N. Economou, M. Sigalas, in [PC126], 143 (1996)
- 16.37. M. Kafesaki, E.N. Economou, Interpretation of the band-structure results for elastic and acoustic waves by analogy with the LCAO approach, *Phys. Rev. B* **52**, 13317 (1995); and, multiple-scattering theory for three-dimensional periodic acoustic composites, *Phys. Rev. B* **60**, 11993 (1999)
- 16.38. M. Kafesaki, R.S. Penciu, E.N. Economou, Air bubbles in water: A strongly multiple scattering medium for acoustic waves, *Phys. Rev. Lett.* **84**, 6050 (2000)
- 16.39. M.M. Sigalas, E.N. Economou, Elastic and acoustic wave band-structure, *J. Sound Vib* **158**, 377 (1992)
- 16.40. M.M. Sigalas, E.N. Economou, Band-structure of elastic-waves in 2-dimensional systems, *Sol. State Commun.* **86**, 141 (1993)
- 16.41. Z.Y. Liu, X.X. Zhang, Y.W. Mao, Y.Y. Zhu, Z.Y. Yang, C.T. Chan, P. Sheng, Locally resonant sonic materials, *Science* **289**, 1734 (2000)
- 16.42. J.B. Pendry, A.J. Holden, W.J. Stewart, I. Youngs, Extremely low frequency plasmons in metallic mesostructures, *Phys. Rev. Lett.* **76**, 4773 (1996); J.B. Pendry A.J. Holden, D.J. Robbins, W.J. Stewart, Low frequency plasmons in thin-wire structures, *J. Phys. Condens. Matter* **10**, 4785 (1998)
- 16.43. J.B. Pendry, A.J. Holden, D.J. Robbins, W.J. Stewart, Magnetism from conductors and enhanced nonlinear phenomena, *Microwave Theory Tech.* **47**, 2075 (1999)
- 16.44. E.N. Economou, T. Koschny, C.M. Soukoulis, Strong diamagnetic response in split-ring-resonator metamaterials: Numerical study and two-loop model, *Phys. Rev. B* **77**, 092401 (2008)

- 16.45. M. Notomi, Theory of light propagation in strongly modulated photonic crystals: Refractionlike behavior in the vicinity of the photonic band gap, *Phys. Rev. B* **62**, 10696 (2000)
- 16.46. S. Foteinopoulou, E.N. Economou, C.M. Soukoulis, Refraction in media with a negative refractive index, *Phys. Rev. Lett.* **90**, 107402 (2003)
- 16.47. S. Foteinopoulou, C.M. Soukoulis, Negative refraction and left-handed behavior in two-dimensional photonic crystals, *Phys. Rev. B* **67**, 235107 (2003)
- 16.48. S.X. Yang, J.H. Page, Z.Y. Liu, M.L. Cowan, C.T. Chan, P. Sheng, Focusing of sound in a 3D phononic crystal, *Phys Rev Lett* **93**, 024301 (2004)
- 16.49. L. Feng, X.P. Liu, M.H. Lu, Y.B. Chen, Y.F. Chen, Y.W. Mao, J. Zi, Y.Y. Zhu, S.N. Zhu, N.B. Ming, Acoustic backward-wave negative refractions in the second band of a sonic crystal, *Phys. Rev. Lett.* **96**, 014301 (2006)
- 16.50. M.S. Thijssen, R. Sprik, J. Wijnhoven, M. Megens, T. Narayanan, A. Lagendijk, W.L. Vos, Inhibited light propagation and broadband reflection in photonic air-sphere crystals, *Phys. Rev. Lett.* **83**, 2730 (1999)
- 16.51. A. Blanco, E. Chomski, S. Grabtchak, M. Ibisate, S. John, S.W. Leonard, C. Lopez, F. Meseguer, H. Miguez, J.P. Mondia, G.A. Ozin, O. Toader, H.M. van Driel, Large-scale synthesis of a silicon photonic crystal with a complete three-dimensional bandgap near 1.5 micrometres, *Nature* **405**, 437 (2000)
- 16.52. See the papers by W.L. Vos, H.M. van Driel, M. Megens, A.F. Koenderink, A. Imhof, p. 191, D.J. Norris, Y.A. Vlasov, p.229, A. van Blaaderen, K.P. Velikov, J.P. Hoogenboom, D.L.J. Vossen, A. Yethiraj, R. Dullens, T. van Dillen, A. Polman, p. 239, S.G. Romanov, T. Maka, C.M. Sotomayor, Torres, M. Müller, R. Zentel, p. 253, R.M. Amos, D.M. Taylor, T.J. Shepherd, T.G. Rarity, P. Tapster, p. 263, V. Yannopapas, A. Modinos, N. Stefanou, p. 383, in [PC124]
- 16.53. J.B. Pendry, D.R. Smith, The quest for the superlens, *Scientific American* **295**, 60 (July 2006)
- 16.54. V.G. Veselago, *Usp. Fiz. Nauk* **92**, 517 (1967); The Electrodynamics of Substances with Simultaneously Negative Values of ϵ and μ *Sov. Phys. Usp.* **10**, 509 (1968)
- 16.55. J. B. Pendry, Negative refraction makes a perfect lens, *Phys. Rev. Lett.* **85**, 3966 (2000)
- 16.56. N. Fang, H. Lee, C. Sun, X. Zhang, Sub-diffraction-limited optical imaging with a silver superlens, *Science* **308**, 534 (2005)
- 16.57. D. Schurig, J.J. Mock, B.J. Justice, S.A. Cummer, J.B. Pendry, A.F. Starr, D.R. Smith, Metamaterial electromagnetic cloak at microwave frequencies, *Science* **314**, 977 (2006); *Optics Express*, **15**, 14772 (2007)
- 16.58. A. Alù, N. Engheta, *J. Opt A: Pure Appl.* **10**, 093002. Plasmonic and metamaterials cloaking (2008)
- 16.59. M. Kafesaki, I. Tsiapa, N. Katsarakis, Th. Koschny, C.M. Soukoulis, E.N. Economou, Left-handed metamaterials: The fishnet structure and its variations, *Phys. Rev. B* **75**, 235114 (2007)
- 16.60. D.R. Smith, W.J. Padilla, D.C. Vier, R. Shelby, S.C. Nemat-Nasser, N. Kroll, S. Schultz, in [PC124], p. 351

- 16.61. R.A. Shelby, D.R. Smith, S.C. Nemat-Nasser, S. Schultz, Microwave transmission through a two-dimensional, isotropic, left-handed metamaterial, *Appl. Phys. Lett.* **78**, 489 (2001)
- 16.62. R.A. Shelby, D.R. Smith, S. Schultz, Experimental verification of a negative index of refraction, *Science* **292**, 77 (2001)
- 16.63. K. Aydin, K. Guven, M. Kafesaki, L. Zhang, C.M. Soukoulis, E. Ozbay, Experimental observation of true left-handed transmission peaks in metamaterials, *Opt. Lett.* **29**, 2623 (2004)
- 16.64. N. Stefanou, V. Karathanos, A. Modinos, Scattering of electromagnetic waves by periodic structures, *J. Phys.: Condens Matter* **4**, 7389 (1992)
- 16.65. A.L. Ingram, A. Parker, A review of the diversity and evolution of photonic structures in butterflies, incorporating the work of John Huxley (The Natural History Museum, London from 1961 to 1990), *Phil. Trans.R. Soc. B* **363**, 2465 (2008)

Chapter 17

- 17.1. H.A. Atwater, *Sci. Am.* **295**, 56 (2007)
- 17.2. S.A. Maier, M.L. Brongersma, P.G. Kik, S. Meltzer, A.A.G. Requicha, H.A. Atwater, *Adv. Mater.* **13**, 1501 (2001)
- 17.3. E. Ozbay, *Science* **311**, 189 (2006)
- 17.4. R. Zia, J.A. Schuller, A. Chandran, M.L. Brongersma, *Mater. Today* **9**, 20 (2006)
- 17.5. S.I. Bozhevolnyi, V.S. Volkov, E. Devaux, T.W. Ebbesen, *Phys. Rev. Lett.* **95**, 046802 (2005)
- 17.6. A. Karalis, E. Lidorikis, M. Ibanescu, J. Joannopoulos, M. Soljacic, *Phys. Rev. Lett.* **95**, 63901 (2005)
- 17.7. J.A. Dionne, L.A. Sweatlock, H.A. Atwater, A. Polman, *Phys. Rev. B* **73**, 035407 (2006)
- 17.8. H. Xu, P. Zhu, H.G. Craighead, W.W. Webb, Resonantly enhanced transmission of light through subwavelength apertures with dielectric filling, to appear in *Optical Society of America*
- 17.9. M. Bai, N. Garcia, *Appl. Phys. Lett.* **89**, 141110 (2006)
- 17.10. E. Hao, G.C. Schatz, *J. Chem. Phys.* **120**, 357 (2004)
- 17.11. J.P. Kottmann, O.J.F. Martin, *Opt. Lett.* **26**, 1096 (2001)
- 17.12. S. Foteinopoulou, J.P. Vigneron, C.V. Vandenbem, *Opt. Express* **15**, 4253 (2007)
- 17.13. I. Romero, J. Aizpurua, G.W. Bryant, F.J. Garcia de Abajo, *Opt. Express* **14**, 9988 (2006)
- 17.14. T.W. Ebbesen, C. Genet, S. Bozhevolnyi, *Phys. Today* **61**, 44 (2008)
- 17.15. J. Vuckovic, M. Loncar, A. Scherer, *IEEE J. Quantum Elec.* **36**, 1131 (2000)
- 17.16. S. Schultz, D.R. Smith, J.J. Mock, D.A. Schultz, *PNAS* **97**, 996 (2000)
- 17.17. L.R. Hirsch, R.J. Stafford, J.A. Bankson, S.R. Sershen, B. Rivera, R.E. Price, J.D. Hazle, N.J. Halas, J.L. West, *PNAS* **100**, 13549 (2003)
- 17.18. E.N. Economou, *Phys. Rev.* **182**, 539 (1969)
- 17.19. E.N. Economou, K.L. Ngai, in *Advances in Chemical Physics*, ed. by I. Prigogine, S.A. Rice, vol **27**, 265, (J. Wiley, New York, 1974), p. 265

Chapter 18

- 18.1. J.C. Phillips, Solid State Phys. **37**, 93 (1982)
- 18.2. M.H. Cohen, G.S. Grest, Phys. Rev. B. **20**, 1077 (1979)
- 18.3. R.C. Zeller, R.O. Pohl, Phys. Rev. B. **4**, 2029 (1971)
- 18.4. W.A. Phillips, Rep. Prog. Phys. **50**, 1657 (1987)
- 18.5. W.A. Phillips, J. low Temp. Phys. **7**, 351 (1972)
- 18.6. P.W. Anderson, B.I. Halperin, C.M. Varma, Philos. Mag. **25**, 1 (1972)
- 18.7. R.O. Pohl, J. Non-Cryst. Solids, **352**, 3363 (2006)
- 18.8. M.H. Cohen, G.S. Grest, Phys. Rev. Lett. **45**, 1271 (1980)
- 18.9. J.C. Lasjaunias et al., Sol. St. Comm. **17**, 1045 (1975)
- 18.10. D. Shechtman, I. Blech, D. Gratias, J.W. Cahn, Phys. Rev. Lett. **53**, 1951 (1984)
- 18.11. A.R. Cortan, in *Encyclopaedia of Applied Physics*, vol. 15, ed. by G.L. Trigg, (VCH, New York, 1996)
- 18.12. M. Gardner, Sci. Am. **236**, 110 (1977)
- 18.13. P.W. Anderson, Phys. Rev. **109**, 1492 (1958)
- 18.14. B.B. Mandelbrot, *The Fractal Geometry of Nature* (Freeman, San Francisco, 1983)
- 18.15. K.J. Falconer, *Fractal Geometry-Mathematical Foundations and Applications* (Wiley, Chichester, 1990)
- 18.16. E.N. Economou, C.M. Soukoulis, Phys. Rev. Lett. **46**, 618 (1981)
- 18.17. D.S. Fisher, P.A. Lee, Phys. Rev. B. **23**, 6851 (1981)
- 18.18. B.J. van Wees, H. Vanhouten, C.W.J. Beenakker, J.G. Williamson, L.P. Kouwenhoven, D. Vandermaarel, C.T. Foxon, Phys. Rev. Lett. **60**, 848 (1988)
- 18.19. M. Büttiker, Y. Imry, R. Landauer, S. Pinhas, Phys. Rev. B. **31**, 6207 (1985)
- 18.20. M. Büttiker, Res. Dev. **32**, 317 (1988)
- 18.21. K.K. Choi, D.C. Tsui, K. Alavi, Phys. Rev. B. **36**, 7751 (1987)
- 18.22. Y. Aharonov, D. Bohm, Phys. Rev. **115**, 485 (1959)
- 18.23. E. Abrahams, P.W. Anderson, D.C. Licciardello, T.V. Ramakrishnan, Phys. Rev. Lett. **42**, 673 (1979)
- 18.24. D.J. Thouless, R. Balian, R. Maynard, G. Toulouse (eds.), *Ill-Condenced Matter* (North Holand, Amsterdam, 1979), pp. 1–62
- 18.25. D.C. Licciardello, D.J. Thouless, J. Phys. C. **11**, 925 (1978)
- 18.26. J.L. Pichard, G. Sarma, J. Phys. C. **14**, L127 (1981)
- 18.27. J.L. Pichard, G. Sarma, J. Phys. C. **14**, L617 (1981)
- 18.28. A. MacKinnon, B. Kramer, Phys. Rev. Lett. **47**, 1546 (1981)
- 18.29. B. Kramer, A. MacKinnon, Rep. Progr. Phys. **56**, 1469 (1993)
- 18.30. C.M. Soukoulis, I. Webman, G.S. Gest, E.N. Economou, Phys. Rev. B. **26**, 1838 (1982)
- 18.31. E.N. Economou, C.M. Soukoulis, A.D. Zdetsis, Phys. Rev. B. **30**, 1686 (1984)
- 18.32. E.N. Economou, C.M. Soukoulis, M.H. Cohen, A.D. Zdetsis, Phys. Rev. B. **31**, 6172 (1985)
- 18.33. E.N. Economou, C.M. Soukoulis, A.D. Zdetsis, Phys. Rev. B. **31**, 6483 (1985)
- 18.34. I. Zambetaki, Q. Li, E.N. Economou, C.M. Soukoulis, Phys. Rev. Lett. **76**, 3614 (1996)

- 18.35. Q. Li, S. Katsoprinakis, E.N. Economou, C.M. Soukoulis, Phys. Rev. B. **56** (8), R4297 (1997)
- 18.36. R.A. Romer, M. Schreiber, in [DSL159], p. 3
- 18.37. T. Ohtsuki, K. Slevin, in [DSL159], p. 31
- 18.38. A. Kawabata, in [DSL159], p. 41
- 18.39. P. Markoš in [DSL159], p. 53
- 18.40. L. Schweitzer in [DSL159], p. 65
- 18.41. E.N. Economou, C.M. Soukoulis, Phys. Rev. B. **28**, 1093 (1983)
- 18.42. E.N. Economou, Phys. Rev. B. **31**, 7710 (1985)
- 18.43. K. von Klitzing, G. Dorda, M. Pepper, Phys. Rev. Lett. **45**, 494 (1980)
- 18.44. D.C. Tsui, H.L. Stormer, A.C. Gossard, Phys. Rev. Lett. **48**, 1559(1982)
- 18.45. M.A. Paalanen, et al., Phys. Rev. **B25**, 5566 (1982)
- 18.46. R.B. Laughlin, Phys. Rev. Lett. **50**, 1395 (1983)
- 18.47. St. Kivelson, D.H. Lee, S.C. Zhang, Sci. Am. **274**, 86 (1996)
- 18.48. S.T. Kivelson, D.H. Lee, S.C. Zhang, Phys. Rev. B. **46**, 2223 (1992)
- 18.49. Y. Hatsugai, Phys. Rev. Lett. **71**, 3697 (1993)
- 18.50. J.K. Jain, *Composite Fermions*, (Cambridge University Press, Cambridge, 2007)
- 18.51. G. Bergmann, Phys. Rev. **B28**, 2914 (1983)
- 18.52. P.A. Lee, T.V. Ramakrishnan, Rev. Mod. Phys. **57**, 297 (1985)
- 18.53. S. Hikami, A.I. Larkin, Y. Nagaoka, Prog. Theor. Phys. **63**, 707 (1980)
- 18.54. R. Kubo, Can. J. Phys. **34**, 1274 (1956)
- 18.55. R. Kubo, J. Phys. Soc. Jpn. **12**, 570 (1957)
- 18.56. A.D. Greenwood, Proc. Phys. Soc. **71**, 585 (1958)

Chapter 19

- 19.1. H.W. Kroto, J.R. Heath, S.C. Obrien, R.F. Curl, R.E. Smalley, Nature **318**, 162 (1985)
- 19.2. T. Takabayashi et al., Science **323**, 1585 (2009)
- 19.3. S. Iijima, Nature **354**, 56 (1991)
- 19.4. M.J. Mehl, D.A. Papaconstantopoulos, Phys. Rev. B **54**, 4519 (1996)
- 19.5. J.L. Elkind, J.M. Alford, F.D. Weiss, R.T. Laaksonen, R.E. Smalley, J. Chem. Phys. **87**, 2397 (1987)
- 19.6. M.F. Jarrold, J.E. Bower, K.M. Creegan, J. Chem. Phys. **90**, 3615(1989)
- 19.7. E. Kaxiras, Chem. Phys. Lett. **163**, 323 (1989)
- 19.8. E. Kaxiras, Phys. Rev. Lett. **64**, 551 (1990)
- 19.9. E. Kaxiras, Phys. Rev. **B56**, 13455 (1997)
- 19.10. N. Binggeli, J.L. Martins, J.R. Chelikowsky, Phys. Rev. Lett. **68**, 2956 (1992)
- 19.11. U. Röthlisberger, W. Andreoni, M. Parinello, Phys. Rev. Lett. **72**, 665 (1994)
- 19.12. J. Jellinek, T.L. Beck, R.S. Berry, J. Chem. Phys. **84**, 2783 (1986)
- 19.13. B.C. Guo, K.P. Kerns, A.W. Castleman, Science **255**, 1411 (1992)
- 19.14. L. Jasak, P. Hawrylak, A. Wojs, *Quantum Dots*, Springer-Verlag, Berlin, (1998)
- 19.15. R. Hanson, L.P. Kouwenhoven, J.R. Petta, S. Tarucha, L.M. Vandersypen, Rev. Mod. Phys., **79**, 1217 (2007)

- 19.16. J.R. Petta, A.C. Johnson, J.M. Taylor, E.A. Laird, A. Yacoby, M.D. Lukin, C.M. Markus, M.P. Hanson, A.C. Gossard, *Science*, **309**, 2180 (2005)
- 19.17. W.G. van der Weil, S. De Franceschi, J.M. Elzerman, T. Fujisawa, S. Tarucha, L.P. Kouwenhoven, *Rev. Mod. Phys.*, **75**, 1 (2003)
- 19.18. M.Grobis, I.G. Rau, R.M. Potok, H. Shtrikman, D. Goldhaber-Gordon, *Phys. Rev. Lett.* **100**, 246601-1, (2008)
- 19.19. V. Fock *Z. Phys.* **47**, 446 (1928)
- 19.20. C.G. Darwin, *Proc. Camb. Phil. Soc.*, **27**, 86 (1930)
- 19.21. P. Avouris, *Physics Today*, **62**, 34 (2009)

Chapter 20

- 20.1. M.N. Baibich, J.M. Broto, A. Fert, F.N. Vandau, F. Petroff, P. Eitenne, G. Creuzet, A. Friederich, J. Chazelas, *Phys. Rev. Lett.* **61**, 2472 (1988)
- 20.2. G. Binasch, P. Grunberg, F. Saurenbach, W. Zinn, *Phys. Rev. B* **39**, 4828 (1989)
- 20.3. M. Jullière, *Phys. Lett. A* **54**, 225 (1975)
- 20.4. T. Miyazaki, N. Tezuka, *J. Magn. Magn. Mater.* **139**, L231 (1995)
- 20.5. X. Hao, J.S. Moodera, R. Meservey, *Phys. Rev. B* **42**, 8235 (1990)
- 20.6. J.S. Moodera, G. Mathon, *J. Magn. Magn. Mater.* **200**, 248 (1999)
- 20.7. S.S.P. Parkin, C. Kaiser, A. Panchula, P.M. Rice, B. Hughes, M. Samant, S.H. Yang, *Nat Mater.* **3**, 862 (2004)
- 20.8. S. Yuasa, T. Nagahama, A. Fukushima, Y. Suzuki, K. Ando, *Nat Mater.* **3**, 868 (2004)
- 20.9. H. Kubota, A. Fukushima, Y. Ootani, S. Yuasa, K. Ando, H. Maehara, K. Tsunekawa, D.D. Djayaprawira, N. Watanabe, Y. Suzuki, *Appl. Phys. Lett.* **89**, 042505(2006)
- 20.10. S. Datta, B. Das, *Appl. Phys. Lett.* **56**, 665 (1990)
- 20.11. R.A. de Groot, F.M. Mueller, P.G. van Engen, K.H.J. Buschow, *Phys. Rev. Lett.* **50**, 2024 (1983)
- 20.12. H. Akinaga, T. Manago, M. Shirai, *Jpn. J. Appl. Phys. Part 2*, **39**, L1118 (2000)
- 20.13. E.I. Rashba, *Phys. Rev. B* **62**, R16267 (2000)
- 20.14. P.V. Dorpe, V. Motsnyi, M. Nijboer, E. Goovaerts, V. Safaron, J. Das, W.V. Roy, G. Borghs, J. De Boeck, *Jpn. J. Appl. Phys., Part 2* **42**, L502 (2003)
- 20.15. H.J. Zhu, M. Ramsteiner, H. Kostial, M. Wassermeier, H.P. Schönherr, K.H. Ploog, *Phys. Rev. Lett.* **87**, 016601 (2001)
- 20.16. A.T. Hanbicki, B.T. Jonker, G. Itskos, G. Kioseoglou, A. Petrou, *Appl. Phys. Lett.* **80**, 1240 (2002)
- 20.17. A.T. Hanbicki, O.M.J. van 't Erve, R. Magno, G. Kioseglou, C.H. Li, B.T. Jonker, G. Itskos, R. Mallory, M. Yasar, A. Petrou, *Appl. Phys. Lett.* **82**, 4092 (2003)
- 20.18. X. Jiang, R. Wang, R.M. Shelby, R.M. Macfarlane, S.R. Bank, J.S. Harris, S.S.P. Parkin, *Phys. Rev. Lett.* **94**, 056601 (2005)
- 20.19. X. Jiang, R. Wang, R.M. Shelby, R.M. Macfarlane, S.R. Bank, J.S. Harris, S.S.P. Parkin, *Phys. Rev. Lett.* **94**(5), 056601 (2005)

- 20.20. M. Bowen, M. Bibes, A. Barthelemy, J-P. Contour, A. Anane, Y. Lemaitre, A. Fert, Appl. Phys. Lett. **82**, 233 (2003)
- 20.21. M. Lezaic, P. Mavropoulos, J. Enkovaara, G. Bihlmayer, S. Bluegel, Phys. Rev. Lett. **97**(2), 026404 (2006)
- 20.22. I. Žutić, J. Fabian, S.D. Sarma, Rev. Mod. Phys. **76**, 323 (2004)
- 20.23. P. Sharma, K. Sreenivas, K.V. Rao, J. Appl. Phys. **93**, 3963 (2003)
- 20.24. D. Chiba, M. Sawicki, Y. Nishitani, Y. Nakatani, F. Matsukura, H. Ohno, Nature. **455**, 515 (2008)
- 20.25. D.D. Awschalom, R. Epstein, R. Hanson, The diamond age of spintronics, Sci. Am. **297**, 84, (2007)

Chapter 21

- 21.1. M.A. Ruderman, Ch. Kittel, Phys. Rev. **96**, 99 (1954)
- 21.2. T. Kasuya, Progr. Theor. Phys. (Kyoto) **16**, 45 (1956)
- 21.3. K. Yosida, Phys. Rev. **106**, 893 (1957)
- 21.4. L. Onsager, Phys. Rev. **65**, 117 (1944)
- 21.5. N.D. Mermin, H. Wagner, Phys. Rev. Lett. **17**, 1133 (1966)
- 21.6. F.D.M. Haldane, Phys. Rev. Lett. **50**, 1153 (1983)
- 21.7. I. Affleck, J. Phys. Condens. Matter **1**, 3047 (1989)
- 21.8. O. Golinelli, T. Jolicoeur, R. Lacaze, Phys. Rev. B **45**, 9798 (1992)
- 21.9. T. Sakai, M. Takahashi, Phys. Rev. B **42**, 4537 (1990)
- 21.10. J. Hubbard, Proc. Roy. Soc. London Ser. A **276**, 238 (1963)
- 21.11. Y. Nagaoka, Phys. Rev. **147**, 392 (1966)
- 21.12. M. Cyrot, C. Lyon-Caen, Le Jour. de Phys. **36**, 253 (1975)
- 21.13. J.E. Hirsch, Phys. Rev. B **31**, 4403 (1985)
- 21.14. P.W. Anderson, Science **235**, 1196 (1987)
- 21.15. V.J. Emery, S.A. Kivelson, Q. Lin, Phys. Rev. Lett. **64**, 475 (1990)
- 21.16. M. Marder, N. Papanikolaou, G.C. Psaltakis, Phys. Rev. B **41**, 6920(1990)
- 21.17. R. Strack, D. Vollhardt, Phys. Rev. Lett. **70**, 2637 (1993)
- 21.18. S.Q. Shen, Z.M. Qiu, Phys. Rev. Lett. **72**, 1280 (1994)
- 21.19. L. Chen, B. Bourbonnais, T. Li, A.M.S. Tremblay, Phys. Rev. Lett. **66**, 369 (1991)

Chapter 22

- 22.1. W. Meissner, R. Ochsenfeld, Die Naturwissenschaften **21**, 787 (1933)
- 22.2. H.K. Onnes, Leiden Communications **120** (1911)
- 22.3. W.E. Pickett, H. Krakauer, R.E. Cohen, D.J. Singh, Science **255**, 46 (1992)
- 22.4. A.Y. Ganin, Y. Takabayashi, Y.Z. Khimyak, S. Margadonna, A. Tamai, M.J. Rosseinsky, K. Prassides, Nature Mater. **7**, 367 (2008)
- 22.5. I.J. Lee, S.E. Brown, M.J. Naughton, J. Phys. Soc. Jap. **75**, 051011(2006)
- 22.6. J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, J. Akimitsu, Nature **410**, 63 (2001)
- 22.7. Y. Kamihara, T. Watanabe, M. Hirano, H. Hosono, J. Am. Chem. Soc. **130**, 3296 (2008)

- 22.8. T.A. Friedmann, M.W. Rabin, J. Giapintzakis, J.P. Rice, D.M. Ginsberg, *Phys. Rev. B* **42**, 6217 (1990)
- 22.9. F. London, H. London, *Proc. Roy. Soc. A* **149**, 71 (1935)
- 22.10. A.B. Pippard, *Proc. Roy. Soc. A* **191**, 385 (1947)
- 22.11. V.L. Ginzburg, L.D. Landau, *JETP USSR* **20**, 1064 (1950)
- 22.12. A.A. Abrikosov, *JETP USSR* **5**, 1174 (1957)
- 22.13. B.S. Deaver, W.M. Fairbank, *Phys. Rev. Lett.* **7**, 43 (1961)
- 22.14. W.E. Pickett, H. Krakauer, R.E. Cohen, D.J. Singh, *Phys. Rev. B* **42**, 8764 (1990)
- 22.15. G.R. Darling, A.Y. Ganin, M.J. Rosseinsky, Y. Takabayashi, K. Prassides, *Phys. Rev. Lett.* **101**, 136404 (2008)
- 22.16. X.H. Chen, T. Wu, G. Wu, R.H. Liu, H. Chen, D.F. Fang, *Nature*, **453**, 761 (2008)
- 22.17. F. London, H. London, *Z. Physik* **96**, 359 (1935)

Chapter 23

- 23.1. K. Ishida, H. Mukuda, Y. Kitaoka, K. Asayama, Z.Q. Mao, Y. Mori, Y. Maeno, *Nature* **396**, 658 (1998)
- 23.2. A.P. Mackenzie, Y. Maeno, *Physica B* **280**, 148 (2000)
- 23.3. D. Jérôme, A. Mazaud, M. Ribault, K. Bechgaard, *J. Phys. Lett. (Paris)* **41**, L95 (1980)
- 23.4. K. Bechgaard, K. Carneiro, M. Olsen, F.B. Rasmussen, C.S. Jacobsen, *Phys. Rev. Lett.* **46**, 852 (1981)
- 23.5. K. Maki, E. Puchkaryov, G.F. Wang, H. Won, *Chin. J. Phys.* **38**, 386 (2000)
- 23.6. I.J. Lee, S.E. Brown, W.G. Clark, M.J. Strouse, M.J. Naughton, W. Kang, P.M. Chaikin, *Phys. Rev. Lett.* **88**, 017004 (2002)
- 23.7. D. Podolsky, E. Altman, T. Rostunov, E. Demler, *Phys. Rev. Lett.* **93**, 246402 (2004)
- 23.8. G.M. Eliashberg, *Sov. Phys. JETP-USSR* **11**, 696 (1960)
- 23.9. W.L. McMillan, *Phys. Rev.* **167**, 331 (1968)
- 23.10. P.B. Allen, R.C. Dynes, *Phys. Rev. B* **12**, 905 (1975)
- 23.11. L.N. Oliveira, E.K.U. Gross, W. Kohn, *Phys. Rev. Lett.* **60**, 2430 (1988)
- 23.12. M. Lüders, M.A.L. Marques, N.N. Lathiotakis, A. Floris, G. Profeta, L. Fast, A. Continenza, S. Massidda, E.K.U. Gross, *Phys. Rev. B* **72**, 024545 (2005)
- 23.13. M.A.L. Marques, M. Luders, N.N. Lathiotakis, G. Profeta, A. Floris, L. Fast, A. Continenza, E.K.U. Gross, S. Massidda, *Phys. Rev. B* **72**, 024546 (2005)
- 23.14. A. Floris, A. Sanna, M. Luders, G. Profeta, N. N. Lathiotakis, M.A.L. Marques, C. Franchini, E.K.U. Gross, *Physica C* **456**, 45 (2007)
- 23.15. B.D. Josephson, *Phys. Lett.* **1**, 251 (1962)
- 23.16. E. Berg, D. Orgad, S.A. Kivelson, *Phys. Rev. B* **78**, 094509 (2008)

Index

- Acceptor impurities, 192, 195–197
Acceptor ionization energies, 195
Acoustic branches, 164, 200
Acoustic modes, 200
Acoustical phonon branch, 253
Acronyms, 762
Adiabatic approximation, 212
Aharonov-Bohm effect, 528, 529, 538
Alkali earths, 354, 397, 417, 423, 741
Alkali halide crystals, 407
Alkali halides, 402, 407
Alloys, 4, 49, 229, 232, 234, 236, 238, 240, 499–501, 538, 577, 591, 614, 630
Almost degenerate case, 311
Amorphous semiconductors, 499, 502, 504, 538
Amorphous silicon dioxide, 378–380
Amorphous solids, *See* Static disorder and localization
Angular frequency, 10, 36, 37, 128, 213, 761
Angular momentum, 27, 129, 130, 137, 319, 320, 369, 558, 559, 614, 638, 702, 705
Anharmonic effects, 232, 252
Anharmonic interactions, 211
Anharmonic terms, *See* Anharmonic effects
Anion, 4, 56, 57, 157, 172, 180, 182, 184, 224, 362, 365, 368, 398, 399, 402, 404, 406, 431, 433, 550, 579, 743, 794
Anisotropy energy, 582, 584–587, 593
Annealing, 472
Annihilation operator, 259
Anomalous skin effect, 644
Antibonding states, 741, 743
Antiferromagnetic materials, 580
Antiferromagnetic order in the JM, 603
Antiferromagnetism, 712
 magnons, 620
 Neel temperature, 577
Antiferromagnets, 581
Anti-Stokes component, 254
Anti-Stokes line, 254
Artificial structures, 52, 231, 233, 234
Atomic configurations, 504
Atomic energy levels, 707
Atomic force microscope, 232
Atomic form factor, 248, 505, 797
Atomic levels, 154, 158, 168, 173, 178, 180, 184, 379, 382, 397, 398, 425, 738, 780
Atomic orbitals, 153, 161, 164, 165, 169, 171, 172, 174, 177–179, 183, 207, 301, 303, 378, 417, 425, 452, 546, 556, 702, 706, 738, 740, 742–746, 748–750, 752, 754
Atomic radii, 25
Atomic radii R of the elements and the ratio $2R/d$, 768
Atomic system of units, 761
Atomic wave functions, *See* Spherically symmetric potentials
Atoms, 4, 18, 21–29, 32

- Augmented plane-wave method, 302, 313, 321
- Avogadro's number (N_A), 30, 33, 212
- AC electrical conductivity, 113, 690
- Band bending, 438
- Band edges, 154–156, 168, 170, 178–180, 182, 189, 192, 207, 282, 302, 417, 421, 513, 610, 657, [791](#), [792](#), [797](#)
- Band gap, 158, 178, 467, 513
- Band index, 73, 274, 278, 279, 289, 291, 297, 675, 676, 756, 758
- Band overlap, 330, 333, 411, 432, 433, 536
- Band repulsion, *See* Level repulsion
- Band structure, 155, 158, 160, 166, 198–200, 281, 285, 318, 329, 353–356, 358, 361, 382, 383, 412–415, 428, 447, 449, 455, 513, 676
- Band structure, semiconductors, 360
- Band width, 169, 359, 396, 411, 412, 422, 426, 432, 434, 513, 657, 659
- Bardeen-Cooper-Schrieffer (BCS) theory, 664
- Base-centered orthorhombic Bravais lattice, 61
- Basic relations of statistical mechanics, 716
- Basis, 63, 68–71, 161, 169–171, 179, 311, 314, 379, 561, 604, 738, 744, 745, 748, [790](#), [812](#)
- BCS theory, *See* Bardeen-Cooper-Schrieffer theory
- Bending of bands, 438
- Biased junction, 491
- Binding energy, 55, 93, 94, 193–195, 235, 237, 372, 373, 387, 389, 399–401, 407, 653, 657, 659, 661–663, 680, 682
- Blackbody radiation, 16, [779](#)
- Bloch electrons, 411, 425
- Bloch equations, 70, 72
- Bloch function, 278, 279, 298, 317, 343, 401
- Bloch theorem, 70, 72, 78, 150, 466, [800](#)
- Bloch T3/2 law, 574
- Bloch wall, 571, 572, 582, 586, 587, 592, 593
- Body-centered cubic, 54, 64, 68, 70, 75, 76, 78, 177, 250, 351–354, 365, 394, 398, 412, 413, 418, 420, 422, 430, 434, 473, 501, 502, 545, 581, [797](#)
- Boer parameter, 395, 407, 549
- Bohm-Staver relation, 98, 342
- Bohr magneton, 129, 137, 759
- Bohr radius (a_B), 17, 21, 193, 194, 760
- Boltzmann equation, 297, 755, 756
- Boltzmann distribution, 196
- Boltzmann's constant (k_B), 15, 16, 29, 716, 759, [779](#)
- Bond susceptibility, 368
- Bonding, 53–58, 85, 158, 169–173, 178, 181–184, 358, 365, 382, 385, 397, 546, 548, 741–743, [790](#), [794](#)
- Bonding states, 741
- Bonding types
 - covalent, 53, 54, 58, 77, 543
 - hydrogen, 49, 53, 58, 77, [785](#)
 - ionic, 53, 58, 77
 - simple metallic, 53
 - transition metallic, 53
 - van der Waals, 53, 54, 57, 58, 77
- Born-Oppenheimer approximation, 212
- Born-von Karman boundary conditions, *See* Periodic boundary conditions
- Bose gas, *See* Non-interacting bosonic particles
- Bose-Einstein condensation, 6, 52
- Boundary conditions, 387, 454, 475, 478, 488, 494, 530, 586, 644, 698, 699
- Bound charge, 686, 690
- Bra and Ket Notation, 700
- Bragg beams, *See* Diffracted beams
- Bragg law, *See* Bragg results
- Bragg planes, 75, 76, 78, 249, 250, 360, 363, 501, 576
- Bragg results, 249
- Bravais lattices
 - crystal planes, 67
 - systems and types, 61
- Breakdown, electric, 40
- Breathers, 238
- Brillouin scattering, 253

- Brillouin zones, 70, 73, 75, 76, 150, 198, 258, 259, 274, 276, 283, 325, 327
- Bulk modulus, 263, 395
- Bulk modulus and compressibility of the elements, 771
- Buttiker formalism, 521
-
- c/a* ratio, 66
- Carbon nanotubes, 53, 551–554, 556, 564
- Casimir limit, *See* Phonon scattering by surfaces
- Cauchy relation, 263, 400, 799
- Causality, 692
- Cell
 - primitive, 60, 62–71, 74, 75, 351, 360
 - unit, 62, 65, 66, 68–71
 - Wigner-Seitz, 60, 62, 68, 71, 75, 78
- Cesium chloride structure, 70, 398
- Chalcogenide glasses, 49
- Charge density, 84, 215, 438, 476, 479, 484, 486, 494, 685, 686, 693, 786, 821
- Classical mechanics, 31, 39, 42, 279
- Clausius-Mossotti relation, 404
- Clusters, 49, 52, 53, 235, 443, 543, 544, 549, 550, 556, 557, 564
- Coercive force, *See* Coercivity
- Coercivity, 573, 577
- Coherence length, superconductors, 645
- Coherence, intrinsic, 645, 647, 653, 660
- Coherent potential approximation (CPA), 222, 522–525, 534, 539
- Cohesive energy, 33, 93
 - Fermi gas, 34, 93
 - of the elements, 423
 - sodium metal, 34
- Collision time, 294, 297
- Collisions, of Bloch electrons, 252
- Colloids, 50, 51
- Color centers, 223
- Common crystal structures, 59, 68, 73
- Compensated solids, 197, 295
- Compound semiconductor, 53, 170–172, 174, 183, 184, 208, 255, 309, 362, 398, 402, 543, 792
- Compressibility, 26, 42, 454
- Concentration
 - electrons, 19, 195, 196, 198, 215, 292, 294, 488, 491–493
 - holes, 196, 293, 483, 486, 492
- Condensed matter, 3, 6, 9, 18, 47–78, 114, 212
- Condensed-matter physics and applications, 6
- Conductance, 38, 519–521, 530, 531, 539, 563, 565
- Conduction band, 159, 168, 187, 320, 425, 494
- Conduction electrons, 131, 238, 598
- Conductivity
 - DC electrical, 692
 - electrical, 113, 114, 120–122, 131, 140, 143, 144, 214, 223, 273, 288, 295, 346, 690
 - ionic, 224, 225
 - tensor, 133, 295–297, 374, 757
 - thermal, 141–145, 385, 504, 638, 639
- Conductivity in doped semiconductors, 197, 373–376
- Configurations, 8, 38, 212, 229, 378, 379, 397, 410, 411, 448, 520, 556, 557, 570, 571, 582, 584, 587, 590, 597, 608, 609, 611, 614, 622, 677, 706
- Contact hyperfine interaction, *See* Knight shift
- Conventional unit cell, *See* Unit cell
- Cooper pair, 222, 235–238, 646–648, 652, 653, 655–661, 664, 665, 670, 677, 678, 680, 682
- Coordination number, 502, 504, 610
- Correlation Functions, 266, 504–506, 538
- Coulomb blockade, 558, 561–565
- Coulomb potential, 9–15, 21, 193, 340, 341, 396, 582, 666, 784
- Coupled pendulums model, 149–152
- Covalent bond, 53, 58, 77, 543
- Covalent crystals, *See* Covalent solids
- Covalent solids, 55
- Creation operators, 269
- Critical exponents, 532, 574, 578, 583, 584, 616
- Critical field, 630, 631, 649, 672
- Critical points, 532, 660, 806
- Critical shear stress, 229, 230

- Crystal field and quenching of L, 137
- Crystal structure, 57, 59–70, 73, 157, 215, 232, 245–272, 316, 354, 397, 424, 426, 433, 581, 585
- Crystal structures of the elements, 766
- Crystal systems, 61
- Crystal systems and Bravais lattices, 61
- Cubic lattices, 67, 261, 285, 398, 579
- Curie constant, *See* Curie law
- Curie law, 137
- Curie-Weiss law, 573, 575, 584
- Current density, electrical, 145, 184, 185, 224, 731
- Cyclotron frequency, 128, 130, 133, 145, 278, 289, 756
- Cyclotron mass, 287, 288
- Cyclotron resonance, 128, 287

- Dangling bonds, 473, 474, 495, 504, 548, 556
- d-band, 432
- d-band conductivity, 432
- De Boer parameter, 395, 407, 549
- Debye T^3 law, *See* Specific heat
- Debye frequency, 99, 103, 395
- Debye model, 99, 102, 475, 801
- Debye model, density of states, 102
- Debye-Scherrer method, *See* Powder method
- Debye temperature, 83, 99, 104, 108, 237, 786, 787, 805
- Debye temperature and thermal conductivity of the elements, 773
- Debye wavenumber, 99
- Debye wave vector, *See* Debye wavenumber
- Debye-Scherrer method, *See* Powder method
- Debye-Waller factor, 263, 265, 343
- Defects, 122, 127, 143, 191, 207, 214, 223–225, 234, 276, 372, 440, 443, 571
- Defects in crystals, *See* Color centers
- Degeneracy, 15, 128, 135, 139, 188, 195, 319, 321, 379, 536, 544, 548, 709
- Degenerate semiconductor, 196
- de Haas-van Alphen effect, 139, 273, 287, 288, 290, 298, 354
- Demagnetization factor, *See* Depolarization coefficient
- Density functional theory, 215
- Density of states
 - Debye model, 102
 - electrons, 91, 92, 106, 120, 159, 189, 198–201, 276, 354
 - phonon, 101, 102, 200–202, 259, 260, 269, 440, 450, 466, 721
- Depletion layer, 488, 591
- Depolarization coefficient, 799
- Diamagnetism, atomic (Larmor), 134
- Diamond structure, 177, 472
- Dielectric constant, 191, 207, 372, 404, 450, 478, 496, 689
- Dielectric function
 - phenomenological expressions, 730
 - Thomas-Fermi, 118, 729
- Diffraction beams, 247
- Diffraction, 250, 506–508, 557
- Diffraction, neutron scattering, 576
- Diffusion, 225, 488, 489, 492, 493, 496, 511–513
- Diffusion coefficient, 226
- Diffusion lengths, 512
- Diffusion region (p–n junction), 492
- Dilute magnetic semiconductors, 591
- Dimensional analysis, 15–17, 21, 32, 36, 38, 83, 97, 125, 395, 400, 780, 781
- Dimensionless e-p coupling λ , 126
- Dipole moment (electric), 690
- Direct gap semiconductor, 189, 190, 199, 371, 438, 492, 551, 558
- Direct lattices, 74–77, 249–251, 276, 277, 354, 364, 381, 420, 797, 798
- Direct optical transition, 558, 559, *See* Optical transition
- Direct term in Hartree-Fock equation, *See* Hartree-Fock approximation
- Disorder and many body effects, 239, 331, 384, 538
- Disordered alloys, 232, 499
- Dispersion curve, 152
- Displacive transition, *See* Structural phase transition
- Distribution function, 504, 505
- Distribution, classical, *See* Boltzmann distribution

- Distribution, Fermi-Dirac, *See* Fermi distribution
- Distribution, Planck, *See* Phonon distribution
- Divalent metals, 354, 388
- Domains, closure, 584, 585
- Donor impurities, 192, 195, 197
- Donor ionization energies, 194
- Donor states, *See* Donor impurities
- Doping, 193
- Doping of semiconductors, 193
- DOS, *See* Density of states
- Double layer, 479, 480, 483
- Dressed electrons, 235
- Drift current, 487–489
- Drift velocity, 294
- Drude formula, 117
- Drude model, *See* Drude formula
- Dulong and Petit law, 103
- Dynamical matrix, 269
- Dynamical structure factor, 265, 269

- Effective Bohr magneton, 137
- Effective Hamiltonian, 189, 191, 194, 276–279, 559, 560
- Effective masses, 29, 154, 174, 186–188, 203, 321, 491
- Effective mass, semiconductors, 186–188
- Eigenfrequencies, phononic DOS, 201–206
- Eigenvalue problem near Bragg planes, *See* Almost degenerate case
- Einstein relation, 224
- Elastic constants
 - cubic crystals, 263, 367
 - in crystals, 262
- Elastic moduli, 90, 91, 94–97
- Elastic scattering, 39, 245, 267, 504, 506, 538, 576, 711
- Elastic strain, 582
- Elastic wave equation, 444, 735, 736
- Electrical resistivity, 4, 38–41, 54–56, 125, 127, 222
- Elastic wave quantization, 264, 269
- Elasticity, theory of elastic constants, 260–263
- Electric conductivity, 723
- Electric induction, 685
- Electrical conductivity, 114, 120–123

- Electrical conductivity and resistivity of the elements, 775
- Electrochemical potential, 140, 519–521, 537
- Electron affinities, 402, 550, 743
- Electron diffraction, 762, 763
- Electron-electron correlations, 235–237, 434, 435, 519, 595
- Electron-electron indirect attraction, 655
- Electron-electron interactions, 218
 - and Hartree-Fock approximation, 708
 - and Hubbard model, 607–613
- Electron gas, 232, 534, 557, 564
- Electronic polarizabilities, 404
- Electron spin, *See* Spin
- Electron-like trajectories, 285
- Electron orbits, *See* Electron-like trajectories
- Electron spin resonance, 129, 130, 762
- Electron, tight-binding, 532, 533
- Electron transport, 510, 512, 513
- Electron work functions, 232
- Electron-electron collisions, *See* El-el interactions
- Electron-hole droplets, 373
- Electron-phonon collisions, *See* Electron-phonon interactions
- Electron-phonon interactions, 237, 238
- Electrostatic approximation, 114, 726
- Electrostatic screening, 123
- Elemental semiconductor, 48, 166, 167, 174, 177, 180, 309, 360, 365, 366, 388
- Elementary excitations, 618–620, 668, 670, 671
- Empirical pseudopotential method, 309
- Empty core model, 305
- Energy band calculation, 154, 155, 158, 162, 165, 181, 281, 285, 303–308, 310–320
- Energy bands, 153, 310
- Energy gap, 41, 321, 386, 445, 549, 646
- Energy gap, superconducting materials, 632–637, 662, 663
- Energy loss, 725
- Entropy, 3, 8, 500, 582, 632, 634, 639, 641, 670, 693, 713–715, 717, 720, 721, 795, 821

- Entropy, current, 639
- Equations of motion, 97, 733, 734
- Equilibrium structures, 8, 10–15, 51
- Ewald construction, 250
- Exchange energy, 585
- Exchange interaction, 582, 585, 597, 599, 601, 611–613, 622
- Exchange term in Hartree-Fock equation, 708
- Excitons
 - binding energies, 373
 - Frenkel, 372, 373, 389
 - Mott-Wannier, 373, 389
- Exclusion principle, *See* Pauli exclusion principle
- Expressions for $\varepsilon(\mathbf{k}, \omega)$ within the JM, 728
- Extended zone scheme, 159, 160, 174, 325, 334
- Extrinsic semiconductors, 193
- Face-centered cubic, 65, 67, 69, 75, 76, 231, 354–356, 358, 361, 363, 364, 394, 413, 448, 473, 501, 502, 549
- Factor, atomic form, 248, [797](#)
- Fermi distribution, 716
- Fermi energy, 12, 88, 90, 101, 156, 159, 289
- Fermi function, *See* Fermi distribution
- Fermi level, 12, 13, 165, 235–237
- Fermi lines, 283, 330–336, 345, 353
- Fermi momentum, 88, 107
- Fermions, heavy, 625, 627
- Fermi parameters, 89
- Fermi sphere, 351, 354, 356, 363–365, 501, 606
- Fermi surface(s)
 - of alkali metals, 351
 - of aluminum, 355
 - of beryllium, 354
- Fermi temperature, 88
- Fermi velocity, 88, 120, 121
- Fermi wave vector, 330
- Fermi-Dirac distribution, *See* Fermi distribution
- Ferrimagnetic materials, 570, 579
- Ferrimagnetism, *See* Ferrimagnets
- Ferrimagnets, 570, 574–576, 579, 592
- Ferrites, 580
- Ferroelectric crystals, 687
- Ferroelectricity, 689
- Ferromagnetic crystals, 578
- Ferromagnetic materials, 235, 570, 577, 578, 582
- Ferromagnetic order in the JM, 599
- Ferromagnetism, *See* Ferromagnets
 - crystals, 578
 - domains, 592
 - Heisenberg model, 623
 - hysteresis, 578, 592
 - order parameter, 236
- Ferromagnets, 434, 462, 571, 573, 574, 577, 578, 582–586, 591, 592, 603, 689
- Fick's law, 224
- Field ion microscope, 232
- Fine structure constant, 759
- Finite systems, 52, 543–565
 - carbon nanotubes, 551–556
 - clusters, 544
 - fullerenes, 545–549
 - fullerides, 549–551
 - other clusters, 556, 557
- First-order transition, 51, 239, 633
- Floquet's theorem, 72
- Fluctuating dipole and Lennard-Jones potential, 393
- Fluctuating dipole, *See* Van der Waals interaction
- Fluxoid, 652, 654
- Force constants, *See* Spring constants
- Fourier analysis, 466
- Fourier transform, 113, 115, 122–124, 236, 246, 247, 266, 306, 506, 507, 510, 656, 673, 681, 691, 692, 728, [787](#), [802](#)
- Fractional quantum Hall effect, 535, 538, 539
- Free electron, 30, 54, 90, 93, 116, 121, 128, 137, 138, 191, 325, 326, 330, 334
- Free electron approximation, 93
- Free energy
 - Gibbs, 8, 18, 37, 51, 500, 582, 584, 587, 592, 640, 641, 645–647, 649, 650, 652, 653, 713, [796](#)
 - Helmholtz, 632, 634, 640, 713
 - Frenkel defect, 223, 224, [796](#)

- Frenkel exciton, 372, 389
 Fullerenes, 53, 543, 545, 547, 548, 551, 564
 Fullerides, 49, 549–551, 564
 Gap
 direct, 166, 189, 190, 199, 319, 371, 437, 438, 492, 551, 558
 indirect, 165, 166, 189, 190, 199, 205, 437
 Gas, *See* Electron gas
 Gas, electron, *See* Jellium model
 Gauge invariance, 686
 Gauge transformation, *See* Gauge invariance
 Gels, 6, 47, 51
 Generation current, 490, 491
 Generation of carriers, 488
 Ginzburg-Landau equation, 646
 Ginzburg-Landau parameter, 645
 Glasses, 6, 8, 49–51, 232, 234, 240, 499, 502
 Grain boundary, small-angle, 230
 Graphite, Graphene, 380
 Group velocity, 152, 201, 259, 279, 281, 282, 284, 285, 329, 333, 457, 458
 Grüneisen constant, 103
 Grneisen parameter, 103
 Gyromagnetic ratio, 130, 145
 Hall coefficient, 133, 273, 293, 294, 299, 357, 376, 377, 388, 389
 Hall effect
 in aluminum, 273, 294
 in semiconductors, 534
 resistance, 38, 132, 534
 Hall effect in compensated materials, 295, 296
 Hall mobility, 377
 Hall resistivity, 132
 Hard matter, 48, 77
 Harmonic approximation, 213, 238
 Harmonic oscillations, 219, 256–258
 Harrison's construction, 336, 337, 345
 Hartree-Fock approximation, 708
 Hartree-Fock equations, 708
 hcp, *See* Hexagonal close-packed structure
 Heat capacity, 503, *See also* Specific heat
 glasses, 503
 phonon, 106
 Heavy fermions, 627
 Heisenberg model, 613, 619, 623
 Heisenberg's uncertainty principle, 10, 11
 Heitler-London approximation, 597
 Helium, 26, 33, 39, 57, 136, 373, 393, 394, 525, 707, 781
 Heterojunction, 231, 233, 558
 Heterostructures, *See* Heterojunction
 Hexagonal close-packed, 55, 66–68, 75, 76, 78, 177, 250, 354, 355, 394, 412, 413, 434, 473, 502
 Hexagonal close-packed structure, 66
 Hexagonal lattice, 60, 63, 67, 811
 High temperature superconductors, 49
 Hole-like trajectories, 285
 Hole orbits, *See* Hole-like trajectories
 Holes, 41, 184, 186, 187, 194–196, 238, 293, 333, 368, 370, 371, 373, 374, 387, 389, 432, 441, 442, 483, 486–492, 496, 557, 559, 561, 564
 Honeycomb network, 381
 Hooke's law, 47, 734
 Hubbard model, 607, 610–612, 622
 Hume-Rothery rules, 500
 Hund's rules, 597
 Hydrogen bond, 49, 53, 58, 77, 785
 Hydrogen molecule, 661
 Hyperfine effects, *See* Knight shift
 Hysteresis, 572, 573, 592
 Ice, 49, 53, 58, 785
 Impurities
 and electrical conductivity, 223
 and Kondo effect, 564
 elastic scattering by, 121
 in semiconductors, 192–195, *See also* Donors; Acceptors; Doping
 Impurity band, 234
 Impurity band conduction, *See* Impurity band
 Impurity levels, 192–195
 Indirect gap, 165, 166, 189, 190, 199, 205, 437

- Indirect optical transitions, 558–561,
 See also Optical transitions
- Indirect photon absorption, 164, 203,
 254, 255
- Inelastic scattering cross-section, 269
- Inelastic scattering, phonons, 201, 252,
 253, 268
- Inert gas crystals, *See* Van der Waals
 solids
- Infrared transmission, 635
- Inhomogeneous semiconductors, *See*
 p–n Homojunction
- Insulator-metal (Mott) transition, *See*
 d-band
- Insulators, 41, 48, 49, 64, 105, 153, 159,
 178, 183, 202, 215, 224, 424, 430,
 432, 549
- Interaction of matter with an external
 electromagnetic field, 711
- Interband transitions, *See* Optical
 transitions
- Interfaces, 48, 225, 231–233, 240, 250,
 314, 387, 438, 439, 457, 458, 461,
 468, 471–498, 584, 585, 589, 591,
 592, 630
- Interstitials, 48, 223–225, 314, 315,
 317, 796
- Intrinsic carrier concentration, *See*
 Intrinsic case
- Intrinsic case, 197
- Intrinsic coherence length, 645, 647,
 653, 660
- Intrinsic semiconductors, 371
- Inverse spinel, 579
- Ionic bond, 53, 58, 77
- Ionic compounds, 49, 208, 255, 397–399,
 401–407, 433
- Ionic conductivity, 224, 225
- Ionic crystals, 226, 255, 401
- Ionic crystals, data, 400
- Ionic crystals II–VI, 397
- Ionic crystals III–V (mixed
 ionic-covalent), 208, 397, 402
- Ionic interactions in real space, 338–340
- Ionic motion, 27–29, 119, 221, 231, 239,
 346, 407
- Ionic oscillations, 97, 256
- Ionic plasma frequency, 730
- Ionic radii, 42, 399, 433
- Ionic radii of the elements, 769
- Ionic solids, 56, 57, 153, 157, 158, 174,
 177, 223, 224, 238, 255, 302, 372,
 373, 397, 399, 402, 406, 407,
 550, 564
- Ionic vibrations, 28, 97, 99, 103, 239,
 245–272, 346
- Ionization energies, 194
 Acceptor, 195
 Donor, 194
- Ionization potentials and values of L, S,
 and J of atoms, 772
- Ising model, 614
- Itinerant exchange, 599
- Jellium model, 83–111, 113–147, 153,
 211, 544, 656, 727, 729, 762
- Jellium model and el-el Coulomb
 repulsion, 599–603, 605–607
- Jones zone (JZ), 363–365
- Josephson effects, 677–681
- Joule heating, 141
- Junction, 231, 487, 491, 636, 677
- Junction, superconducting, 495, 635
- k_B (Boltzmann's constant), 15, 16, 29,
 320, 322, 716, 759, 779
- Kelvin relation, 141, 145
- Kinetic energy, 7, 10, 18, 21, 22, 25–27,
 53, 86, 90, 92, 218, 258, 276, 372,
 396, 558, 600, 648
- Kinetic theory of gases, 471
- Kohler's rule, 300
- Knight shift, 131
- Kohn anomalies, 604
- Kohn, Rostoker method, 302, 315–317,
 322
- Kondo theory, 564
- Korringa, 302, 315–317, 322
- Korringa-Kohn-Rostoker (KKR)
 method, 302, 315–317, 322
- K-p perturbation theory, 320, 322
- Kramers degeneracy, 321
- Kramers-Kronig relations, 188, 404, 692
- Kronig-Penney model, 327
- Lagrangian equations, 116, 527
- LA modes, 200
- Landau diamagnetism, 138, 370

- Landauer formula, 518, 539
- Landau levels, 139, 288, 289, 536–538
- Landau levels for free electrons, 288
- Landau theory of a Fermi liquid, *See* Dressed electrons
- Landau theory, phase transition, 649
- Landau-Ginzburg equations, 646, 647
- Landau-Ginzburg theory, 645, 652, 653, 665, 675, *See also* Ginzburg-Landau
- Lande factor, 129
- Langevin diamagnetism, 134
- Langevin function, 368, 369
- Langevin susceptibility, 136, 145
- Larmor diamagnetism, 134
- Larmor frequency, *See* NMR frequency
- Lasers, 6, 231, 253, 254, 440, 443, 688
- Latent heats of melting and vaporization of the elements, 774
- Lattice conductivity, 183
- Lattice constant(s), 62, 68, 71, 76, 100, 166, 167, 179, 278, 464
- Lattice dynamics, *See* Ionic oscillations
- Lattice frequencies, 97, 278
- Lattice momentum, 268, 311
- Lattice planes, 225, 227, 231, 495, 798, 812, *See also* Miller indices; Reciprocal lattice
- Lattices
 - cubic, 67, 261, 285, 398
 - direct, 74–77, 249–251, 276, 277, 354, 364, 381, 420, 797, 798
- Lattice planes, correspondence with reciprocal lattice vectors, 306, 308
- Lattice planes. *See also* Miller indices; Reciprocal lattice, 798, 812
- Lattice specific heat, *See* Specific heat
- Lattice sums, 394
- Lattice sums of inverse powers, 394
- Lattice types, 60–62, 67
- Lattice vacancies, 223
- Lattice vibrations
 - and specific heat, 104, 105
 - and superconductivity, 637
 - and thermal conductivity, 142
 - and thermal expansion, 106, 107
 - and thermopower, 140, 142
 - Bohm-Staver relation, 98
 - by light scattering, 252
 - by neutron scattering, 245
 - by X-ray scattering, 245
 - optical branch, 200
 - quantum theory of, 618
 - van Hove singularities, 282, 501, 538
- Lattice with a basis, 63
- Laue condition, *See* Laue's equations
- Laue's equations, 251
- Law of mass action, 196
- LCAO method, 152, 153, 169, 173, 174, 183, 301, 302, 321, 360, 371, 420, 426, 474, 556, 737–754
- Left-handed metamaterials (LHM), 52, 456–466, 468
- Lennard-Jones 6-12 potential, 407, 556
- Level repulsion, 169
- Linear combination of atomic orbitals (LCAO), 152, 153, 161, 169, 173, 174, 182, 183, 301, 302, 360, 378, 404, 426, 474, 607, 677, 737–754, *See also* Tight-binding method
- Light, scattering, *See* Brillouin scattering; Raman scattering
- Line defects, 214, 225, 240
- Line width, 780
- Linear chain, *See* One-dimensional system
- Liquid crystals, 6, 47, 51
- Local electric field, 585, 690, 731
- Localization, 232, 234, 235, 384, 440, 511, 513, 516–518, 523, 526, 527, 529–534, 540
- Localized moments, 411
- Localized states, 514
- LO modes, 200, 201
- London equation, 236, 642, 643, 653
- London gauge, 642
- London penetration depth, 643
- Longitudinal acoustic (LA) phonons, 119, 120
- Longitudinal oscillations, 119, 405
- Longitudinal plasma, 144
- Long-range order, 49, 51, 229, 505, 576, 592
- Lorentz force, 128, 685
- Low-angle grain boundary, 230
- Lorenz number, the rhs of the Wiedemann-Franz relation, 143

- Low energy electron diffraction (LEED), 232
- Lower critical field, 649
- LST relation, 203, 208, 404, 407, *See also* Lyddane-Sachs-Teller relation
- Lyddane-Sachs-Teller relation, 203, 208, 404, 407
- Lyddane-Sachs-Teller relation and soft modes, 208

- Macroscopic electric field, 731
- Madelung constant, 399, 401, 433, 550
- Madelung energy, *See* Madelung constant
- Magnetic alloys (dilute), *See* Dilute magnetic semiconductors
- Magnetic anisotropy and domain formation, 584
- Magnetic breakdown, 278
- Magnetic domains, 570–572, 582, 584–587, 592, 593
- Magnetic flux quantum, 647, 649, 650, 652, 679, 759
- Magnetic interactions
 - and mean field theory, 584
 - and nuclear magnetic resonance, 130
 - and spin-orbit coupling, 590
 - susceptibility, 602, 603
- Magnetic ions, 579
- Magnetic properties of superconductors, 627, 629
- Magnetic resonance, 128, 461–465
- Magnetic susceptibility, 128, 130, 133, 136, 137, 145, 288, 368, 370, 389, 412, 462, 573–577, 601, 603, 622, 689
- Magnetite, 443, 575, 576, 579
- Magnetization, 133, 138, 145, 370, 409, 569–574, 578, 580, 582–590, 592, 593, 599–601, 606, 614–616, 618, 619, 621, 623, 629, 632, 685, 712, 761
- Magnetization-stress interaction, 582
- Magnetoconductivity, 131, 132, 589
- Magnetoconductivity, tensor, 377
- Magneton, Bohr, 129, 137
- Magneton numbers, 137
- Magnetoresistance, *See also* Magnetoconductivity
 - giant, 589, 593
 - two carrier types, 376, 377
- Magnetostriction, *See* Magnetization-stress interaction
- Magnons, antiferromagnetic, dispersion relation, 618
- Many body problem, 217, 235
- Mass density, 33, 84, 94, 97, 450, 475, 761
- Material - specific calculations of superconducting quantities, 674–676
- Matthiessen's rule, 122
- Maxwell-Boltzmann distribution, 225, 374, 482, *See also* Boltzmann distribution
- Maxwell equations, 444, 456, 461, 466, 477, 495, 584, 641, 645, 685–688
- Mean field approximation, 583, 584, 608, 610–613, 615, 616, 622, 623
- Mean field theory, 584, 593, 645, 665
- Mean free path, 39, 121, 122, 234, 374, 510, 512, 518, 534, 644, 691
- Mechanical properties, 54–57, 222, 225–231, 365, 366, 389, 399–401, 407
- Meissner (Meissner-Ochsenfeld) effect, 627
- Melting
 - points, 409
 - temperature, 37, 38, 42
- Mesoscopic regime, 48, 52, *See* Nanostructures
- Metal-insulator transition (Mott transition), *See* d-band conductivity
- Metal-insulator transition, 835, *See also* Mott transition
- Metallic bond, 53, 77
- Metals, 30, 39, 54, 55, 59, 86, 113–147, 174, 183–185, 230, 295, 302, 340–343, 351, 409, 473, 477, 544, 557, 589, 720
- Microscopic mobility, 375
- Miller indices, 67–70, 75, 798
- Minority carriers, 489–492, 494, 496, 497, *See also* p-n junction; Semiconductors
- Mixed state in superconductors, 630

- Mobilities, 376, 384
- Mobility edges, 514, 517, 523
- Mobility gap, *See* Localized states
- Molecular crystals, *See* Molecular solids
- Molecular hydrogen, 238, 661
- Molecular solids, 49, 53, 58, 177, 406
- Momentum conservation, 165
- Momentum, crystal, 72, 165, 185, 239, 251, 253, 254, 258, 274, 384, 618, 656, 755
- Monocrystalline solids, 129, 263
- MOSFET, 494
- Mott exciton, 373, 389
- Mott transition, **835**, *See also* d-band conductivity
- Mott-Wannier excitons, 373, 389
- Muffin tin potential, 313, 467
- Multiphonon processes, 254
- Multiplet, *See* Triplet state

- Nanostructures, 500, 543
- Nanotubes, 53, 543, 551–556, 564
- Nearest neighbor, 68, 71
- Nearly free electron approximation, *See* Pseudopotential
- Neel temperature, 577
- Neel wall, 572
- Negative effective mass, 155
- Negative index materials, *See* Left-handed metamaterials (LHM)
- Neutron, 663
 - and magnetic ordering, 245
 - and phonon polarizations, 268
 - cold (thermal), 245
 - Diffraction, 245, 247, 250
 - energy-momentum, 663
 - magnetic reflections, 576
 - one-phonon scattering, 267
 - scattering length, 267
- NMR frequency, 130
- NMR tomography, 130, 131
- Noble gas solids
 - data, 395
 - Debye temperature, **806**
 - freezing and boiling points, 394
- Noble metals
 - band structure and Fermi surface, 351–359
- Nondegenerate semiconductors, 371
- Non-interacting bosonic particles, 720
- Non-interacting electrons, distribution, 718
- Normal mode enumeration, 28, 29
- Normal modes of harmonic crystal, 266, *See also* Harmonic approximation; Phonons
- Normal process, 251, *See also* Phonon umklapp process
- Normal spinel, 579
- n.p product, 196, 197
- Nuclear magnetic resonance, 130, 131
- Nuclear spins and magnetic moments, 776
- Number of states, 73, 74, 86–90, 107, 109, 159, 187, 201, 234, 276, 330, 514, 669, 673, 700
- Numerical relations and correspondences, 764

- One-dimensional system, 150
- Onsager relations, 614
- Open orbits, 295–297, 299, 357
- Optical branch, 164, 200
- Optical measurement of phonon spectra, 253, 255
- Optical modes, *See* Optical branch
- Optical phonon branch, 175
- Optical phonons, 200
- Optical phonons, soft, 164, 254, *See also* Soft modes
- Optical transitions, 199
- Optical threshold in alkali metals, 119
- Orbital angular momentum, quenching of, 137
- Orbitals, linear combination of atomic, 152, 738
- Order
 - long-range, 49, 51, 229, 505, 576
 - short-range, 49, 229
- Order parameter, 235, 236, 587, 632, 645, 648
- Organic semiconductors, 386, 387, 389, 391
- Oscillations, Friedel, 340
- Oscillator raising and lowering operators, *See* Phonon creation and annihilation operators
- Overlap integrals, 301, 597

- Oxides, 49, 51, 430–435, 534, 591, 627, 677
- Packing fraction, *See* Volume fraction
- Pairing, 664, 675
- Paramagnetism, 134, 137
- Paramagnetism, VanVleck, 134, 369
- Particle diffusion, electron, 487
- Particle diffusion, ion, 225
- Pauli exclusion principle, 11–15, 18, 706
- Pauli exclusion principle and inertness of filled bands, 185
- Pauli spin magnetization, 370
- Peierls instability, 162, 415, 793
- Peltier coefficient, 141, 145
- Peltier effect, *See* Peltier coefficient
- Penetration depth, 627, 645, 651
- Penetration depth, London, 643
- Periodic boundary conditions, 150, 162, 553, 555, 644, 698–700
- Perovskite(s), 49, 423–428, 435, 591
- Periodic table of the elements, 765
- Periodic zone scheme, *See* Repeated zone scheme
- Perovskite structure, 627
- Persistent currents, *See* Surface currents
- Perturbation formulas, *See* Perturbation results
- Perturbation results, 706–709
- Perturbation theory, 222, 240, 310–313, 317, 318, 320–322, 325, 332, 345
- Phase diagrams, 185, 610, 611, 806
- Phase space, 606, 700
- Phase transitions, 51, 52, 433, 527, 574, 577, 614, 633, 689
- Phase transitions, structural, 239, 240, 538
- Phonon creation and annihilation operators, 270
- Phonon distribution, 720, 721
- Phononic crystals, 52, 450–453, 455, 456, 461, 467
- Phononic crystals, gaps, 451
- Phononic dispersions in metals, 340–342
- Phonon-phonon interactions, 238–240
- Phonons
 - coordinates, 258, 264
 - dispersion relations, 201, 251, 256–263
 - distribution, 721
 - heat capacity, 104
 - in metals, 342–345
 - inelastic scattering, 201, 252, 254
 - mean free path, 342–344
 - momentum, 143
 - normal processes, 251
 - soft modes, 239
- Phonon scattering by surfaces, 143
- Phonon umklapp process, 143, 239, 251
- Photonic crystals, 52, 439–450, 466
- Photons, 164, 246, 253, 255, 267, 371–373, 440, 476, 481, 482, 492, 727
- Photovoltaic, 387, 492, 551, 558, 810
- Physical constants, 759
- Piezoelectricity, 688
- Planck distribution, *See* Phonon distribution
- Plane wave expansion, 303, 309, 310, 446
- Plane waves, 70, 73, 75, 86, 150, 245, 301–303, 309–311, 314, 315, 322, 360, 446, 451, 510, 603, 604, 622, 711, 735
- Plasma frequency, 191
- Plasma oscillation (plasmon), 119, 120, 143, 238
- Plasmon at interface, 478
- Plasmon frequency, 478, 498
- Plasmon, surface, 477, 478, 498
- Plastic deformation, critical stress, 229
- p–n Homojunction, 483–492, 496, 498
- p–n junction(s), 471, 488, 491–493, 498, *See also* Bending of bands; Depletion layer; Recombination current; Rectification; Reverse bias; Saturation current
- Point defect, 207, 510
- Poise, 503
- Poisson equation, 123, 484, 488, 494
- Poisson's ratio, 736
- Polar semiconductors, *See* Compound semiconductors
- Polaritons, 255, 268, 373
- Polarizabilities, 723
 - electronic polarizabilities, 404
 - ionic, 404
- Polaron, coupling constant, 238
- Polaron or bipolaron, 238

- Polarons, 238
- Polycrystalline solids, 49, 214, 262, 263
- Polycrystalline state, 48
- Polymers, 50, 51, 443, 450
- Polyvalent metals, 302, 342, 345, 346
- Potential energy, 7, 9, 11, 26, 92, 93, 256, 338, 341, 596, 602, 702, 728, 734
- Potential, periodic, 109, 133, 149, 154, 222, 274, 277, 288, 291, 313, 326, 330–332, 475
- Potential well analogy, 533, 534
- Powder method, 250
- Pressures, 7, 8, 95, 96, 103, 459, 471, 640, 722
- Primitive cell, *See* Cell, primitive
- Primitive cell, pseudopotential, 361
- Primitive vectors, 59, 62, 63, 67, 68, 70, 71, 351, 381, 495, 552–554
- Pseudopotential(s), 325–328
 - form factors, 362
 - form factors, tables, 362
 - ionic, 303, 304, 306, 307, 337
 - method, 305, 309, 341, 342, 353, 356, 363, 371
 - total, 303, 307
- Pyroelectric, 689
- Pyroelectric crystals, pyroelectric materials, 689
- QHE, *See* Quantum Hall effect
- Quantization
 - elastic wave, 269, 270
 - orbits in magnetic field, 289
 - spin waves, 138
- Quantization of orbits, 289
- Quantum dots, 52, 53, 385, 543, 557–559, 564, 565, 589
- Quantum Hall effect, 38, 384, 534, 536, 537, 539
- Quantum informatics, 240
- Quantum interference, 510, 512, 513, 526
- Quantum kinetic energy, 7, 10, 54, 77, 96
- Quantum mechanics, 5, 10, 30, 153, 154, 279, 511, 697–712
- Quantum of flux, 129, 647–650, 652, 654, 759
- Quantum theory
 - Diamagnetism, 135
 - Paramagnetism, 137–139
- Quasi-crystals, 500, 506, 508, 509, 538
- Quasi-particles, 120, 235, 623, 665
- Quenching, orbital angular momentum, 137
- Radial distribution function, 506
- Radius of a sphere whose volume is the volume per atom, 767
- Radius, ionic, 42, 399, 433, *See also* Ionic radii
- Raman effect, *See* Raman scattering
- Raman scattering, 253, *See also* Brillouin scattering
- Random network, 551
- Random stacking, 231
- Rare earth ions, 627
- Rare earth ions, and indirect exchange, 599
- Rayleigh attenuation, *See* Rayleigh scattering
- Rayleigh scattering, 445
- Reciprocal lattice
 - and Miller indices, 75, 798
 - of body-centered cubic, 75, 351
 - of face-centered cubic, 351, 354, 364
 - vectors, 74, 75, 77, 150, 155, 159, 247, 251, 253, 258, 268, 309, 311, 326, 328, 337, 352, 354, 475, 554, 656, 798
- Recombination current, 491, 497
- Recombination radiation, 488
- Recombination time, 488
- Reconstruction, 231, 472, 474, 495, 556
- Rectification, 488
- Rectification by p–n junction, 488
- Reduced zone scheme, 159, 160, 283, 284, 325–329, 332–335, 352–354, 356, 357, 360, 361
- Reflection, 9, 61, 114, 250, 292, 458, 459, 518, 519, 748, 750
- Reflection coefficient, 518
- Refractive index, 114, 190, 215, 456, 464, 468, 724, 842
- Relaxation, 231, 472, 473, 479, 495
- Relaxation time, 116, 375–377, 512, 526, 540, 638, 755

- Relaxation-time approximation, 526
- Remanence, 573
- Repeated zone scheme, 281, 283–285, 287, 295, 298, 331, 334–336, 357, 418, [798](#)
- Residual resistivity, 127
- Resistance, electrical, 38, 761
- Resistance minimum, 661
- Resistance quantum, 516
- Resistivity, 775
 - DC electrical, 38, 42
 - electrical, 4, 38–40, 55, 56, 125, 127, 222
- Response, electron gas, 113, 127, 140, 534, 564
- Response function, 462, 726
- Reverse bias, 278, 487, 488, 490
- RHEED, 232
- Richardson-Dushman equation, 481, 493
- RKKY interaction, 500, 599
- RKKY theory, *See* RKKY interaction
- Rotating coordinate system, 188, [785](#)
- Rotating crystal method, 250
- Rydberg (Ry), 275, 361, 416, 561

- Saturation current, 490, 491
- Saturation current, in p–n junction, 490
- Saturation magnetization, 572–574, 578, 580, 582, 584, 592
- Scaling approach to localization, 529, 540
- Scanning electron microscope, 763
- Scanning tunneling, 763
- Schottky barrier, 493, 591
- Schottky defect, 223, 224, [795](#)
- Schottky vacancies, 224
- Schrödinger equation, 73, 152, 155, 157, 160, 174, 194, 212, 220, 274, 303, 309, 313–316, 321, 382, 443, 446, 560, 646, 647, 698, 701, 702, 705, 737, [824](#)
- Screened Coulomb potential, 115, 340, 666
- Screening, electrostatic, 115
- Screening, Thomas - Fermi, 118, 729
- Screw dislocation, 228
- Second-order transition, 574, 614, 633, 689

- Seebeck effect, 140
- Self-assembled soft matter, 51, 52
- Self-diffusion, 226
- Self-trapping, *See* Polaron or bipolaron
- Semiclassical approximation, 276, 278, 755
- Semiclassical trajectories, 280, 283, 285–287
- Semiconductor(s)
 - crystals, 177
 - degenerate, 196
 - dielectric constant, 191
 - doping impurities, 192
 - mobilities, 376
 - various data, 194, 195
- Semimetals, 106, 153, 215, 273, 661
- Semimetals, valence bands, 333
- Shear
 - modulus, 34, 35, 47, 54–57, 97, 100, 215, 229, 239, 259, 736, [785](#)
 - strain, 47, 48, 735
 - stress, 47, 48
- Shell model, *See* Shell structure
- Shell structure, 238
- Short-range order, 49
- Shubnikov-de Haas effect, 288
- Silicon dioxide, 49, 51, 378, 389, 450, 494, 499, 502, 503
- Single-domain particles, 570, 587
- Single-electron transistor, 558
- Singularities, Van Hove, 73, 259, 260, 269, 276, 282, 284, 286, 501, 513, 538
- SI vs. G-CGS systems, 278
- Size and energy, atoms, 21, 23, 41
- Size effects, *See* Finite systems
- Slater approximation to exchange term, *See* X- α approximation
- Slater determinant, 314
- Slip, 225–228
- Small oscillations approximation, 27, 36, 37, *See* Harmonic approximation
- Sodium chloride structure, 69, 398
- Soft matter, 48, 50–52, 77, 214, 499
- Soft modes, 239
- Solar cells, 192
- Solitons, 238, 239, 387
- Solutions of Helmholtz equation, 778
- Sound velocities, 37, 98

- Space charge region, *See* Depletion layer
- Spaghetti diagrams, 327
- Specific heat, 29–31, 83, 104–108, 125, 138, 142, 145, 215, 273, 412, 502–504, 626, 632–634, 652, 671, 713, 722, [821](#), [824](#)
- Specific heat (electronic), 30, 125, 142, 145, 626, 652
- Specific heat (lattice), 104
- Specific heat coefficient Y_c , 106
- Spectral discreteness, 14
- Spheres, close packing of, 32
- Spherical harmonics, 704
- Spherically symmetric potentials, 313, 319, 660, 700–706
- sp1 Hybrid atomic orbitals, 744
- sp2 Hybrid atomic orbitals, 745, 748, 750
- sp3 Hybrid atomic orbitals, 749
- Spin, 11, 13, 30, 86, 104, 129, 130, 134, 137, 138, 186, 219, 319, 320, 370, 413, 559, 569, 589, 591, 597, 600, 603, 608, 612, 614, 615, 617, 620, 638, 660, 712, [819](#)
- Spin density wave, 604–606, 622
- Spinel, 579
- Spin-orbit coupling, 188, 319, 320, 388
- Spintronics, 588–592
- Spin wave, 596, 618, 619
- Spontaneous magnetization, 409, 619, 621
- Spring constants, 213, 777
- SQUID, 677–680
- Stacking fault, 231
- Static disorder and localization, 513
- Statistical mechanics (SM), 5, 713–722, 763
- STM, 232, 763
- Stokes component, *See* Stokes line
- Stokes line, 254
- Strain components, 733
- Strain tensor, 48, 260, 366, 367, 733, 734
- Strength of alloys, 229
- Stress and strain, 734, 735
- Structural phase transitions, 238, 239, 538
- Structure factor, 247, 265, 269, [797](#)
- Sublattices, 177, 224, 398, 587, 588, 592, 593
- Substrate, 439, 499, 557, 558, 564
- Superconducting quantum interference devices (SQUID), 677–680
- Superconductivity, 630, 632, 640, 641, 646, 649, 650, 652
 - coherence length, 645, 653, 660
 - concentration ns, 674
 - critical current, 631
 - critical T_c , 430
 - Ginzburg - Landau Theory, 645–651
 - infrared absorption, *See* infrared transmission
 - intermediate state, 630
 - magnetic field, critical value, 629–632
 - mixed state, 630
 - order parameter, 235, 236, 675
 - perfect diamagnetism, 236, 426
 - Pippard's generalization, 644, 645
 - quantization of the magnetic flux, 651
 - relaxation times for nuclear spin, 638
 - specific heat, 632–634
 - strong coupling, 664, 672
 - temperature dependence of the superconducting gap, 635–637
 - thermal conductivity, 639
 - thermodynamic relations, 639–641
 - thermoelectric coefficients, 638, 639
 - triplet pairing, 660
 - tunneling current in metal/ insulator/ superconductor junctions, 635
 - type I, 630–633, 640, 645, 646, 648–650, 652, 653
 - type II, 631, 645, 646, 649, 652
 - ultrasound attenuation, 635
 - vortex lines, 630, 632, 640, 641, 646, 649, 650, 652, *See also* Vortex state
 - zero DC resistivity, 627
- Superconductors
 - gap, 637
 - high T_c , 427
 - isotope effect α , 638
- Superlattices, 437–439
- Surface currents, 627
- Surface dipole layer, 480
- Surface electronic structure, 476
- Surface levels, *See* surface states

- Surface plasmon(s), 477, 478, 498
- Surface relaxation, 473
- Surfaces, experimental techniques, 232
- Surface states, 474–479
- Surfaces of constant energy, 286, 287
- Susceptibilities, 577
- Susceptibility, Larmor, 136

- TA modes, 200
- TB method, *See* LCAO
- Temperature, 8, 16, 18, 30, 31, 37, 41, 88, 237, 502, 522, 549, 574, 575, 577, 616, 628, 629, 633, 662, 664, 761, [781](#)
- Temperature, Debye, 83, 99, 104, 108, 237, [786](#), [787](#), [805](#)
- Tetrahedral angles, 749
- Tetravalent metals, 358, 359
- Thermal conductivity, 141–145, 385, 504, 638, 639
- Thermal equilibrium, 265, 519, 638
- Thermal expansion, 107, 108, 215, 238, 239, 714
- Thermal expansion and Grüneisen parameter, 103, 107, 108
- Thermal resistivity, phonon, 239
- Thermionic emission, 481, 482, 496
- Thermodynamic potentials, 101, 581, 665, 668, 669, 713
- Thermodynamic relations, [817](#)
- Thermodynamics, 5, 7, 8, 26, 587, 588, 594, 713–722
- Thermoelectric effects, 141–143, 688
- Thermoelectric response, 140–143
- Thermopower, 140, 141, 145, 273
- Thomas Fermi dielectric constant, 115, 118
- Thomas-Fermi screening constant, 728
- Thomson effect, 141
- Tight binding model (TBM), 241, 281–287, 514, 522, 529, 530, 533, 622, 763
- Tight-binding method (TB), 281
- TO modes, 200, 201
- Tomography, 130
- Transistor, MOS, 762
- Transition
 - first-order, 51
 - metal-insulator, 106, 330
 - second-order, 689
- Transition metal alloys, 53
- Transition metals
 - and compounds, 411
 - cohesive energies, 423
 - parameters, 420
- Transition temperature, glass, 50
- Translation operation, 59
- Translation vector, 72
- Transmission coefficient, 443, 502
- Transmission probability, *See* Transmission coefficient
- Transparency, alkali metals, 119
- Transport, 42, 55, 85, 120–122, 125, 144, 221, 237, 343, 371, 385, 387, 389, 432, 434, 510–513, 522, 523, 557, 558, 563, 564, 591, 674
- Transport properties, 42, 55, 122, 125, 221, 223, 237, 238, 371–377, 385, 434, 522, 557, 563, 564, 674
- Transverse acoustic (TA) phonon, 200
- Transverse optical (TO) modes, 200, 201
- Transverse optical (TO) phonon, 203, 255, 256
- Transverse optical modes, 200
- Triplet excited states, 388, 597, 598, 613, 622
- Triplet state, 597
- Trivalent metals, 354, 356, 357, 388
- Tunneling, 8, 278, 589, 635
- Tunneling, Josephson, 677
- Tunneling probability, 677
- Twinning, 231
- Type I superconductors, 630, 633, 640, 645, 646
- Type II superconductors, 630, 632, 633, 641, 646, 649, 652

- Ultrasonic attenuation, 238
- Umklapp processes, 143, 239, 344
- Unit cell, 62, 64–66, 68–71, 78, 163, 248, 351, 364, 430, 431, 433, 437–439, 450, 461–466, 530, 550, 557, 575, 579, 592, 730, 738, [797](#)
- Upper critical field, 630
- UPS, 232, 763
- Useful mathematical formulae, 777

- Vacancies, 48, 122, 223, 226, 428, 796
- Valence, 85
- Valence band edge, 791
- Valence bands, 40, 41, 159, 167, 168, 184, 187, 188, 207, 319, 320, 333, 365, 369, 375, 426, 486, 488, 730
- Valence electrons, 54, 55, 73, 84, 93, 119, 129, 302–305, 307, 321, 352, 353, 368, 424, 462, 483, 741
- Values of s-, p-, d- energy levels in atoms, 707
- Van der Waals force, 49, 57, 58, 380, 389
- Van der Waals interaction, 24
- Van der Waals solids, 393, 397
- Van Hove singularities, 73, 259, 269, 276, 282, 284, 286, 501, 513, 538
- Van Vleck paramagnetism, 134, 369
- Variational principle, 315
- Vector potential, 527, 581, 642–644, 646, 678, 711, 712
- Velocity of Bloch electrons, 73
- Vibrations, 28, 30, 37, 99, 103, 108, 144, 145, 163, 200, 239, 245, 258, 346, 504, 618, 637, 638, 652, 785, 805, *See* Harmonic oscillations
- Viscoelastic, 48
- Viscosity, 47–49, 502, 503, 538, 785
- Vitreous silica, *See* Amorphous silicon dioxide
- Volume fraction, 69
- Volume per atom, 26, 27, 32, 33, 84, 107, 569
- Von Laue' equations, 251
- Von Laue formulation of X-ray diffraction, *See* Von Laue' equations
- Von Laue method, *See* Von Laue' equations
- Vortex state, 630, 632, 640, 641, 646, 649, 650, 652
- Weak localization, 384, 526, 527, 532, 540
- Wiedemann-Franz law, 143, 638
- Wigner-Seitz cell, 62, 78
- Work function, 232, 233, 479–481, 483, 493, 495
- Work hardening, 230
- Wurtzite structure, 66, 67, 205, 206
- X-a approximation, 219
- X rays, 245, 248, 252, 506, 538, 576
- X-ray diffraction, 506, 763
- Yukawa potential, *See* Screened Coulomb potential
- Zener breakdown, 487
- Zero point motion of ions, 743
- Zincblende structure, 177, 239, 398
- Zones, Brillouin, 70, 75, 76, 150, 198, 258, 259, 274, 276, 325, 327