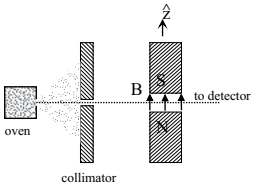
Introduction

State vectors

Stern Gerlach experiment



In the Stern Gerlach experiment

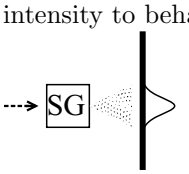
- silver atoms are heated in an oven, from which they escape through a narrow slit,
- the atoms pass through a collimator and enter an inhomogenous magnetic field, we assume the field to be uniform in the xy-plane and to vary in the z-direction,
- a detector measures the intensity of the electrons emerging from the magnetic field as a function of z.

We know that

- 46 of the 47 electrons of a silver atom form a spherically symmetric shell and the angular momentum of the electron outside the shell is zero, so the magnetic moment due to the orbital motion of the electrons is zero,
- the magnetic moment of an electron is $c\boldsymbol{S}$, where $\boldsymbol{S}$ is the spin of an electron,
- the spins of electrons cancel pairwise,
- thus the magnetic moment $\boldsymbol{\mu}$ of an silver atom is almost solely due to the spin of a single electron, i.e. $\boldsymbol{\mu} = c\boldsymbol{S}$,
- the potential energy of a magnetic moment in the magnetic field $\boldsymbol{B}$ is $-\boldsymbol{\mu} \cdot \boldsymbol{B}$, so the force acting in the z-direction on the silver atoms is

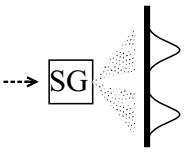
$$F_z = \mu_z \frac{\partial B_z}{\partial z}.$$

So the measurement of the intensity tells how the z-component the angular momentum of the silver atoms passing through the magnetic field is distributed. Because the atoms emerging from the oven are randomly oriented we would expect the intensity to behave as shown below.



classically

In reality the beam is observed to split into two components.



in reality

Based on the measurements one can evaluate the z-components S_z of the angular momentum of the atoms and find out that

- for the upper distribution $S_z = \hbar/2$.
- for the lower distribution $S_z = -\hbar/2$.

In quantum mechanics we say that the atoms are in the angular momentum *states* $\hbar/2$ and $-\hbar/2$.
The *state vector* is a mathematical tool used to represent the states. Atoms reaching the detector can be described, for example, by the *ket*-vectors $|S_z;\uparrow\rangle$ and $|S_z;\downarrow\rangle$.
Associated with the ket-vectors there are dual *bra*-vectors $\langle S_z;\uparrow|$ and $\langle S_z;\downarrow|$. State vectors are assumed

- to be a complete description of the described system,
- to form a linear (Hilbert) space, so the associated mathematics is the theory of (infinite dimensional) linear spaces.

When the atoms leave the oven there is no reason to expect the angular momentum of each atom to be oriented along the z-axis. Since the state vectors form a linear space also the superposition

$$c_\uparrow|S_z;\uparrow\rangle + c_\downarrow|S_z;\downarrow\rangle$$

is a state vector which obviously describes an atom with angular momentum along both positive and negative z-axis.
The magnet in the Stern Gerlach experiment can be thought as an apparatus measuring the z-component of the angular momentum. We saw that after the measurement the atoms are in a definite angular momentum state, i.e. in the measurement the state

$$c_\uparrow|S_z;\uparrow\rangle + c_\downarrow|S_z;\downarrow\rangle$$

collapses either to the state $|S_z;\uparrow\rangle$ or to the state $|S_z;\downarrow\rangle$.
A generalization leads us to the measuring postulates of quantum mechanics:
Postulate 1 *Every measurable quantity is associated with a Hermitean operator whose eigenvectors form a complete basis (of a Hilbert space),*
and
Postulate 2 *In a measurement the system makes a transition to an eigenstate of the corresponding operator and the result is the eigenvalue associated with that eigenvector.*
If $\mathcal{A}$ is a measurable quantity and A the corresponding Hermitean operator then an arbitrary state $|\alpha\rangle$ can be described as the superposition

$$|\alpha\rangle = \sum_{a'} c_{a'}|a'\rangle,$$

where the vectors $|a'\rangle$ satisfy

$$A|a'\rangle = a'|a'\rangle.$$

The measuring event $\mathcal{A}$ can be depicted symbolically as

$$|\alpha\rangle \xrightarrow{\mathcal{A}} |a'\rangle.$$

In the Stern Gerlach experiment the measurable quantity is the z-component of the spin. We denote the measuring event by $\boxed{\mathrm{SG}\hat{\boldsymbol{z}}}$ and the corresponding Hermitean operator by S_z. We get

$$\begin{aligned}
S_z|S_z;\uparrow\rangle &= \frac{\hbar}{2}|S_z;\uparrow\rangle \\
S_z|S_z;\downarrow\rangle &= -\frac{\hbar}{2}|S_z;\downarrow\rangle \\
|S_z;\alpha\rangle &= c_\uparrow|S_z;\uparrow\rangle + c_\downarrow|S_z;\downarrow\rangle \\
|S_z;\alpha\rangle &\xrightarrow{\boxed{\mathrm{SG}\hat{\boldsymbol{z}}}} |S_z;\uparrow\rangle \quad \text{or} \\
|S_z;\alpha\rangle &\xrightarrow{\boxed{\mathrm{SG}\hat{\boldsymbol{z}}}} |S_z;\downarrow\rangle.
\end{aligned}$$

Because the vectors $|a'\rangle$ in the relation

$$A|a'\rangle = a'|a'\rangle$$

are eigenvectors of an Hermitean operator they are orthognal with each other. We also suppose that they are normalized, i.e.

$$\langle a'|a''\rangle = \delta_{a'a''}.$$

Due to the completeness of the vector set they satisfy

$$\sum_{a'} |a'\rangle\langle a'| = 1,$$

where 1 stands for the identity operator. This property is called the *closure*. Using the orthonormality the coefficients in the superposition

$$|\alpha\rangle = \sum_{a'} c_{a'}|a'\rangle$$

can be written as the scalar product

$$c_{a'} = \langle a'|\alpha\rangle.$$

An arbitrary linear operator B can in turn be written with the help of a complete basis $\{|a'\rangle\}$ as

$$B = \sum_{a',a''} |a'\rangle\langle a'|B|a''\rangle\langle a''|.$$

Abstract operators can be *represented* as matrices:

$$B \mapsto \begin{array}{c} \\ \langle a_1| \\ \langle a_2| \\ \langle a_3| \\ \vdots \end{array} \begin{array}{c} \begin{array}{cccc} |a_1\rangle & |a_2\rangle & |a_3\rangle & \dots \end{array} \\ \begin{pmatrix} \langle a_1|B|a_1\rangle & \langle a_1|B|a_2\rangle & \langle a_1|B|a_3\rangle & \dots \\ \langle a_2|B|a_1\rangle & \langle a_2|B|a_2\rangle & \langle a_2|B|a_3\rangle & \dots \\ \langle a_3|B|a_1\rangle & \langle a_3|B|a_2\rangle & \langle a_3|B|a_3\rangle & \dots \\ \vdots & \vdots & \vdots & \vdots \end{pmatrix} \end{array}.$$

Note The matrix representation is *not* unique, but depends on the basis. In the case of our example we get the 2×2-matrix representation

$$S_z \mapsto \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},$$

when we use the set $\{|S_z;\uparrow\rangle, |S_z;\downarrow\rangle\}$ as the basis. The base vectors map then to the unit vectors

$$\begin{aligned}
|S_z;\uparrow\rangle &\mapsto \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\
|S_z;\downarrow\rangle &\mapsto \begin{pmatrix} 0 \\ 1 \end{pmatrix}
\end{aligned}$$

of the two dimensional Euclidean space.
Although the matrix representations are not unique they are related in a rather simple way. Namely, we know that
Theorem 1 *If both of the basis $\{|a'\rangle\}$ and $\{|b'\rangle\}$ are orthonormalized and complete then there exists a unitary operator U so that*

$$|b_1\rangle = U|a_1\rangle, |b_2\rangle = U|a_2\rangle, |b_3\rangle = U|a_3\rangle, \dots$$

If now X is the representation of an operaor A in the basis $\{|a'\rangle\}$ the representation X' in the basis $\{|b'\rangle\}$ is obtained by the similarity transformation

$$X' = T^\dagger X T,$$

where T is the representation of the base transformation operator U in the basis $\{|a'\rangle\}$. Due to the unitarity of the operator U the matrix T is a unitary matrix.
Since

- an abstract state vector, excluding an arbitrary phase factor, uniquely describes the physical system,
- the states can be written as superpositions of different base sets, and so the abstract operators can take different matrix forms,

the physics must be contained in the invariant propertices of these matrices. We know that
Theorem 2 *If T is a unitary matrix, then the matrices X and $T^\dagger X T$ have the same trace and the same eigenvalues.*
The same theorem is valid also for operators when the trace is defined as

$$\mathrm{tr}A = \sum_{a'} \langle a'|A|a'\rangle.$$

Since

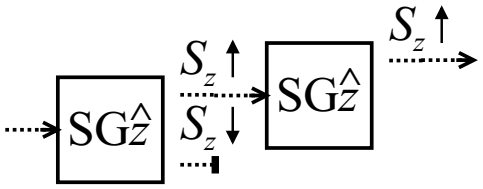
- quite obviously operators and matrices representing them have the same trace and the same eigenvalues,
- due to the postulates 1 and 2 corresponding to a measurable quantity there exists an Hermitean operator and the measuring results are eigenvalues of this operator,

the results of measurements are independent on the particular representation and, in addition, every measuring event corresponding to an operator reachable by a similarity transformation, gives the same results. Which one of the possible eigenvalues will be the result of a measurement is clarified by

Postulate 3 *If A is the Hermitean operator corresponding to the measurement $\mathcal{A}$, $\{|a'\rangle\}$ the eigenvectors of A associated with the eigenvalues $\{a'\}$, then the probability for the result a' is $|c_{a'}|^2$ when the system to be measured is in the state*

$$|\alpha\rangle = \sum_{a'} c_{a'}|a'\rangle.$$

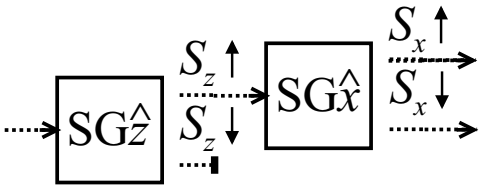
Only if the system already before the measurement is in a definite eigenstate the result can be predicted exactly. For example, in the Stern Gerlach experiment $\boxed{\mathrm{SG}\hat{\boldsymbol{z}}}$ we can block the emerging lower beam so that the spins of the remaining atoms are oriented along the positive z-axis. We say that the system is *prepared* to the state $|S_z;\uparrow\rangle$.



If we now let the polarized beam to pass through a new $\boxed{\mathrm{SG}\hat{\boldsymbol{z}}}$ experiment we see that the beam from the latter experiment does not split any more. According to the postulate this result can be predicted exactly.
We see that

- the postulate can also be interpreted so that the quantities $|c_{a'}|^2$ tell the probability for the system being in the state $|a'\rangle$,
- the physical meaning of the matrix element $\langle\alpha|A|\alpha\rangle$ is then the expectation value (average) of the measurement and
- the normalization condition $\langle\alpha|\alpha\rangle = 1$ says that the system is in one of the states $|a'\rangle$.

Instead of measuring the spin z-component of the atoms with spin polarized along the z-axis we let this polarized beam go through the $\boxed{\mathrm{SG}\hat{\boldsymbol{x}}}$ experiment. The result is exactly like in a single $\boxed{\mathrm{SG}\hat{\boldsymbol{z}}}$ experiment: the beam is again splitted into two components of equal intensity, this time, however, in the x-direction.



So, we have performed the experiment

$$|S_z;\uparrow\rangle \xrightarrow{\boxed{\mathrm{SG}\hat{\boldsymbol{x}}}} |S_x;\uparrow\rangle \quad \text{or}$$

$$|S_z;\uparrow\rangle \xrightarrow{\boxed{\mathrm{SG}\hat{\boldsymbol{x}}}} |S_x;\downarrow\rangle.$$

Again the analysis of the experiment gives $S_x = \hbar/2$ and $S_x = -\hbar/2$ as the x-components of the angular momenta. We can thus deduce that the state $|S_z;\uparrow\rangle$ is, in fact, the superposition

$$|S_z;\uparrow\rangle = c_{\uparrow\uparrow}|S_x;\uparrow\rangle + c_{\uparrow\downarrow}|S_x;\downarrow\rangle.$$

For the other component we have correspondingly

$$|S_z;\downarrow\rangle = c_{\downarrow\uparrow}|S_x;\uparrow\rangle + c_{\downarrow\downarrow}|S_x;\downarrow\rangle.$$

When the intensities are equal the coeffiecients satisfy

$$\begin{aligned} |c_{\uparrow\uparrow}| &= |c_{\uparrow\downarrow}| = \frac{1}{\sqrt{2}} \\ |c_{\downarrow\uparrow}| &= |c_{\downarrow\downarrow}| = \frac{1}{\sqrt{2}} \end{aligned}$$

according to the postulate 3. Excluding a phase factor, our postulates determine the transformation coefficients. When we also take into account the orthogonality of the state vectors $|S_z;\uparrow\rangle$ and $|S_z;\downarrow\rangle$ we can write

$$\begin{aligned} |S_z;\uparrow\rangle &= \frac{1}{\sqrt{2}}|S_x;\uparrow\rangle + \frac{1}{\sqrt{2}}|S_x;\downarrow\rangle \\ |S_z;\downarrow\rangle &= e^{i\delta_1}\left(\frac{1}{\sqrt{2}}|S_x;\uparrow\rangle - \frac{1}{\sqrt{2}}|S_x;\downarrow\rangle\right). \end{aligned}$$

There is nothing special in the direction $\hat{\boldsymbol{x}}$, nor for that matter, in any other direction. We could equally well let the beam pass through a $\boxed{\mathrm{SG}\hat{\boldsymbol{y}}}$ experiment, from which we could deduce the relations

$$\begin{aligned} |S_z;\uparrow\rangle &= \frac{1}{\sqrt{2}}|S_y;\uparrow\rangle + \frac{1}{\sqrt{2}}|S_y;\downarrow\rangle \\ |S_z;\downarrow\rangle &= e^{i\delta_2}\left(\frac{1}{\sqrt{2}}|S_y;\uparrow\rangle - \frac{1}{\sqrt{2}}|S_y;\downarrow\rangle\right), \end{aligned}$$

or we could first do the $\boxed{\mathrm{SG}\hat{\boldsymbol{x}}}$ experiment and then the $\boxed{\mathrm{SG}\hat{\boldsymbol{y}}}$ experiment which would give us

$$\begin{aligned} |S_x;\uparrow\rangle &= \frac{e^{i\delta_3}}{\sqrt{2}}|S_y;\uparrow\rangle + \frac{e^{i\delta_4}}{\sqrt{2}}|S_y;\downarrow\rangle \\ |S_x;\downarrow\rangle &= \frac{e^{i\delta_3}}{\sqrt{2}}|S_y;\uparrow\rangle - \frac{e^{i\delta_4}}{\sqrt{2}}|S_y;\downarrow\rangle. \end{aligned}$$

In other words

$$\begin{aligned} |\langle S_y;\uparrow|S_x;\uparrow\rangle| &= |\langle S_y;\downarrow|S_x;\uparrow\rangle| = \frac{1}{\sqrt{2}} \\ |\langle S_y;\uparrow|S_x;\downarrow\rangle| &= |\langle S_y;\downarrow|S_x;\downarrow\rangle| = \frac{1}{\sqrt{2}}. \end{aligned}$$

We can now deduce that the unknown phase factors must satisfy

$$\delta_2 - \delta_1 = \pi/2 \text{ or } -\pi/2.$$

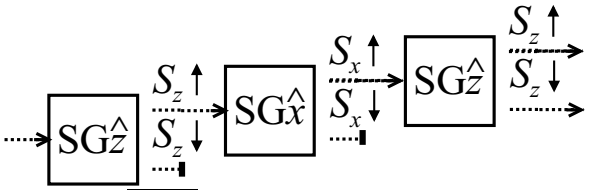
A common choice is $\delta_1 = 0$, so we get, for example,

$$\begin{aligned} |S_z;\uparrow\rangle &= \frac{1}{\sqrt{2}}|S_x;\uparrow\rangle + \frac{1}{\sqrt{2}}|S_x;\downarrow\rangle \\ |S_z;\downarrow\rangle &= \frac{1}{\sqrt{2}}|S_x;\uparrow\rangle - \frac{1}{\sqrt{2}}|S_x;\downarrow\rangle. \end{aligned}$$

Thinking like in classical mechanics, we would expect both the z- and x-components of the spin of the atoms in the upper beam passed through the $\boxed{\text{SG}\hat{\boldsymbol{z}}}$ and $\boxed{\text{SG}\hat{\boldsymbol{x}}}$ experiments to be $S_{x,z} = \hbar/2$. On the other hand, we can reverse the relations above and get

$$|S_x;\uparrow\rangle = \frac{1}{\sqrt{2}}|S_z;\uparrow\rangle + \frac{1}{\sqrt{2}}|S_z;\downarrow\rangle,$$

so the spin state parallel to the positive x-axis is actually a superposition of the spin states parallel to the positive and negative z-axis. A Stern Gerlach experiment confirms this.



After the last $\boxed{\text{SG}\hat{\boldsymbol{z}}}$ measurement we see the beam splitting again into two equally intensive componenents. The experiment tells us that there are quantitities which cannot be measured simultaneously. In this case it is impossible to determine simultaneously both the z- and x-components of the spin. Measuring the one causes the atom to go to a state where both possible results of the other are present.
We know that

Theorem 3 *Commuting operators have common eigenvectors.*

When we measure the quantity associated with an operator A the system goes to an eigenstate $|a'\rangle$ of A. If now B commutes with A, i.e.

$$[A, B] = 0,$$

then $|a'\rangle$ is also an eigenstate of B. When we measure the quantity associated with the operator B while the system is already in an eigenstate of B we get as the result the corresponding eigenvalue of B. So, in this case we can measure both quantities simultaneously.
On the other hand, S_x and S_z cannot be measured simultaneously, so we can deduce that

$$[S_x, S_z] \neq 0.$$

So, in our example a single Stern Gerlach experiment gives as much information as possible (as far as only the spin is concerned), consecutive Stern Gerlach experiments cannot reveal anything new.
In general, if we are interested in quantities associated with commuting operators, the states must be characterized by eigenvalues of all these operators. In many cases quantum mechanical problems can be reduced to the tasks to find the set of all possible commuting operators (and their eigenvalues). Once this set is found the states can be classified completely using the eigenvalues of the operators.

Translations

The previous discrete spectrum state vector formalism can be generalized also to continuos cases, in practice, by replacing

- summations with integrations
- Kronecker's δ-function with Dirac's δ-function.

A typical continuous case is the measurement of position:

- the operator x corresponding to the measurement of the x-coordinate of the position is Hermitean,
- the eigenvalues $\{x'\}$ of x are real,
- the eigenvectors $\{|x'\rangle\}$ form a complete basis.

So, we have

$$\begin{aligned} x|x'\rangle &= x'|x'\rangle \\ 1 &= \int_{-\infty}^{\infty} dx' \, |x'\rangle\langle x'| \\ |\alpha\rangle &= \int_{-\infty}^{\infty} dx' \, |x'\rangle\langle x'|\alpha\rangle, \end{aligned}$$

where $|\alpha\rangle$ is an arbitrary state vector. The quantity $\langle x'|\alpha\rangle$ is called a *wave function* and is usually written down using the function notation

$$\langle x'|\alpha\rangle = \psi_\alpha(x').$$

Obviously, looking at the expansion

$$|\alpha\rangle = \int_{-\infty}^{\infty} dx' \, |x'\rangle\langle x'|\alpha\rangle,$$

the quantity $|\psi_\alpha(x')|^2 dx'$ can be interpreted according to the postulate 3 as the probability for the state being localized in the neighborhood $(x', x' + dx')$ of the point x'. The position can be generalized to three dimension. We denote by $|\boldsymbol{x}'\rangle$ the *simultaneous* eigenvector of the operators x, y and z, i.e.

$$\begin{aligned} |\boldsymbol{x}'\rangle &\equiv |x', y', z'\rangle \\ x|\boldsymbol{x}'\rangle &= x'|\boldsymbol{x}'\rangle, \quad y|\boldsymbol{x}'\rangle = y'|\boldsymbol{x}'\rangle, \quad z|\boldsymbol{x}'\rangle = z'|\boldsymbol{x}'\rangle. \end{aligned}$$

The exsistence of the common eigenvector requires commutativity of the corresponding operators:

$$[x_i, x_j] = 0.$$

Let us suppose that the state of the system is localized at the point $\boldsymbol{x}'$. We consider an operation which transforms this state to another state, this time localized at the point $\boldsymbol{x}' + d\boldsymbol{x}'$, all other observables keeping their values. This operation is called an *infinitesimal translation.* The corresponding operator is denoted by $\mathcal{T}(d\boldsymbol{x}')$:

$$\mathcal{T}(d\boldsymbol{x}')|\boldsymbol{x}'\rangle = |\boldsymbol{x}' + d\boldsymbol{x}'\rangle.$$

The state vector on the right hand side is again an eigenstate of the position operator. Quite obviously, the vector $|\boldsymbol{x}'\rangle$ is *not* an eigenstate of the operator $\mathcal{T}(d\boldsymbol{x}')$.

The effect of an infinitesimal translation on an arbitrary state can be seen by expanding it using position eigenstates:

$$\begin{aligned} |\alpha\rangle \longrightarrow \mathcal{T}(d\boldsymbol{x}'')|\alpha\rangle &= \mathcal{T}(d\boldsymbol{x}'') \int d^3x' \, |\boldsymbol{x}'\rangle\langle\boldsymbol{x}'|\alpha\rangle \\ &= \int d^3x' \, |\boldsymbol{x}' + d\boldsymbol{x}''\rangle\langle\boldsymbol{x}'|\alpha\rangle \\ &= \int d^3x' \, |\boldsymbol{x}'\rangle\langle\boldsymbol{x}' - d\boldsymbol{x}''|\alpha\rangle, \end{aligned}$$

because $\boldsymbol{x}'$ is an ordinary integration variable.
To construct $\mathcal{T}(d\boldsymbol{x}')$ explicitely we need extra constraints:

1. it is natural to require that it preserves the normalization (i.e. the conservation of probability) of the state vectors:

   $$\langle\alpha|\alpha\rangle = \langle\alpha|\mathcal{T}^\dagger(d\boldsymbol{x}')\mathcal{T}(d\boldsymbol{x}')|\alpha\rangle.$$

   This is satisfied if $\mathcal{T}(d\boldsymbol{x}')$is unitary, i.e.

   $$\mathcal{T}^\dagger(d\boldsymbol{x}')\mathcal{T}(d\boldsymbol{x}') = 1.$$

2. we require that two consecutive translations are equivalent to a single combined transformation:

   $$\mathcal{T}(d\boldsymbol{x}')\mathcal{T}(d\boldsymbol{x}'') = \mathcal{T}(d\boldsymbol{x}' + d\boldsymbol{x}'').$$

3. the translation to the opposite direction is equivalent to the inverse of the original translation:

   $$\mathcal{T}(-d\boldsymbol{x}') = \mathcal{T}^{-1}(d\boldsymbol{x}').$$

4. we end up with the identity operator when $d\boldsymbol{x}' \to 0$:

   $$\lim_{d\boldsymbol{x}'\to 0} \mathcal{T}(d\boldsymbol{x}') = 1.$$

It is easy to see that the operator

$$\mathcal{T}(d\boldsymbol{x}') = 1 - i\boldsymbol{K} \cdot d\boldsymbol{x}',$$

where the components K_x, K_y and K_z of the vector $\boldsymbol{K}$ are *Hermitean operators*, satisfies all four conditions. Using the definition

$$\mathcal{T}(d\boldsymbol{x}')|\boldsymbol{x}'\rangle = |\boldsymbol{x}' + d\boldsymbol{x}'\rangle$$

we can show that

$$[\boldsymbol{x}, \mathcal{T}(d\boldsymbol{x}')] = d\boldsymbol{x}'.$$

Substituting the explicit reprersentation

$$\mathcal{T}(d\boldsymbol{x}') = 1 - i\boldsymbol{K} \cdot d\boldsymbol{x}'$$

it is now easy to prove the commutation relation

$$[x_i, K_j] = i\delta_{ij}.$$

The equations

$$\begin{aligned} \mathcal{T}(d\boldsymbol{x}') &= 1 - i\boldsymbol{K} \cdot d\boldsymbol{x}' \\ \mathcal{T}(d\boldsymbol{x}')|\boldsymbol{x}'\rangle &= |\boldsymbol{x}' + d\boldsymbol{x}'\rangle \end{aligned}$$

can be considered as the definition of $\boldsymbol{K}$.
One would expect the operator $\boldsymbol{K}$ to have something to do with the momentum. It is, however, not quite the momentum, because its dimension is 1/length. Writing

$$\boldsymbol{p} = \hbar \boldsymbol{K}$$

we get an operator $\boldsymbol{p}$, with dimension of momentum. We take this as the definition of the momemtum. The commutation relation

$$[x_i, K_j] = i\delta_{ij}$$

can now be written in a familiar form like

$$[x_i, p_j] = i\hbar\delta_{ij}.$$

Finite translations
Consider translation of the distance $\Delta x'$ along the x-axis:

$$\mathcal{T}(\Delta x'\hat{\boldsymbol{x}})|\boldsymbol{x}'\rangle = |\boldsymbol{x}' + \Delta x'\hat{\boldsymbol{x}}\rangle.$$

We construct this translation combining infinitesimal translations of distance $\Delta x'/N$ letting $N \to \infty$:

$$\begin{aligned}\mathcal{T}(\Delta x'\hat{\boldsymbol{x}}) &= \lim_{N\to\infty}\left(1 - \frac{ip_x\Delta x'}{N\hbar}\right)^N \\ &= \exp\left(-\frac{ip_x\Delta x'}{\hbar}\right).\end{aligned}$$

It is relatively easy to show that the translation operators satisfy

$$[\mathcal{T}(\Delta y'\hat{\boldsymbol{y}}), \mathcal{T}(\Delta x'\hat{\boldsymbol{x}})] = 0,$$

so it follows that

$$[p_y, p_x] = 0.$$

Generally

$$[p_i, p_j] = 0.$$

This commutation relation tells that it is possible to construct a state vector which is a simultaneous eigenvector of all components of the momentum operator, i.e. there exists a vector

$$|\boldsymbol{p}'\rangle \equiv |p'_x, p'_y, p'_z\rangle,$$

so that

$$p_x|\boldsymbol{p}'\rangle = p'_x|\boldsymbol{p}'\rangle, \quad p_y|\boldsymbol{p}'\rangle = p'_y|\boldsymbol{p}'\rangle, \quad p_z|\boldsymbol{p}'\rangle = p'_z|\boldsymbol{p}'\rangle.$$

The effect of the translation $\mathcal{T}(d\boldsymbol{x}')$ on an eigenstate of the momentum operator is

$$\mathcal{T}(d\boldsymbol{x}')|\boldsymbol{p}'\rangle = \left(1 - \frac{i\boldsymbol{p}\cdot d\boldsymbol{x}'}{\hbar}\right)|\boldsymbol{p}'\rangle = \left(1 - \frac{i\boldsymbol{p}'\cdot d\boldsymbol{x}'}{\hbar}\right)|\boldsymbol{p}'\rangle.$$

The state $|\boldsymbol{p}'\rangle$ is thus an eigenstate of $\mathcal{T}(d\boldsymbol{x}')$: a result, which we could have predicted because

$$[\boldsymbol{p}, \mathcal{T}(d\boldsymbol{x}')] = 0.$$

Note The eigenvalues of $\mathcal{T}(d\boldsymbol{x}')$ are complex because it is not Hermitean.

So, we have derived the *canonical commutation relations* or *fundamental commutation relations*

$$[x_i, x_j] = 0, \quad [p_i, p_j] = 0, \quad [x_i, p_j] = i\hbar\delta_{ij}.$$

Recall, that the projection of the state $|\alpha\rangle$ along the state vector $|x'\rangle$ was called the *wave function* and was denoted like $\psi_\alpha(x')$. Since the vectors $|x'\rangle$ form a complete basis the scalar product between the states $|\alpha\rangle$ and $|\beta\rangle$ can be written with the help of the wave functions as

$$\langle\beta|\alpha\rangle = \int dx'\,\langle\beta|x'\rangle\langle x'|\alpha\rangle = \int dx'\,\psi^*_\beta(x')\psi_\alpha(x'),$$

i.e. $\langle\beta|\alpha\rangle$ tells how much the wave functions overlap. If $|a'\rangle$ is an eigenstate of A we define the corresponding *eigenfunction* $u_{a'}(x')$ like

$$u_{a'}(x') = \langle x'|a'\rangle.$$

An arbitrary wave function $\psi_\alpha(x')$ can be expanded using eigenfunctions as

$$\psi_\alpha(x') = \sum_{a'} c_{a'}u_{a'}(x').$$

The matrix element $\langle\beta|A|\alpha\rangle$ of an operator A can also be expressed with the help of eigenfunctions like

$$\begin{aligned}\langle\beta|A|\alpha\rangle &= \int dx' \int dx''\,\langle\beta|x'\rangle\langle x'|A|x''\rangle\langle x''|\alpha\rangle \\ &= \int dx' \int dx''\,\psi^*_\beta(x')\langle x'|A|x''\rangle\psi_\alpha(x'').\end{aligned}$$

To apply this formula we have to evaluate the matrix elements $\langle x'|A|x''\rangle$, which in general are functions of the two variables x' and x''. When A depends only on the position operator x,

$$A = f(x),$$

the calculations are much simpler:

$$\langle\beta|f(x)|\alpha\rangle = \int dx'\,\psi^*_\beta(x')f(x')\psi_\alpha(x').$$

Note $f(x)$ on the left hand side is an operator while $f(x')$ on the right hand side is an ordinary number.

Momentum operator p in position basis $\{|\boldsymbol{x}'\rangle\}$
For simplicity we consider the one dimensional case. According to the equation

$$\begin{aligned}\mathcal{T}(d\boldsymbol{x}'')|\alpha\rangle &= \mathcal{T}(d\boldsymbol{x}'')\int d^3x'\,|\boldsymbol{x}'\rangle\langle\boldsymbol{x}'|\alpha\rangle \\ &= \int d^3x'\,|\boldsymbol{x}' + d\boldsymbol{x}''\rangle\langle\boldsymbol{x}'|\alpha\rangle \\ &= \int d^3x'\,|\boldsymbol{x}'\rangle\langle\boldsymbol{x}' - d\boldsymbol{x}''|\alpha\rangle\end{aligned}$$

we can write

$$\left(1 - \frac{ip\,dx''}{\hbar}\right)|\alpha\rangle$$

$$
\begin{aligned}
&= \int dx'\, \mathcal{T}(dx'')|x'\rangle\langle x'|\alpha\rangle \\
&= \int dx'\, |x'\rangle\langle x' - dx''|\alpha\rangle \\
&= \int dx'\, |x'\rangle \left(\langle x'|\alpha\rangle - dx'' \frac{\partial}{\partial x'}\langle x'|\alpha\rangle \right).
\end{aligned}
$$

In the last step we have expanded $\langle x' - dx''|\alpha\rangle$ as Taylor series. Comparing both sides of the equation we see that

$$
p|\alpha\rangle = \int dx'\, |x'\rangle \left(-i\hbar \frac{\partial}{\partial x'}\langle x'|\alpha\rangle \right),
$$

or, taking scalar product with a position eigenstate on both sides,

$$
\langle x'|p|\alpha\rangle = -i\hbar \frac{\partial}{\partial x'}\langle x'|\alpha\rangle.
$$

In particular, if we choose $|\alpha\rangle = |x'\rangle$ we get

$$
\langle x'|p|x''\rangle = -i\hbar \frac{\partial}{\partial x'}\delta(x' - x'').
$$

Taking scalar product with an arbitrary state vector $|\beta\rangle$ on both sides of

$$
p|\alpha\rangle = \int dx'\, |x'\rangle \left(-i\hbar \frac{\partial}{\partial x'}\langle x'|\alpha\rangle \right)
$$

we get the important relation

$$
\langle \beta|p|\alpha\rangle = \int dx' \psi^*_\beta(x') \left(-i\hbar \frac{\partial}{\partial x'} \right) \psi_\alpha(x').
$$

Just like the position eigenvalues also the momentum eigenvalues p' comprise a continuum. Analogically we can define the *momentum space wave function* as

$$
\langle p'|\alpha\rangle = \phi_\alpha(p').
$$

We can move between the momentum and configuration space representations with help of the relations

$$
\begin{aligned}
\psi_\alpha(x') &= \langle x'|\alpha\rangle = \int dp'\, \langle x'|p'\rangle\langle p'|\alpha\rangle \\
\phi_\alpha(p') &= \langle p'|\alpha\rangle = \int dx'\, \langle p'|x'\rangle\langle x'|\alpha\rangle.
\end{aligned}
$$

The transformation function $\langle x'|p'\rangle$ can be evaluated by substituting a momentum eigenvector $|p'\rangle$ for $|\alpha\rangle$ into

$$
\langle x'|p|\alpha\rangle = -i\hbar \frac{\partial}{\partial x'}\langle x'|\alpha\rangle.
$$

Then

$$
\langle x'|p|p'\rangle = p'\langle x'|p'\rangle = -i\hbar \frac{\partial}{\partial x'}\langle x'|p'\rangle.
$$

The solution of this differential equation is

$$
\langle x'|p'\rangle = C \exp\left(\frac{ip'x'}{\hbar} \right),
$$

where the normalization factor C can be determined from the identity

$$
\langle x'|x''\rangle = \int dp'\, \langle x'|p'\rangle\langle p'|x''\rangle.
$$

Here the left hand side is simply $\delta(x' - x'')$ and the integration of the left hand side gives $2\pi\hbar|C|^2\delta(x' - x'')$. Thus the transformation function is

$$
\langle x'|p'\rangle = \frac{1}{\sqrt{2\pi\hbar}} \exp\left(\frac{ip'x'}{\hbar} \right),
$$

and the relations

$$
\begin{aligned}
\psi_\alpha(x') &= \langle x'|\alpha\rangle = \int dp'\, \langle x'|p'\rangle\langle p'|\alpha\rangle \\
\phi_\alpha(p') &= \langle p'|\alpha\rangle = \int dx'\, \langle p'|x'\rangle\langle x'|\alpha\rangle.
\end{aligned}
$$

can be written as familiar Fourier transforms

$$
\begin{aligned}
\psi_\alpha(x') &= \left[\frac{1}{\sqrt{2\pi\hbar}} \right] \int dp'\, \exp\left(\frac{ip'x'}{\hbar} \right) \phi_\alpha(p') \\
\phi_\alpha(p') &= \left[\frac{1}{\sqrt{2\pi\hbar}} \right] \int dx'\, \exp\left(-\frac{ip'x'}{\hbar} \right) \psi_\alpha(x').
\end{aligned}
$$

Time evolution operator

In quantum mechanics

- unlike position, time is *not* an observable.
- there is no Hermitean operator whose eigenvalues were the time of the system.
- time appears only as a parameter, not as a measurable quantity.

So, contradictory to teachings of the relativity theory, time and position are not on equal standing. In relativistic quantum field theories the equality is restored by degrading also the position down to the parameter level.

We consider a system which at the moment t_0 is in the state $|\alpha\rangle$. When time goes on there is no reason to expect it to remain in this state. We suppose that at a later moment t the system is described by the state

$$|\alpha, t_0; t\rangle, \quad (t > t_0),$$

where the parameter t_0 reminds us that exactly at that moment the system was in the state $|\alpha\rangle$. Since the time is a continuous parameter we obviously have

$$\lim_{t\to t_0} |\alpha, t_0; t\rangle = |\alpha\rangle,$$

and can use the shorter notation

$$|\alpha, t_0; t_0\rangle = |\alpha, t_0\rangle.$$

Let's see, how state vectors evolve when time goes on:

$$|\alpha, t_0\rangle \overset{\text{evolution}}{\longrightarrow} |\alpha, t_0; t\rangle.$$

We work like we did with translations. We define the *time evolution operator* $\mathcal{U}(t, t_0)$:

$$|\alpha, t_0; t\rangle = \mathcal{U}(t, t_0)|\alpha, t_0\rangle,$$

which must satisfy physically relevant conditions.

1. Conservation of probability

We expand the state at the moment t_0 with the help of the eigenstates of an observable A:

$$|\alpha, t_0\rangle = \sum_{a'} c_{a'}(t_0)|a'\rangle.$$

At a later moment we get the expansion

$$|\alpha, t_0; t\rangle = \sum_{a'} c_{a'}(t)|a'\rangle.$$

In general, we cannot expect the probability for the system being in a specific state $|a'\rangle$ to remain constant, i.e. in most cases

$$|c_{a'}(t)| \neq |c_{a'}(t_0)|.$$

For example, when a spin $\frac{1}{2}$ particle, which at the moment t_0 is in the state $|S_x; \uparrow\rangle$, is subjected to an external constant magnetic field parallel to the z-axis, it will precess in the xy-plane: the probability for the result $\hbar/2$ in the measurement $\boxed{\text{SG}\hat{\boldsymbol{x}}}$ oscillates between 0 and 1 as a function of time. In any case, the probability for the result $\hbar/2$ *or* $-\hbar/2$ remains always as the constant 1. Generalizing, it is natural to require that

$$\sum_{a'} |c_{a'}(t_0)|^2 = \sum_{a'} |c_{a'}(t)|^2.$$

In other words, the normalization of the states does not depend on time:

$$\begin{aligned} \langle\alpha, t_0|\alpha, t_0\rangle &= \langle\alpha, t_0; t|\alpha, t_0; t\rangle \\ &= \langle\alpha, t_0|\mathcal{U}^\dagger(t, t_0)\mathcal{U}(t, t_0)|\alpha, t_0\rangle. \end{aligned}$$

This is satisfied if we require $\mathcal{U}(t, t_0)$ to be unitary, i.e.

$$\mathcal{U}^\dagger(t, t_0)\mathcal{U}(t, t_0) = 1.$$

2. Composition property

The evolution from the time t_0 to a later time t_2 should be equivalent to the evolution from the initial time t_0 to an intermediate time t_1 followed by the evolution from t_1 to the final time t_2, i.e.

$$\mathcal{U}(t_2, t_0) = \mathcal{U}(t_2, t_1)\mathcal{U}(t_1, t_0), \quad (t_2 > t_1 > t_0).$$

Like in the case of the translation operator we will first look at the infinitesimal evolution

$$|\alpha, t_0; t_0 + dt\rangle = \mathcal{U}(t_0 + dt, t_0)|\alpha, t_0\rangle.$$

Due to the continuity condition

$$\lim_{t\to t_0} |\alpha, t_0; t\rangle = |\alpha\rangle$$

we have

$$\lim_{dt\to 0} \mathcal{U}(t_0 + dt, t_0) = 1.$$

So, we can assume the deviations of the operator $\mathcal{U}(t_0 + dt, t_0)$ from the identity operator to be of the order dt. When we now set

$$\mathcal{U}(t_0 + dt, t_0) = 1 - i\Omega dt,$$

where Ω is a Hermitean operator, we see that it satisfies the composition condition

$$\mathcal{U}(t_2, t_0) = \mathcal{U}(t_2, t_1)\mathcal{U}(t_1, t_0), \quad (t_2 > t_1 > t_0),$$

is unitary and deviates from the identity operator by the term $\mathcal{O}(dt)$.

The physical meaning of Ω will be revealed when we recall that in classical mechanics the Hamiltonian generates the time evolution. From the definition

$$\mathcal{U}(t_0 + dt, t_0) = 1 - i\Omega dt$$

we see that the dimension of Ω is frequency, so it must be multiplied by a factor before associating it with the Hamiltonian operator H:

$$H = \hbar\Omega,$$

or

$$\mathcal{U}(t_0 + dt, t_0) = 1 - \frac{iH\,dt}{\hbar}.$$

The factor $\hbar$ here is not necessarily the same as the factor $\hbar$ in the case of translations. It turns out, however, that in order to recover Newton's equations of motion in the classical limit both coefficients must be equal.
Applying the composition property

$$\mathcal{U}(t_2, t_0) = \mathcal{U}(t_2, t_1)\mathcal{U}(t_1, t_0), \quad (t_2 > t_1 > t_0)$$

we get

$$\begin{aligned}\mathcal{U}(t + dt, t_0) &= \mathcal{U}(t + dt, t)\mathcal{U}(t, t_0) \\ &= \left(1 - \frac{iH\,dt}{\hbar}\right)\mathcal{U}(t, t_0),\end{aligned}$$

where the time difference $t - t_0$ does not need to be infinitesimal. This can be written as

$$\mathcal{U}(t + dt, t_0) - \mathcal{U}(t, t_0) = -i\left(\frac{H}{\hbar}\right)dt\,\mathcal{U}(t, t_0).$$

Expanding the left hand side as the Taylor series we end up with

$$i\hbar\frac{\partial}{\partial t}\mathcal{U}(t, t_0) = H\mathcal{U}(t, t_0).$$

This is the *Schrödinger equation of the time evolution operator*. Multiplying both sides by the state vector $|\alpha, t_0\rangle$ we get

$$i\hbar\frac{\partial}{\partial t}\mathcal{U}(t, t_0)|\alpha, t_0\rangle = H\mathcal{U}(t, t_0)|\alpha, t_0\rangle.$$

Since the state $|\alpha, t_0\rangle$ is independent on the time t we can write the Schrödinger equation of the state vectors in the form

$$i\hbar\frac{\partial}{\partial t}|\alpha, t_0; t\rangle = H|\alpha, t_0; t\rangle.$$

In fact, in most cases the state vector Schrödinger equation is unnecessary because all information about the dynamics of the system is contained in the time evolution operator $\mathcal{U}(t, t_0)$. When this operator is known the state of the system at any moment is obtained by applying the definition

$$|\alpha, t_0; t\rangle = \mathcal{U}(t, t_0)|\alpha, t_0\rangle,$$

We consider three cases:
(**i**) The Hamiltonian does not depend on time. For example, a spin $\frac{1}{2}$ particle in a time independent magnetic field belongs to this category. The solution of the equation

$$i\hbar\frac{\partial}{\partial t}\mathcal{U}(t, t_0) = H\mathcal{U}(t, t_0)$$

is

$$\mathcal{U}(t, t_0) = \exp\left[-\frac{iH(t - t_0)}{\hbar}\right]$$

as can be shown by expanding the exponential function as the Taylor series and differentiating term by term with respect to the time. Another way to get the solution is to compose the finite evolution from the infinitesimal ones:

$$\lim_{N\to\infty}\left[1 - \frac{(iH/\hbar(t - t_0)}{N}\right]^N = \exp\left[-\frac{iH(t - t_0)}{\hbar}\right].$$

(**ii**) The Hamiltonain H depends on time but the operators H corresponding to different moments of time commute. For example, a spin $\frac{1}{2}$ particle in the magnetic field whose strength varies but direction remains constant as a function of time. A formal solution of the equation

$$i\hbar\frac{\partial}{\partial t}\mathcal{U}(t, t_0) = H\mathcal{U}(t, t_0)$$

is now

$$\mathcal{U}(t, t_0) = \exp\left[-\left(\frac{i}{\hbar}\right)\int_{t_0}^{t} dt'\,H(t')\right],$$

which, again, can be proved by expanding the exponential function as the series.
(**iii**) The operators H evaluated at different moments of time *do not* commute For example, a spin $\frac{1}{2}$ particle in a magnetic field whose direction changes in the course of time: H is proportional to the term $\boldsymbol{S}\cdot\boldsymbol{B}$ and if now, at the moment $t = t_1$ the magnetic field is parallel to the x-axis and, at the moment $t = t_2$ parallel to the y-axis, then $H(t_1) \propto BS_x$ and $H(t_2) \propto BS_y$, or $[H(t_1), H(t_2)] \propto B^2[S_x, S_y] \neq 0$. It can be shown that the formal solution of the Schrödinger equation is now

$$\begin{aligned}&\mathcal{U}(t, t_0) = \\ &\quad 1 + \sum_{n=1}^{\infty}\left(\frac{-i}{\hbar}\right)^n\int_{t_0}^{t} dt_1\int_{t_0}^{t_1} dt_2\cdots \\ &\quad \int_{t_0}^{t_{n-1}} dt_n\,H(t_1)H(t_2)\cdots H(t_n).\end{aligned}$$

This expansion is called the *Dyson series*. We will assume that our Hamiltonians are time independent until we start working with the so called interaction picture. Suppose that A is an Hermitean operator and

$$[A, H] = 0.$$

Then the eigenstates of A are also eigenstates of H, called *energy eigenstates*. Denoting corresponding eigenvalues of the Hamiltonian as $E_{a'}$ we have

$$H|a'\rangle = E_{a'}|a'\rangle.$$

The time evolution operator can now be written with the help of these eigenstates. Choosing $t_0 = 0$ we get

$$\begin{aligned}\exp\left(-\frac{iHt}{\hbar}\right) &= \sum_{a'}\sum_{a''}|a''\rangle\langle a''|\exp\left(-\frac{iHt}{\hbar}\right)|a'\rangle\langle a'| \\ &= \sum_{a'}|a'\rangle\exp\left(-\frac{iE_{a'}t}{\hbar}\right)\langle a'|.\end{aligned}$$

Using this form for the time evolution operator we can solve every intial value problem provided that we can expand the initial state with the set $\{|a'\rangle\}$. If, for example, the initial state can be expanded as

$$|\alpha, t_0 = 0\rangle = \sum_{a'}|a'\rangle\langle a'|\alpha\rangle = \sum_{a'}c_{a'}|a'\rangle,$$

we get

$$\begin{aligned} |\alpha, t_0 = 0; t\rangle &= \exp\left(-\frac{iHt}{\hbar}\right)|\alpha, t_0 = 0\rangle \\ &= \sum_{a'} |a'\rangle\langle a'|\alpha\rangle \exp\left(-\frac{iE_{a'}t}{\hbar}\right). \end{aligned}$$

In other words, the expansion coefficients evolve in the course of time as

$$c_{a'}(t=0) \longrightarrow c_{a'}(t) = c_{a'}(t=0)\exp\left(-\frac{iE_{a'}t}{\hbar}\right).$$

So, the absolute values of the coefficients remain constant. The relative phase between different components will, however, change in the course of time because the oscillation frequencies of different components differ from each other.
As a special case we consider an initial state consisting of a single eigenstate:

$$|\alpha, t_0 = 0\rangle = |a'\rangle.$$

At some later moment this state has evolved to the state

$$|\alpha, t_0 = 0; t\rangle = |a'\rangle \exp\left(-\frac{iE_{a'}t}{\hbar}\right).$$

Hence, if the system originally is in an eigenstate of the Hamiltonian H and the operator A it stays there forever. Only the phase factor $\exp(-iE_{a'}t/\hbar)$ can vary. In this sense the observables whose corresponding operators commute with the Hamiltonian, are *constants of motion*. Observables (or operators) associated with mutually commuting operators are called *compatible*. As mentioned before, the treatment of a physical problem can in many cases be reduced to the search for a maximal set of compatible operators. If the operators $A, B, C, \ldots$ belong to this set, i.e.

$$[A, B] = [B, C] = [A, C] = \cdots = 0,$$

and if, furthermore,

$$[A, H] = [B, H] = [C, H] = \cdots = 0,$$

that is, also the Hamiltonian is compatible with other operators, then the time evolution operator can be written as

$$\exp\left(-\frac{iHt}{\hbar}\right) = \sum_{K'} |K'\rangle \exp\left(-\frac{iE_{K'}t}{\hbar}\right)\langle K'|.$$

Here K' stands for the collective index:

$$A|K'\rangle = a'|K'\rangle,\ B|K'\rangle = b'|K'\rangle,\ C|K'\rangle = c'|K'\rangle,\ \ldots$$

Thus, the quantum dynamics is completely solved (when H does not depend on time) if we only can find *a maximal set of compatible operators commuting also with the Hamiltonian*.
Let's now look at the expectation value of an operator. We first assume, that at the moment $t = 0$ the system is in an eigenstate $|a'\rangle$ of an operator A commuting with the Hamiltonian H. Suppose, we are interested in the expectation value of an operator B which does not necessarily commute either with A or with H. At the moment t the system is in the state

$$|a', t_0 = 0; t\rangle = \mathcal{U}(t, 0)|a'\rangle.$$

In this special case we have

$$\begin{aligned} \langle B\rangle &= \langle a'|\mathcal{U}^\dagger(t,0)B\mathcal{U}(t,0)|a'\rangle \\ &= \langle a'|\exp\left(\frac{iE_{a'}t}{\hbar}\right)B\exp\left(-\frac{iE_{a'}t}{\hbar}\right)|a'\rangle \\ &= \langle a'|B|a'\rangle, \end{aligned}$$

that is, the expectation value *does not depend on time*. For this reason the energy eigenstates are usually called *stationary states*
We now look at the expectation value in a superposition of energy eigenstates, in a *non stationary state*

$$|\alpha, t_0 = 0\rangle = \sum_{a'} c_{a'}|a'\rangle.$$

It is easy to see, that the expectation value of B is now

$$\langle B\rangle = \sum_{a'}\sum_{a''} c^*_{a'}c_{a''}\langle a'|B|a''\rangle \exp\left[-\frac{i(E_{a''} - E_{a'})t}{\hbar}\right].$$

This time the expectation value consists of terms which oscillate with frequences determind by the Bohr frequency condition

$$\omega_{a''a'} = \frac{E_{a''} - E_{a'}}{\hbar}.$$

As an application we look at how spin $\frac{1}{2}$ particles behave in a constant magnetic field. When we assume the magnetic moments of the particles to be $e\hbar/2m_ec$ (like electrons), the Hamiltonian is

$$H = -\left(\frac{e}{m_ec}\right)\boldsymbol{S}\cdot\boldsymbol{B}.$$

If we choose $\boldsymbol{B} \parallel \hat{\boldsymbol{z}}$, we have

$$H = -\left(\frac{eB}{m_ec}\right)S_z.$$

The operators H and S_z differ only by a constant factor, so they obviously commute and the eigenstates of S_z are also energy eigenstates with energies

$$\begin{aligned} E_\uparrow &= -\frac{e\hbar B}{2m_ec} \quad \text{for state } |S_z;\uparrow\rangle \\ E_\downarrow &= +\frac{e\hbar B}{2m_ec} \quad \text{for state } |S_z;\downarrow\rangle. \end{aligned}$$

We define the *cyclotron frequency* ω_c so that the energy difference between the states is $\hbar\omega_c$:

$$\omega_c \equiv \frac{|e|B}{m_ec}.$$

The Hamiltonian H can now be written as

$$H = \omega_c S_z,$$

when we assume that $e < 0$.
All information about the evolution of the system is contained in the operator

$$\mathcal{U}(t,0) = \exp\left(-\frac{i\omega_c S_z t}{\hbar}\right).$$

If at the moment $t = 0$ the system is in the state

$$|\alpha\rangle = c_\uparrow |S_z;\uparrow\rangle + c_\downarrow |S_z;\downarrow\rangle,$$

it is easy to see that at the moment t it is in the state

$$\begin{aligned} |\alpha, t_0 = 0; t\rangle &= c_\uparrow \exp\left(-\frac{i\omega_c t}{2}\right)|S_z;\uparrow\rangle \\ &\quad + c_\downarrow \exp\left(+\frac{i\omega_c t}{2}\right)|S_z;\downarrow\rangle. \end{aligned}$$

If the initial state happens to be $|S_z;\uparrow\rangle$, meaning that in the previous equation

$$c_\uparrow = 1, \quad c_\downarrow = 0,$$

we see that the system will stay in this state at all times. This was to be expected because the state is stationary.
We now assume that the initial state is $|S_x;\uparrow\rangle$. From the relation

$$|S_x;\uparrow\rangle = \frac{1}{\sqrt{2}}|S_z;\uparrow\rangle + \frac{1}{\sqrt{2}}|S_z;\downarrow\rangle$$

we see that

$$c_\uparrow = c_\downarrow = \frac{1}{\sqrt{2}}.$$

For the probabilities that at the moment t the system is in eigenstates of S_x we get

$$\begin{aligned} |\langle S_x;\uparrow |\alpha, t_0 = 0; t\rangle|^2 &= \cos^2\frac{\omega_c t}{2} \\ |\langle S_x;\downarrow |\alpha, t_0 = 0; t\rangle|^2 &= \sin^2\frac{\omega_c t}{2}. \end{aligned}$$

Even if the spin originally were parallel to the positive x-axis a magnetic field parallel to the z-axis makes the direction of the spin to rotate. There is a finite probability for finding the system at some later moment in the state $|S_x;\downarrow\rangle$. The sum of probabilities corresponding to different orientations is 1.
It is easy to see that the expectation values of the operator $\boldsymbol{S}$ satisfy

$$\begin{aligned} \langle S_x\rangle &= \left(\frac{\hbar}{2}\right)\cos\omega_c t \\ \langle S_y\rangle &= \left(\frac{\hbar}{2}\right)\sin\omega_c t \\ \langle S_z\rangle &= 0. \end{aligned}$$

Physically this means that the spin *precesses* in the xy-plane.

Lastly we look at how the statevectors corresponding to different times are correlated. Suppose that at the moment $t = 0$ the system is described by the state vector $|\alpha\rangle$, which in the course of time evolves to the state $|\alpha, t_0 = 0; t\rangle$. We define the *correlation amplitude* $C(t)$ as

$$\begin{aligned} C(t) &= \langle\alpha|\alpha, t_0 = 0; t\rangle \\ &= \langle\alpha|\mathcal{U}(t,0)|\alpha\rangle. \end{aligned}$$

The absolute value of the correlation amplitude tells us how much the states associated with different moments of time resemble each other.
In particular, if the initial state is an energy eigenstate $|a'\rangle$, then

$$C(t) = \exp\left(-\frac{iE_{a'}t}{\hbar}\right),$$

and the absolute value of the correlation amplitude is 1 at all times. When the initial state is a superposition of energy eigenstates we get

$$C(t) = \sum_{a'} |c_{a'}|^2 \exp\left(-\frac{iE_{a'}t}{\hbar}\right).$$

When t is relatively large the terms in the sum oscillate rapidly with different frequencies and hence most probably cancel each other. Thus we expect the correlation amplitude decreasing rather rapidly from its initial value 1 at the moment $t = 0$.
We can estimate the value of the expression

$$C(t) = \sum_{a'} |c_{a'}|^2 \exp\left(-\frac{iE_{a'}t}{\hbar}\right)$$

more concretely when we suppose that the statevectors of the system comprise so many, nearly degenerate, energy eigenvectors that we can think them almost to form a continuum. Then the summation can be replaced by the integration

$$\sum_{a'} \longrightarrow \int dE\,\rho(E), \quad c_{a'} \longrightarrow g(E)\Big|_{E\approx E_{a'}},$$

where $\rho(E)$ is the density of the energy eigenstates. The expression

$$C(t) = \sum_{a'} |c_{a'}|^2 \exp\left(-\frac{iE_{a'}t}{\hbar}\right)$$

can now be written as

$$C(t) = \int dE\,|g(E)|^2\rho(E)\exp\left(-\frac{iEt}{\hbar}\right),$$

which must satisfy the normalization condition

$$\int dE\,|g(E)|^2\rho(E) = 1.$$

In many realistic physical cases $|g(E)|^2\rho(E)$ is concentrated into a small neighborhood (size ΔE) of a

point $E = E_0$. Rewriting the integral representation as

$$C(t) = \exp\left(-\frac{iE_0t}{\hbar}\right) \times \int dE\,|g(E)|^2\rho(E)\exp\left[-\frac{i(E-E_0)t}{\hbar}\right],$$

we see that when t increases the integrand oscillates very rapidly except when the energy interval $|E - E_0|$ is small as compared with $\hbar/t$. If the interval, which satisfies $|E - E_0| \approx \hbar/t$, is much shorter than ΔE —the interval from which the integral picks up its contribution—, the correlation amplitudes practically vanishes. The characteristic time, after which the absolute value of the correlation amplitude deviates significantly from its initial value 1, is

$$t \approx \frac{\hbar}{\Delta E}.$$

Although this equation was derived for a quasi continuous energy spectrum it is also valid for the two state system in our spin precession example: the initial state $|S_x;\uparrow\rangle$ starts to lose its identity after the time $\approx 1/\omega_c = \hbar/(E_\uparrow - E_\downarrow)$ as we can see from the equation

$$|\langle S_x;\uparrow|\alpha, t_0 = 0; t\rangle|^2 = \cos^2\frac{\omega_c t}{2}.$$

As a summary we can say that due to the evolution the state vector describing the initial state of the system will not any more describe it after a time interval of order $\hbar/\Delta E$. This property is often called the *time and energy uncertainty relation*. Note, however, that this relation is of completely different character than the uncertainty relation concerning position and momentum because time is not a quantum mechanical observable.

Quantum statistics

Density operator:

$$\rho \equiv \sum_i w_i |\alpha_i\rangle\langle\alpha_i|$$

is

- Hermitean:
$$\rho^\dagger = \rho$$
- normalized:
$$\mathrm{tr}\rho = 1.$$

Density matrix:

$$\langle b''|\rho|b'\rangle = \sum_i w_i \langle b''|\alpha_i\rangle\langle\alpha_i|b'\rangle.$$

Ensemble average:

$$\begin{aligned}[A] &= \sum_{b'}\sum_{b''}\langle b''|\rho|b'\rangle\langle b'|A|b''\rangle \\ &= \mathrm{tr}(\rho A).\end{aligned}$$

Dynamics

$$|\alpha_i\rangle = |\alpha_i; t_0\rangle \longrightarrow |\alpha_i, t_0; t\rangle$$

We suppose that the occupation of states is conserved, i.e.

$$w_i = \text{constant}.$$

Now

$$\rho(t) = \sum_i w_i |\alpha_i, t_0; t\rangle\langle\alpha_i, t_0; t|,$$

so

$$\begin{aligned}i\hbar\frac{\partial\rho}{\partial t} &= \sum_i w_i \left(i\hbar\frac{\partial}{\partial t}|\alpha_i, t_0; t\rangle\right)\langle\alpha_i, t_0; t| \\ &\quad + \sum_i w_i |\alpha_i, t_0; t\rangle\left(-i\hbar\frac{\partial}{\partial t}|\alpha_i, t_0; t\rangle\right)^\dagger \\ &= H\rho - \rho H = -[\rho, H].\end{aligned}$$

Like Heisenberg's equation of motion, but wrong sign! OK, since ρ is not an observable.

Continuum

Example:

$$[A] = \int d^3x' \int d^3x''\, \langle \boldsymbol{x}''|\rho|\boldsymbol{x}'\rangle\langle\boldsymbol{x}'|A|\boldsymbol{x}''\rangle.$$

Here the density matrix is

$$\begin{aligned}\langle \boldsymbol{x}''|\rho|\boldsymbol{x}'\rangle &= \langle\boldsymbol{x}''|\left(\sum_i w_i|\alpha_i\rangle\langle\alpha_i|\right)|\boldsymbol{x}'\rangle \\ &= \sum_i w_i \psi_i(\boldsymbol{x}'')\psi_i^*(\boldsymbol{x}').\end{aligned}$$

Note

$$\langle \boldsymbol{x}'|\rho|\boldsymbol{x}'\rangle = \sum_i w_i |\psi_i(\boldsymbol{x}')|^2.$$

Thermodynamics

We define

$$\sigma = -\mathrm{tr}(\rho\ln\rho).$$

One can show that

- for a completely stochastic ensemble
$$\sigma = \ln N,$$
when N is the number of the independent states in the system.
- for a pure ensemble
$$\sigma = 0.$$

Hence σ measures disorder $\Longrightarrow$ it has something to do with the entropy.
The entropy is defined by

$$S = k\sigma.$$

In a thermodynamical equilibrium

$$\frac{\partial\rho}{\partial t} = 0,$$

so

$$[\rho, H] = 0$$

and the operators ρ and H have common eigenstates $|k\rangle$:

$$\begin{aligned}H|k\rangle &= E_k|k\rangle \\ \rho|k\rangle &= w_k|k\rangle.\end{aligned}$$

Using these eigenstates the density matrix can be represented as

$$\rho = \sum_k w_k |k\rangle\langle k|$$

and

$$\sigma = -\sum_k \rho_{kk}\ln\rho_{kk},$$

where the diagonal elements of the density matrix are

$$\rho_{kk} = w_k.$$

In the equilibrium the entropy is at maximum.
We maximize σ under conditions

- $U = [H] = \mathrm{tr}\rho H = \sum_k \rho_{kk}E_k$.
- $\mathrm{tr}\rho = 1$.

Hence

$$\begin{aligned}\delta\sigma &= -\sum_k \delta\rho_{kk}(\ln\rho_{kk} + 1) = 0 \\ \delta[H] &= \sum_k \delta\rho_{kk}E_k = 0 \\ \delta(\mathrm{tr}\rho) &= \sum_k \delta\rho_{kk} = 0.\end{aligned}$$

With the help of Lagrange multipliers we get

$$\sum_k \delta\rho_{kk}\left[(\ln\rho_{kk}+1)+\beta E_k+\gamma\right]=0,$$

so

$$\rho_{kk}=e^{-\beta E_k-\gamma-1}.$$

The normalization ($\mathrm{tr}\rho=1$) gives

$$\rho_{kk}=\frac{e^{-\beta E_k}}{\sum_l^N e^{-\beta E_l}} \quad \text{(canonical ensemble)}.$$

It turns out that

$$\beta=\frac{1}{k_B T},$$

where T is the thermodynamical temperature and k_B the Boltzmann constant.
In statistical mechanics we define *the canonical partition function* Z:

$$Z=\mathrm{tr}e^{-\beta H}=\sum_k^N e^{-\beta E_k}.$$

Now

$$\rho=\frac{e^{-\beta H}}{Z}.$$

The ensemble average can be written as

$$\begin{aligned}[A] &= \mathrm{tr}\rho A=\frac{\mathrm{tr}\left(e^{-\beta H}A\right)}{Z}\\ &= \frac{\left[\sum_k^N \langle k|A|k\rangle e^{-\beta E_k}\right]}{\sum_k^N e^{-\beta E_k}}.\end{aligned}$$

In particular we have

$$\begin{aligned}U &= [H]=\frac{\sum_k^N E_k e^{-\beta E_k}}{\sum_k^N e^{-\beta E_k}}\\ &= -\frac{\partial}{\partial\beta}(\ln Z).\end{aligned}$$

Example Electrons in a magnetic field parallel to z axis. In the basis $\{|S_z;\uparrow\rangle,|S_z;\downarrow\rangle\}$ of the eigenstates of the Hamiltonian

$$H=\omega_c S_z$$

we have

$$\rho\mapsto\frac{\begin{pmatrix} e^{-\beta\hbar\omega_c/2} & 0\\ 0 & e^{\beta\hbar\omega_c/2}\end{pmatrix}}{Z},$$

where

$$Z=e^{-\beta\hbar\omega_c/2}+e^{\beta\hbar\omega_c/2}.$$

For example the ensemble averages are

$$\begin{aligned}[S_x] &= [S_y]=0,\\ [S_z] &= -\left(\frac{\hbar}{2}\right)\tanh\left(\frac{\beta\hbar\omega_c}{2}\right).\end{aligned}$$

Angular momentum

O(3)

We consider *active* rotations.
3×3 orthogonal matrix $R \Longleftrightarrow$ rotation in$\mathcal{R}^3$.

Number of parameters

1. RR^T symmetric $\Rightarrow$ RR^T has 6 independent parameters $\Rightarrow$ orthogonality condition $RR^T = 1$ gives 6 independent equations $\Rightarrow$ R has $9 - 6 = 3$ free parameters.

2. Rotation around $\hat{\boldsymbol{n}}$ (2 angles) by the angle $\phi \Rightarrow 3$ parameters.

3. $\hat{\boldsymbol{n}}\phi$ vector $\Rightarrow$ 3 parameters.

3×3 orthogonal matrices form a group with respect to the matrix multiplication:

1. $R_1 R_2$ is orthogonal if R_1 and R_2 are orthogonnal.

2. $R_1(R_2 R_3) = (R_1 R_2)R_3$, associativity.

3. $\exists$ identity $I =$ the unit matrix.

4. if R is orthogonal, then also the inverse matrix $R^{-1} = R^T$ is orthogonal.

The group is called O(3).
Generally rotations do not commute,

$$R_1 R_2 \neq R_2 R_1,$$

so the group is non-Abelian.
Rotations around a common axis commute.
Rotation around z-axis:

$$\begin{aligned} R_z(\phi) &= \begin{pmatrix} \cos\phi & -\sin\phi & 0 \\ \sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix} \\ R_z \begin{pmatrix} x \\ y \\ z \end{pmatrix} &= \begin{pmatrix} x\cos\phi - y\sin\phi \\ x\sin\phi + y\cos\phi \\ z \end{pmatrix}. \end{aligned}$$

Infinitesimal rotations up to the order $\mathcal{O}(\epsilon^2)$:

$$\begin{aligned} R_z(\epsilon) &= \begin{pmatrix} 1 - \frac{\epsilon^2}{2} & -\epsilon & 0 \\ \epsilon & 1 - \frac{\epsilon^2}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}, \\ R_x(\epsilon) &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 - \frac{\epsilon^2}{2} & -\epsilon \\ 0 & \epsilon & 1 - \frac{\epsilon^2}{2} \end{pmatrix}, \\ R_y(\epsilon) &= \begin{pmatrix} 1 - \frac{\epsilon^2}{2} & 0 & \epsilon \\ 0 & 1 & 0 \\ -\epsilon & 0 & 1 - \frac{\epsilon^2}{2} \end{pmatrix}. \end{aligned}$$

We see that

$$\begin{aligned} R_x(\epsilon)R_y(\epsilon) - R_y(\epsilon)R_x(\epsilon) &= \begin{pmatrix} 0 & -\epsilon^2 & 0 \\ \epsilon^2 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \\ &= R_z(\epsilon^2) - 1. \end{aligned}$$

In a Hilbert space we associate

$$R \longleftrightarrow \mathcal{D}(R),$$

i.e.

$$|\alpha\rangle_R = \mathcal{D}(R)|\alpha\rangle.$$

We define the angular momentum (J) so that (we are not employing properties of the classical angular momentum $\boldsymbol{x} \times \boldsymbol{p}$)

$$\mathcal{D}(\hat{\boldsymbol{n}}, d\phi) = 1 - i\left(\frac{\boldsymbol{J}\cdot\hat{\boldsymbol{n}}}{\hbar}\right) d\phi$$

and require that the rotation operator $\mathcal{D}$

- is unitary,
- is decomposable,
- $\mathcal{D} \to 1$, when $d\phi \to 0$.

We see that $\boldsymbol{J}$ must be Hermitean, i.e.

$$\boldsymbol{J}^\dagger = \boldsymbol{J}.$$

Moreover, we require that $\mathcal{D}$ satisfies the same group properties as R, i.e.

$$\mathcal{D}_x(\epsilon)\mathcal{D}_y(\epsilon) - \mathcal{D}_y(\epsilon)\mathcal{D}_x(\epsilon) = \mathcal{D}_z(\epsilon^2) - 1.$$

Since rotations around a common axis commute a finite rotation can be constructed as

$$\begin{aligned} \mathcal{D}(\hat{\boldsymbol{n}}\phi) &= \lim_{N\to\infty}\left[1 - i\left(\frac{\boldsymbol{J}\cdot\hat{\boldsymbol{n}}}{\hbar}\right)\left(\frac{\phi}{N}\right)\right]^N \\ &= \exp\left(-\frac{i\boldsymbol{J}\cdot\hat{\boldsymbol{n}}\phi}{\hbar}\right) \\ &= 1 - i\frac{\boldsymbol{J}\cdot\hat{\boldsymbol{n}}\phi}{\hbar} - \frac{(\boldsymbol{J}\cdot\hat{\boldsymbol{n}})^2\phi^2}{2\hbar^2} + \cdots. \end{aligned}$$

We apply this up to the order $\mathcal{O}(\epsilon^2)$:

$$\begin{aligned} &\left(1 - \frac{iJ_x\epsilon}{\hbar} - \frac{J_x^2\epsilon^2}{2\hbar^2}\right)\left(1 - \frac{iJ_y\epsilon}{\hbar} - \frac{J_y^2\epsilon^2}{2\hbar^2}\right) \\ &\quad - \left(1 - \frac{iJ_y\epsilon}{\hbar} - \frac{J_y^2\epsilon^2}{2\hbar^2}\right)\left(1 - \frac{iJ_x\epsilon}{\hbar} - \frac{J_x^2\epsilon^2}{2\hbar^2}\right) \\ &= -\frac{1}{\hbar^2}J_xJ_y\epsilon^2 + \frac{1}{\hbar^2}J_yJ_x + \mathcal{O}(\epsilon^3) \\ &= 1 - i\frac{J_z\epsilon^2}{\hbar} - 1. \end{aligned}$$

We see that

$$[J_x, J_y] = i\hbar J_z.$$

Similarly for other components:

$$[J_i, J_j] = i\hbar\epsilon_{ijk}J_k.$$

We consider:

$$\begin{aligned}\langle J_x\rangle \equiv \langle\alpha|J_x|\alpha\rangle \longrightarrow \\ {}_R\langle\alpha|J_x|\alpha\rangle_R = \langle\alpha|\mathcal{D}_z^\dagger(\phi)J_x\mathcal{D}_z(\phi)|\alpha\rangle.\end{aligned}$$

We evaluate

$$\mathcal{D}_z^\dagger(\phi)J_x\mathcal{D}_z(\phi) = \exp\left(\frac{iJ_z\phi}{\hbar}\right)J_x\exp\left(-\frac{iJ_z\phi}{\hbar}\right)$$

applying the Baker-Hausdorff lemma

$$\begin{aligned}e^{iG\lambda}Ae^{-iG\lambda} = \\ A + i\lambda[G,A] + \left(\frac{i^2\lambda^2}{2!}\right)[G,[G,A]] + \cdots \\ + \left(\frac{i^n\lambda^n}{n!}\right)[G,[G,[G,\ldots[G,A]]]\ldots] + \cdots\end{aligned}$$

where G is Hermitean. So we need the commutators

$$\begin{aligned}[J_z,J_x] &= i\hbar J_y \\ [J_z,[J_z,J_x]] &= i\hbar[J_z,J_y] = \hbar^2 J_x \\ [J_z,[J_z,[J_z,J_x]]] &= \hbar^2[J_z,J_x] = i\hbar^3 J_y \\ &\vdots\end{aligned}$$

Substituting into the Baker-Hausdorff lemma we get

$$\mathcal{D}_z^\dagger(\phi)J_x\mathcal{D}_z(\phi) = J_x\cos\phi - J_y\sin\phi.$$

Thus the expectation value is

$$\langle J_x\rangle \longrightarrow {}_R\langle\alpha|J_x|\alpha\rangle_R = \langle J_x\rangle\cos\phi - \langle J_y\rangle\sin\phi.$$

Correspondingly we get for the other components

$$\begin{aligned}\langle J_y\rangle &\longrightarrow \langle J_y\rangle\cos\phi + \langle J_x\rangle\sin\phi \\ \langle J_z\rangle &\longrightarrow \langle J_z\rangle.\end{aligned}$$

We see that the components of the expectation value of the angular momentum operator transform in rotations like a vector in $\mathcal{R}^3$:

$$\langle J_k\rangle \longrightarrow \sum_l R_{kl}\langle J_l\rangle.$$

Euler angles

1. Rotate the system counterclockwise by the angle α around the z-axis. The y-axis of of the system coordinates rotates then to a new position y'.
2. Rotate the system counterclockwise by the angle β around the y'-axis. The system z-axis rotates now to a new position z'.
3. Rotate the system counterclockwise by the angle γ around the z'-axis.

Using matrices:

$$R(\alpha,\beta,\gamma) \equiv R_{z'}(\gamma)R_{y'}(\beta)R_z(\alpha).$$

Now

$$\begin{aligned}R_{y'}(\beta) &= R_z(\alpha)R_y(\beta)R_z^{-1}(\alpha) \\ R_{z'}(\gamma) &= R_{y'}(\beta)R_z(\gamma)R_{y'}^{-1}(\beta),\end{aligned}$$

so

$$\begin{aligned}R(\alpha,\beta,\gamma) &= R_{y'}(\beta)R_z(\gamma)R_{y'}^{-1}(\beta)R_{y'}(\beta)R_z(\alpha) \\ &= R_{y'}(\beta)R_z(\alpha)R_z(\gamma) \\ &= R_z(\alpha)R_y(\beta)R_z^{-1}(\alpha)R_z(\alpha)R_z(\gamma) \\ &= R_z(\alpha)R_y(\beta)R_z(\gamma).\end{aligned}$$

Correspondingly

$$\mathcal{D}(\alpha,\beta,\gamma) = \mathcal{D}_z(\alpha)\mathcal{D}_y(\beta)\mathcal{D}_z(\gamma).$$

SU(2)

In the two dimensional space

$$\{|S_z;\uparrow\rangle, |S_z;\downarrow\rangle\}$$

the spin operators

$$\begin{aligned} S_x &= \left(\frac{\hbar}{2}\right)\{(|S_z;\uparrow\rangle\langle S_z;\downarrow|) + (|S_z;\downarrow\rangle\langle S_z;\uparrow|)\} \\ S_y &= \left(\frac{i\hbar}{2}\right)\{-(|S_z;\uparrow\rangle\langle S_z;\downarrow|) + (|S_z;\downarrow\rangle\langle S_z;\uparrow|)\} \\ S_z &= \left(\frac{\hbar}{2}\right)\{(|S_z;\uparrow\rangle\langle S_z;\uparrow|) - (|S_z;\downarrow\rangle\langle S_z;\downarrow|)\} \end{aligned}$$

satisfy the angular momentum commutation relations

$$[S_x, S_y] = i\hbar S_z + \text{cyclic permutations.}$$

Thus the smallest dimension where these commutation relations can be realized is 2.
The state

$$|\alpha\rangle = |S_z;\uparrow\rangle\langle S_z;\uparrow|\alpha\rangle + |S_z;\downarrow\rangle\langle S_z;\downarrow|\alpha\rangle$$

behaves in the rotation

$$\mathcal{D}_z(\phi) = \exp\left(-\frac{iS_z\phi}{\hbar}\right)$$

like

$$\begin{aligned} \mathcal{D}_z(\phi)|\alpha\rangle &= \exp\left(-\frac{iS_z\phi}{\hbar}\right)|\alpha\rangle \\ &= e^{-i\phi/2}|S_z;\uparrow\rangle\langle S_z;\uparrow|\alpha\rangle \\ &\quad + e^{i\phi/2}|S_z;\downarrow\rangle\langle S_z;\downarrow|\alpha\rangle. \end{aligned}$$

In particular:

$$\mathcal{D}_z(2\pi)|\alpha\rangle = -|\alpha\rangle.$$

Spin precession
When the Hamiltonian is

$$H = \omega_c S_z$$

the time evolution operator is

$$\mathcal{U}(t,0) = \exp\left(-\frac{iS_z\omega_c t}{\hbar}\right) = \mathcal{D}_z(\omega_c t).$$

Looking at the equations

$$\begin{aligned} \langle J_x\rangle &\longrightarrow_R \langle J_x\rangle\cos\phi - \langle J_y\rangle\sin\phi \\ \langle J_y\rangle &\longrightarrow_R \langle J_y\rangle\cos\phi + \langle J_x\rangle\sin\phi \\ \langle J_z\rangle &\longrightarrow_R \langle J_z\rangle \end{aligned}$$

one can read that

$$\begin{aligned} \langle S_x\rangle_t &= \langle S_x\rangle_{t=0}\cos\omega_c t - \langle S_y\rangle_{t=0}\sin\omega_c t \\ \langle S_y\rangle_t &= \langle S_y\rangle_{t=0}\cos\omega_c t + \langle S_x\rangle_{t=0}\sin\omega_c t \\ \langle S_z\rangle_t &= \langle S_z\rangle_{t=0}. \end{aligned}$$

We see that

- the spin returns to its original direction after time $t = 2\pi/\omega_c$.
- the wave vector returns to its original value after time $t = 4\pi/\omega_c$.

Matrix representation
In the basis $\{|S_z;\uparrow\rangle, |S_z;\downarrow\rangle\}$ the base vectors are represented as

$$\begin{aligned} |S_z;\uparrow\rangle &\mapsto \begin{pmatrix} 1 \\ 0 \end{pmatrix} \equiv \chi_\uparrow \qquad |S_z;\downarrow\rangle \mapsto \begin{pmatrix} 0 \\ 1 \end{pmatrix} \equiv \chi_\downarrow \\ \langle S_z;\uparrow| &\mapsto (1,0) \equiv \chi_\uparrow^\dagger \qquad \langle S_z;\downarrow| \mapsto (0,1) \equiv \chi_\downarrow^\dagger, \end{aligned}$$

so an arbitrary state vector is represented as

$$\begin{aligned} |\alpha\rangle &\mapsto \begin{pmatrix} \langle S_z;\uparrow|\alpha\rangle \\ \langle S_z;\downarrow|\alpha\rangle \end{pmatrix} \\ \langle\alpha| &\mapsto (\langle\alpha|S_z;\uparrow\rangle, \langle\alpha|S_z;\downarrow\rangle). \end{aligned}$$

The column vector

$$\chi = \begin{pmatrix} \langle S_z;\uparrow|\alpha\rangle \\ \langle S_z;\downarrow|\alpha\rangle \end{pmatrix} \equiv \begin{pmatrix} c_\uparrow \\ c_\downarrow \end{pmatrix}$$

is called the *two component spinor*

Pauli's spin matrices
Pauli's spin matrices σ_i are defined via the relations

$$(S_k)_{ij} \equiv \left(\frac{\hbar}{2}\right)(\sigma_k)_{ij},$$

where the matrix elements are evaluated in the basis $\{|S_z;\uparrow\rangle, |S_z;\downarrow\rangle\}$.
For example

$$S_1 = S_x = \left(\frac{\hbar}{2}\right)\{(|S_z;\uparrow\rangle\langle S_z;\downarrow|) + (|S_z;\downarrow\rangle\langle S_z;\uparrow|)\},$$

so

$$\begin{aligned} (S_1)_{11} = (S_1)_{22} &= 0 \\ (S_1)_{12} = (S_1)_{21} &= \frac{\hbar}{2}, \end{aligned}$$

or

$$(S_1) = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.$$

Thus we get

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix},\ \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix},\ \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

The spin matrices satisfy the anticommutation relations

$$\{\sigma_i, \sigma_j\} \equiv \sigma_i\sigma_j + \sigma_j\sigma_i = 2\delta_{ij}$$

and the commutation relations

$$[\sigma_i, \sigma_j] = 2i\epsilon_{ijk}\sigma_k.$$

Moreover, we see that

$$\begin{aligned}\sigma_i^\dagger &= \sigma_i,\\ \det(\sigma_i) &= -1,\\ \mathrm{tr}(\sigma_i) &= 0.\end{aligned}$$

Often the collective vector notation

$$\boldsymbol{\sigma} \equiv \sigma_1\hat{\boldsymbol{x}} + \sigma_2\hat{\boldsymbol{y}} + \sigma_3\hat{\boldsymbol{z}}.$$

is used for spin matrices. For example we get

$$\begin{aligned}\boldsymbol{\sigma}\cdot\boldsymbol{a} &\equiv \sum_k a_k\sigma_k\\ &= \begin{pmatrix} +a_3 & a_1 - ia_2 \\ a_1 + ia_2 & -a_3 \end{pmatrix}.\end{aligned}$$

and

$$\begin{aligned}(\boldsymbol{\sigma}\cdot\boldsymbol{a})(\boldsymbol{\sigma}\cdot\boldsymbol{b}) &= \sum_{j,k}\sigma_j a_j \sigma_k b_k\\ &= \sum_{j,k}\frac{1}{2}\left(\{\sigma_j,\sigma_k\} + [\sigma_j,\sigma_k]\right)a_j b_k\\ &= \sum_{j,k}(\delta_{jk} + i\epsilon_{jki}\sigma_i)a_j b_k\\ &= \boldsymbol{a}\cdot\boldsymbol{b} + i\boldsymbol{\sigma}\cdot(\boldsymbol{a}\times\boldsymbol{b}).\end{aligned}$$

A special case of the latter formula is

$$(\boldsymbol{\sigma}\cdot\boldsymbol{a})^2 = |\boldsymbol{a}|^2.$$

Now

$$\mathcal{D}(\hat{\boldsymbol{n}},\phi) = \exp\left(-\frac{i\boldsymbol{S}\cdot\hat{\boldsymbol{n}}\phi}{\hbar}\right) \mapsto \exp\left(-\frac{i\boldsymbol{\sigma}\cdot\hat{\boldsymbol{n}}\phi}{2}\right) =$$
$$\mathbf{1}\cos\left(\frac{\phi}{2}\right) - i\boldsymbol{\sigma}\cdot\hat{\boldsymbol{n}}\sin\left(\frac{\phi}{2}\right) =$$
$$\begin{pmatrix} \cos\left(\frac{\phi}{2}\right) - in_z\sin\left(\frac{\phi}{2}\right) & (-in_x - n_y)\sin\left(\frac{\phi}{2}\right) \\ (-in_x + n_y)\sin\left(\frac{\phi}{2}\right) & \cos\left(\frac{\phi}{2}\right) + in_z\sin\left(\frac{\phi}{2}\right) \end{pmatrix}$$

and the spinors behave in rotations like

$$\chi \longrightarrow \exp\left(-\frac{i\boldsymbol{\sigma}\cdot\hat{\boldsymbol{n}}\phi}{2}\right)\chi.$$

Note the notation $\boldsymbol{\sigma}$ *does not* mean that $\boldsymbol{\sigma}$ would behave in rotations like a vector, $\sigma_k \longrightarrow {}_R\sigma_k$. Instead we have

$$\chi^\dagger\sigma_k\chi \longrightarrow \sum_l R_{kl}\chi^\dagger\sigma_l\chi.$$

For all directions $\hat{\boldsymbol{n}}$ one has

$$\exp\left(-\frac{i\boldsymbol{\sigma}\cdot\hat{\boldsymbol{n}}\phi}{2}\right)\Big|_{\phi=2\pi} = -\mathbf{1}, \quad \text{for any } \hat{\boldsymbol{n}}.$$

Euler's angles
The spinor rotation matrices corresponding to rotations around z and y axes are

$$\begin{aligned}\mathcal{D}_z(\alpha) &\mapsto \begin{pmatrix} e^{-i\alpha/2} & 0 \\ 0 & e^{i\alpha/2} \end{pmatrix}\\ \mathcal{D}_y(\beta) &\mapsto \begin{pmatrix} \cos\beta/2 & -\sin\beta/2 \\ \sin\beta/2 & \cos\beta/2 \end{pmatrix}.\end{aligned}$$

With the help of Euler's angles α, β and γ the rotation matrices can be written as

$$\mathcal{D}(\alpha,\beta,\gamma) \mapsto \mathcal{D}^{(\frac{1}{2})}(\alpha,\beta,\gamma) =$$
$$\begin{pmatrix} e^{-i(\alpha+\gamma)/2}\cos\left(\frac{\beta}{2}\right) & -e^{-i(\alpha-\gamma)/2}\sin\left(\frac{\beta}{2}\right) \\ e^{i(\alpha-\gamma)/2}\sin\left(\frac{\beta}{2}\right) & e^{i(\alpha+\gamma)/2}\cos\left(\frac{\beta}{2}\right) \end{pmatrix}.$$

We seek for the eigenspinor of the matrix $\boldsymbol{\sigma}\cdot\hat{\boldsymbol{n}}$:

$$\boldsymbol{\sigma}\cdot\hat{\boldsymbol{n}}\chi = \chi.$$

Now

$$\hat{\boldsymbol{n}} = \begin{pmatrix} \sin\beta\cos\alpha \\ \sin\beta\sin\alpha \\ \cos\beta \end{pmatrix},$$

so

$$\boldsymbol{\sigma}\cdot\hat{\boldsymbol{n}} = \begin{pmatrix} \cos\beta & \sin\beta e^{-i\alpha} \\ \sin\beta e^{i\alpha} & -\cos\beta \end{pmatrix}.$$

The state where the spin is parallel to the unit vector $\hat{\boldsymbol{n}}$, is obviously invariant under rotations

$$\mathcal{D}_{\hat{\boldsymbol{n}}}(\phi) = e^{-i\boldsymbol{S}\cdot\hat{\boldsymbol{n}}/\hbar}$$

and thus an eigenstate of the operator $\boldsymbol{S}\cdot\hat{\boldsymbol{n}}$.
This kind of state can be obtained by rotating the state $|S_z;\uparrow\rangle$

1. angle β around y axis,
2. angle α around z axis,

i.e.

$$\begin{aligned}\boldsymbol{S}\cdot\hat{\boldsymbol{n}}|\boldsymbol{S}\cdot\hat{\boldsymbol{n}};\uparrow\rangle &= \boldsymbol{S}\cdot\hat{\boldsymbol{n}}\mathcal{D}(\alpha,\beta,0)|S_z;\uparrow\rangle\\ &= \left(\frac{\hbar}{2}\right)\mathcal{D}(\alpha,\beta,0)|S_z;\uparrow\rangle\\ &= \left(\frac{\hbar}{2}\right)|\boldsymbol{S}\cdot\hat{\boldsymbol{n}};\uparrow\rangle.\end{aligned}$$

Correspondingly for spinors the vector

$$\chi = \mathcal{D}^{(\frac{1}{2})}(\alpha,\beta,0)|S_z;\uparrow\rangle = \begin{pmatrix} \cos\left(\frac{\beta}{2}\right)e^{-i\alpha/2} \\ \sin\left(\frac{\beta}{2}\right)e^{i\alpha/2} \end{pmatrix}$$

is an eigenstate of the matrix $\boldsymbol{\sigma}\cdot\hat{\boldsymbol{n}}$.

SU(2)
As a representation of rotations the 2×2-matrices

$$\mathcal{D}^{(\frac{1}{2})}(\hat{\boldsymbol{n}},\phi) = e^{-i\boldsymbol{\sigma}\cdot\hat{\boldsymbol{n}}\phi/2}$$

form obviously a group. These matrices have two characteristic properties:

1. unitarity
$$\left(\mathcal{D}^{(\frac{1}{2})}\right)^{\dagger} = \left(\mathcal{D}^{(\frac{1}{2})}\right)^{-1},$$
2. unimodularity
$$\left|\mathcal{D}^{(\frac{1}{2})}\right| = 1.$$

A unitary unimodular matrix can be written as

$$U(a,b) = \begin{pmatrix} a & b \\ -b^* & a^* \end{pmatrix}.$$

The unimodularity condition gives

$$1 = |U| = |a|^2 + |b|^2,$$

and we are left with 3 free parameters.
The unitarity condition is automatically satisfied because

$$\begin{aligned} U(a,b)^{\dagger}U(a,b) &= \begin{pmatrix} a^* & -b \\ b^* & a \end{pmatrix}\begin{pmatrix} a & b \\ -b^* & a^* \end{pmatrix} \\ &= \begin{pmatrix} |a|^2+|b|^2 & 0 \\ 0 & |a|^2+|b|^2 \end{pmatrix} = 1. \end{aligned}$$

Matrices $U(a,b)$ form a group since

- the matrix
$$U(a_1,b_1)U(a_2,b_2) = U(a_1a_2 - b_1b_2^*, a_1b_2 + a_2^*b_1)$$
is unimodular because
$$\begin{aligned} &|U(a_1a_2 - b_1b_2^*, a_1b_2 + a_2^*b_1)| = \\ &\quad |a_1a_2 - b_1b_2^*|^2 + |a_1b_2 + a_2^*b_1|^2 = 1, \end{aligned}$$
and thus also unitary.
- as a unitary matrix U has the inverse matrix:
$$U^{-1}(a,b) = U^{\dagger}(a,b) = U(a^*,-b).$$
- the unit matrix 1 is unitary and unimodular.

The group is called SU(2).
Comparing with the previous spinor representation

$$\mathcal{D}^{(\frac{1}{2})}(\hat{\boldsymbol{n}},\phi) = \begin{pmatrix} \cos\left(\frac{\phi}{2}\right) - in_z\sin\left(\frac{\phi}{2}\right) & (-in_x - n_y)\sin\left(\frac{\phi}{2}\right) \\ (-in_x + n_y)\sin\left(\frac{\phi}{2}\right) & \cos\left(\frac{\phi}{2}\right) + in_z\sin\left(\frac{\phi}{2}\right) \end{pmatrix}$$

we see that

$$\begin{aligned} \mathrm{Re}(a) &= \cos\left(\frac{\phi}{2}\right) & \mathrm{Im}(a) &= -n_z\sin\left(\frac{\phi}{2}\right) \\ \mathrm{Re}(b) &= -n_y\sin\left(\frac{\phi}{2}\right) & \mathrm{Im}(b) &= -n_x\sin\left(\frac{\phi}{2}\right). \end{aligned}$$

The complex numbers a and b are known as
Cayley-Klein's parameters.
Note O(3) and SU(2) are *not* isomorphic.
Example
In O(3): 2π- and 4π-rotations $\mapsto 1$
In SU(2): 2π-rotation $\mapsto -1$ and 4π-rotation $\mapsto 1$.
The operations $U(a,b)$ and $U(-a,-b)$ in SU(2) correspond to a single matrix of O(3). The map SU(2) $\mapsto$ O(3) is thus 2 to 1. The groups are, however, locally isomorphic.

Angular momentum algebra

It is easy to see that the operator

$$\boldsymbol{J}^2 = J_x J_x + J_y J_y + J_z J_z$$

commutes with the operators J_x, J_y and J_z,

$$[\boldsymbol{J}^2, J_i] = 0.$$

We choose the component J_z and denote the common eigenstate of the operators $\boldsymbol{J}^2$ and J_z by $|j,m\rangle$. We know (QM II) that

$$\begin{aligned} \boldsymbol{J}^2|j,m\rangle &= j(j+1)\hbar^2|j,m\rangle,\ j = 0, \frac{1}{2}, 1, \frac{3}{2}, \dots \\ J_z|j,m\rangle &= m\hbar|j,m\rangle,\ m = -j, -j+1, \dots, j-1, j. \end{aligned}$$

We define the ladder operators J_+ and J_-:

$$J_\pm \equiv J_x \pm iJ_y.$$

They satisfy the commutation relations

$$\begin{aligned} [J_+, J_-] &= 2\hbar J_z \\ [J_z, J_\pm] &= \pm\hbar J_\pm \\ \left[\boldsymbol{J}^2, J_\pm\right] &= 0. \end{aligned}$$

We see that

$$J_z J_+|j,m\rangle = \hbar J_+ J_z|j,m\rangle = (m+1)\hbar J_+|j,m\rangle$$

and

$$\boldsymbol{J}^2 J_+|j,m\rangle = J_+\boldsymbol{J}^2|j,m\rangle = j(j+1)\hbar J_+|j,m\rangle,$$

so we must have

$$J_+|j,m\rangle = c_+|j,m+1\rangle$$

The factor c_+ can be deduced from the normalization condition

$$\langle j,m|j',m'\rangle = \delta_{jj'}\delta_{mm'}.$$

We end up with

$$J_\pm|j,m\rangle = \sqrt{(j\mp m)(j\pm m+1)}\hbar|j,m\pm 1\rangle.$$

Matrix elements will be

$$\begin{aligned} \langle j',m'|\boldsymbol{J}^2|j,m\rangle &= j(j+1)\hbar^2\delta_{j'j}\delta_{m'm} \\ \langle j',m'|J_z|j,m\rangle &= m\hbar\delta_{j'j}\delta_{m'm} \\ \langle j',m'|J_\pm|j,m\rangle &= \sqrt{(j\mp m)(j\pm m+1)}\hbar\delta_{j'j}\delta_{m',m\pm 1}. \end{aligned}$$

We define *Wigner's function*:

$$\mathcal{D}^{(j)}_{m'm}(R) = \langle j,m'|\exp\left(-\frac{i\boldsymbol{J}\cdot\hat{\boldsymbol{n}}\phi}{\hbar}\right)|j,m\rangle.$$

Since

$$[\boldsymbol{J}^2, \mathcal{D}(R)] = [\boldsymbol{J}^2, \exp\left(-\frac{i\boldsymbol{J}\cdot\hat{\boldsymbol{n}}\phi}{\hbar}\right)] = 0,$$

we see that $\mathcal{D}(R)$ does not chance the j-quantum number, so it cannot have non zero matrix elements between states with different j values.

The matrix with matrix elements $\mathcal{D}^{(j)}_{m'm}(R)$ is the $(2j+1)$-dimensional irreducible representation of the rotation operator $\mathcal{D}(R)$.

The matrices $\mathcal{D}^{(j)}_{m'm}(R)$ form a group:

- The product of matrices belongs to the group:
$$\mathcal{D}^{(j)}_{m''m}(R_1R_2) = \sum_{m'} \mathcal{D}^{(j)}_{m''m'}(R_1)\mathcal{D}^{(j)}_{m'm}(R_2),$$
where R_1R_2 is the combined rotation of the rotations R_1 and R_2,
- the inverse operation belongs to the group:
$$\mathcal{D}^{(j)}_{m'm}(R^{-1}) = \mathcal{D}^{(j)^*}_{mm'}(R).$$

The state vectors $|j,m\rangle$ transform in rotations like

$$\begin{aligned} \mathcal{D}(R)|j,m\rangle &= \sum_{m'} |j,m'\rangle\langle j,m'|\mathcal{D}(R)|j,m\rangle \\ &= \sum_{m'} |j,m'\rangle\mathcal{D}^{(j)}_{m'm}(R). \end{aligned}$$

With the help of the Euler angles

$$\begin{aligned} &\mathcal{D}^{(j)}_{m'm}(R) = \\ &\quad \langle j,m'|\exp\left(-\frac{iJ_z\alpha}{\hbar}\right)\exp\left(-\frac{iJ_y\beta}{\hbar}\right)\exp\left(-\frac{iJ_z\gamma}{\hbar}\right)|j,m\rangle \\ &\quad = e^{-i(m'\alpha+m\gamma)}d^{(j)}_{m'm}(\beta), \end{aligned}$$

where

$$d^{(j)}_{m'm}(\beta) \equiv \langle j,m'|\exp\left(-\frac{iJ_y\beta}{\hbar}\right)|j,m\rangle.$$

Functions $d^{(j)}_{m'm}$ can be evaluated using *Wigner's formula*

$$\begin{aligned} &d^{(j)}_{m'm}(\beta) = \\ &\quad \sum_k (-1)^{k-m+m'} \\ &\quad \times \frac{\sqrt{(j+m)!(j-m)!(j+m')!(j-m')!}}{(j+m-k)!k!(j-k-m')!(k-m+m')!} \\ &\quad \times \left(\cos\frac{\beta}{2}\right)^{2j-2k+m-m'} \times \left(\sin\frac{\beta}{2}\right)^{2k-m+m'}. \end{aligned}$$

Orbital angular momentum

The components of the classically analogous operator $\boldsymbol{L} = \boldsymbol{x}\times\boldsymbol{p}$ satisfy the commutation relations

$$[L_i, L_j] = i\epsilon_{ijk}\hbar L_k.$$

Using the spherical coordinates to label the position eigenstates,

$$|\boldsymbol{x}'\rangle = |r,\theta,\phi\rangle,$$

one can show that

$$\begin{aligned} \langle\boldsymbol{x}'|L_z|\alpha\rangle &= -i\hbar\frac{\partial}{\partial\phi}\langle\boldsymbol{x}'|\alpha\rangle \\ \langle\boldsymbol{x}'|L_x|\alpha\rangle &= -i\hbar\left(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)\langle\boldsymbol{x}'|\alpha\rangle \\ \langle\boldsymbol{x}'|L_y|\alpha\rangle &= -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)\langle\boldsymbol{x}'|\alpha\rangle \\ \langle\boldsymbol{x}'|L_\pm|\alpha\rangle &= -i\hbar e^{\pm i\phi}\left(\pm i\frac{\partial}{\partial\theta} - \cot\theta\frac{\partial}{\partial\phi}\right)\langle\boldsymbol{x}'|\alpha\rangle \\ \langle\boldsymbol{x}'|\boldsymbol{L}^2|\alpha\rangle &= -\hbar^2\left[\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\right] \\ &\quad \times\langle\boldsymbol{x}'|\alpha\rangle. \end{aligned}$$

We denote the common eigenstate of the operators $\boldsymbol{L}^2$ and L_z by the ket-vector $|l,m\rangle$, i.e.

$$\begin{aligned} L_z|l,m\rangle &= m\hbar|l,m\rangle \\ \boldsymbol{L}^2|l,m\rangle &= l(l+1)\hbar^2|l,m\rangle. \end{aligned}$$

Since $\mathcal{R}^3$ can be represented as the direct product

$$\mathcal{R}^3 = \mathcal{R} \times \Omega,$$

where Ω is the surface of the unit sphere (position=distance from the origin and direction) the position eigenstates can be written correspondingly as

$$|\boldsymbol{x}'\rangle = |r\rangle|\hat{\boldsymbol{n}}\rangle.$$

Here the state vectors $|\hat{\boldsymbol{n}}\rangle$ form a complete basis on the surface of the sphere, i.e.

$$\int d\Omega_{\hat{\boldsymbol{n}}}\, |\hat{\boldsymbol{n}}\rangle\langle\hat{\boldsymbol{n}}| = 1.$$

We define the spherical harmonic function:

$$Y_l^m(\theta,\phi) = Y_l^m(\hat{\boldsymbol{n}}) = \langle\hat{\boldsymbol{n}}|l,m\rangle.$$

The scalar product of the vector $\langle\hat{\boldsymbol{n}}|$ with the equations

$$\begin{aligned} L_z|l,m\rangle &= m\hbar|l,m\rangle \\ \boldsymbol{L}^2|l,m\rangle &= l(l+1)\hbar^2|l,m\rangle \end{aligned}$$

gives

$$-i\hbar\frac{\partial}{\partial\phi}Y_l^m(\theta,\phi) = m\hbar Y_l^m(\theta,\phi)$$

and

$$\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + l(l+1)\right]Y_l^m = 0.$$

Y_l^m and $\mathcal{D}^{(l)}$
The state

$$|\hat{\boldsymbol{n}}\rangle = |\theta,\phi\rangle$$

is obtained from the state $|\hat{\boldsymbol{z}}\rangle$ rotating it first by the angle θ around y-axis and then by the angle ϕ around z-axis:

$$\begin{aligned} |\hat{\boldsymbol{n}}\rangle &= \mathcal{D}(R)|\hat{\boldsymbol{z}}\rangle \\ &= \mathcal{D}(\alpha=\phi,\beta=\theta,\gamma=0)|\hat{\boldsymbol{z}}\rangle \\ &= \sum_{l,m}\mathcal{D}(\phi,\theta,0)|l,m\rangle\langle l,m|\hat{\boldsymbol{z}}\rangle. \end{aligned}$$

Furthermore

$$\langle l,m|\hat{\boldsymbol{n}}\rangle = Y_l^{m*}(\theta,\phi) = \sum_m \mathcal{D}^{(l)}_{m'm}(\phi,\theta,0)\langle l,m|\hat{\boldsymbol{z}}\rangle.$$

Now

$$\langle l,m|\hat{\boldsymbol{z}}\rangle = Y_l^{m*}(0,\phi) = \sqrt{\frac{(2l+1)}{4\pi}}\delta_{m0},$$

so

$$Y_l^{m*}(\theta,\phi) = \sqrt{\frac{(2l+1)}{4\pi}}\mathcal{D}^{(l)}_{m0}(\phi,\theta,\gamma=0)$$

or

$$\mathcal{D}^{(l)}_{m0}(\alpha,\beta,0) = \sqrt{\frac{4\pi}{(2l+1)}}Y_l^{m*}(\theta,\phi)\Big|_{\beta,\alpha}.$$

As a special case

$$\mathcal{D}^{(l)}_{00}(\theta,\phi,0) = d^{(l)}_{00}(\theta) = P_l(\cos\theta).$$

Coupling of angular momenta
We consider two Hilbert spaces $\mathcal{H}_1$ and $\mathcal{H}_2$. If now A_i is an operator in the space $\mathcal{H}_i$, the notation $A_1 \otimes A_2$ means the operator

$$A_1 \otimes A_2|\alpha\rangle_1 \otimes |\beta\rangle_2 = (A_1|\alpha\rangle_1) \otimes (A_2|\beta\rangle_2)$$

in the product space. Here $|\alpha\rangle_i \in \mathcal{H}_i$. In particular,

$$A_1 \otimes 1_2|\alpha\rangle_1 \otimes |\beta\rangle_2 = (A_1|\alpha\rangle_1) \otimes |\beta\rangle_2,$$

where 1_i is the identity operator of the space $\mathcal{H}_i$. Correspondingly $1_1 \otimes A_2$ operates only in the subspace $\mathcal{H}_2$ of the product space. Usually the subspace of the identity operators, or even the identity operator itself, is not shown, for example

$$A_1 \otimes 1_2 = A_1 \otimes 1 = A_1.$$

It is easy to verify that operators operating in different subspace commute, i.e.

$$[A_1 \otimes 1_2, 1_1 \otimes A_2] = [A_1, A_2] = 0.$$

In particular we consider two angular momenta $\boldsymbol{J_1}$ and $\boldsymbol{J_2}$ operating in two different Hilbert spaces. They commute:

$$[J_{1i}, J_{2j}] = 0.$$

The infinitesimal rotation affecting both Hilbert spaces is

$$\left(1 - \frac{i\boldsymbol{J}_1\cdot\hat{\boldsymbol{n}}\delta\phi}{\hbar}\right) \otimes \left(1 - \frac{i\boldsymbol{J}_2\cdot\hat{\boldsymbol{n}}\delta\phi}{\hbar}\right) = 1 - \frac{i(\boldsymbol{J}_1\otimes 1 + 1\otimes\boldsymbol{J}_2)\cdot\hat{\boldsymbol{n}}\delta\phi}{\hbar}.$$

The components of the total angular momentum

$$\boldsymbol{J} = \boldsymbol{J}_1 \otimes 1 + 1 \otimes \boldsymbol{J}_2 = \boldsymbol{J}_1 + \boldsymbol{J}_2$$

obey the commutation relations

$$[J_i, J_j] = i\hbar\epsilon_{ijk}J_k,$$

i.e. $\boldsymbol{J}$ *is angular momentum.*
A finite rotation is constructed analogously:

$$\mathcal{D}_1(R) \otimes \mathcal{D}_2(R) = \exp\left(-\frac{\boldsymbol{J}_1\cdot\hat{\boldsymbol{n}}\phi}{\hbar}\right) \otimes \exp\left(-\frac{\boldsymbol{J}_2\cdot\hat{\boldsymbol{n}}\phi}{\hbar}\right).$$

Base vectors of the whole system
We seek in the product space $\{|j_1m_1\rangle \otimes |j_2m_2\rangle\}$ for the maximal set of commuting operators.
(i) $\boldsymbol{J}_1^2$, $\boldsymbol{J}_2^2$, J_{1z} and J_{2z}.

Their common eigenstates are simply direct products

$$|j_1 j_2; m_1 m_2\rangle \equiv |j_1, m_1\rangle \otimes |j_2, m_2\rangle.$$

If j_1 and j_2 can be deduced from the context we often denote

$$|m_1 m_2\rangle = |j_1 j_2; m_1 m_2\rangle.$$

The quantum numbers are obtained from the (eigen)equations

$$\begin{aligned}
\boldsymbol{J}_1^2|j_1 j_2; m_1 m_2\rangle &= j_1(j_1+1)\hbar^2|j_1 j_2; m_1 m_2\rangle \\
J_{1z}|j_1 j_2; m_1 m_2\rangle &= m_1\hbar|j_1 j_2; m_1 m_2\rangle \\
\boldsymbol{J}_2^2|j_1 j_2; m_1 m_2\rangle &= j_2(j_2+1)\hbar^2|j_1 j_2; m_1 m_2\rangle \\
J_{2z}|j_1 j_2; m_1 m_2\rangle &= m_2\hbar|j_1 j_2; m_1 m_2\rangle.
\end{aligned}$$

(ii) $\boldsymbol{J}^2$, $\boldsymbol{J}_1^2$, $\boldsymbol{J}_2^2$ and J_z.
Their common eigenstate is denoted as

$$|j_1 j_2; jm\rangle$$

or shortly

$$|jm\rangle = |j_1 j_2; jm\rangle$$

if the quantum numbers j_1 and j_2 can be deduced from the context. The quantum numbers are obtained from the equations

$$\begin{aligned}
\boldsymbol{J}_1^2|j_1 j_2; jm\rangle &= j_1(j_1+1)\hbar^2|j_1 j_2; jm\rangle \\
\boldsymbol{J}_2^2|j_1 j_2; jm\rangle &= j_2(j_2+1)\hbar^2|j_1 j_2; jm\rangle \\
\boldsymbol{J}^2|j_1 j_2; jm\rangle &= j(j+1)\hbar^2|j_1 j_2; jm\rangle \\
J_z|j_1 j_2; jm\rangle &= m\hbar|j_1 j_2; jm\rangle.
\end{aligned}$$

Now

$$[\boldsymbol{J}^2, J_{1z}] \neq 0, \quad [\boldsymbol{J}^2, J_{2z}] \neq 0,$$

so we cannot add to the set (i) the operator $\boldsymbol{J}^2$, nor to the set (ii) the operators J_{1z} or J_{2z}. Both sets are thus maximal and the corresponding bases complete (and orthonormal), i.e.

$$\begin{aligned}
\sum_{j_1 j_2}\sum_{m_1 m_2} |j_1 j_2; m_1 m_2\rangle\langle j_1 j_2; m_1 m_2| &= 1 \\
\sum_{j_1 j_2}\sum_{jm} |j_1 j_2; jm\rangle\langle j_1 j_2; jm| &= 1.
\end{aligned}$$

In the subspace where the quantum numbers j_1 and j_2 are fixed we have the completeness relations

$$\begin{aligned}
\sum_{m_1 m_2} |j_1 j_2; m_1 m_2\rangle\langle j_1 j_2; m_1 m_2| &= 1 \\
\sum_{jm} |j_1 j_2; jm\rangle\langle j_1 j_2; jm| &= 1.
\end{aligned}$$

One can go from the basis (i) to the basis (ii) via the unitary transformation

$$|j_1 j_2; jm\rangle = \sum_{m_1 m_2} |j_1 j_2; m_1 m_2\rangle\langle j_1 j_2; m_1 m_2|j_1 j_2; jm\rangle,$$

so also the transformation matrix

$$(C)_{jm,m_1 m_2} = \langle j_1 j_2; m_1 m_2|j_1 j_2; jm\rangle$$

is unitary. The elements $\langle j_1 j_2; m_1 m_2|j_1 j_2; jm\rangle$ of the transformation matrix are called *Clebsch-Gordan's coefficients.*
Since

$$J_z = J_{1z} + J_{2z},$$

we must have

$$m = m_1 + m_2,$$

so the Clebsch-Gordan coefficients satisfy the condition

$$\langle j_1 j_2; m_1 m_2|j_1 j_2; jm\rangle = 0, \text{ if } m \neq m_1 + m_2.$$

Further, we must have (QM II)

$$|j_1 - j_2| \leq j \leq j_1 + j_2.$$

It turns out, that the C-G coefficients can be chosen to be real, so the transformation matrix C is in fact orthogonal:

$$\begin{aligned}
&\sum_{jm}\langle j_1 j_2; m_1 m_2|j_1 j_2; jm\rangle\langle j_1 j_2; m_1' m_2'|j_1 j_2; jm\rangle \\
&\quad = \delta_{m_1 m_1'}\delta_{m_2 m_2'} \\
&\sum_{m_1 m_2} \langle j_1 j_2; m_1 m_2|j_1 j_2; jm\rangle\langle j_1 j_2; m_1 m_2|j_1 j_2; j'm'\rangle \\
&\quad = \delta_{jj'}\delta_{mm'}.
\end{aligned}$$

As a special case ($j' = j$ and $m' = m = m_1 + m_2$) we get the normalization condition

$$\sum_{m_1 m_2} |\langle j_1 j_2; m_1 m_2|j_1 j_2; jm\rangle|^2 = 1.$$

Recursion formulas
Operating with the ladder operators to the state $|j_1 j_2; jm\rangle$ we get

$$\begin{aligned}
&J_\pm|j_1 j_2; jm\rangle = \\
&\quad (J_{1\pm} + J_{2\pm}) \sum_{m_1 m_2} |j_1 j_2; m_1 m_2\rangle \\
&\qquad \times\langle j_1 j_2; m_1 m_2|j_1 j_2; jm\rangle,
\end{aligned}$$

or

$$\begin{aligned}
&\sqrt{(j\mp m)(j\pm m+1)}|j_1 j_2; j, m\pm 1\rangle \\
&\quad = \sum_{m_1'}\sum_{m_2'}\Big(\sqrt{(j_1\mp m_1')(j_1\pm m_1'+1)} \\
&\qquad \times|j_1 j_2; m_1'\pm 1, m_2'\rangle \\
&\qquad + \sqrt{(j_2\pm m_2')(j_2\pm m_2'+1)} \\
&\qquad \times|j_1 j_2; m_1', m_2'\pm 1\rangle\Big) \\
&\qquad \times\langle j_1 j_2; m_1' m_2'|j_1 j_2; jm\rangle.
\end{aligned}$$

Taking the scalar product on the both sides with the vector $\langle j_1 j_2; m_1 m_2|$ we get

$$\begin{aligned}
&\sqrt{(j\mp m)(j\pm m+1)}\langle j_1 j_2; m_1 m_2|j_1 j_2; j, m\pm 1\rangle \\
&\quad = \sqrt{(j_1\mp m_1+1)(j_1\pm m_1)} \\
&\qquad \times\langle j_1 j_2; m_1\mp 1, m_2|j_1 j_2; jm\rangle \\
&\qquad + \sqrt{(j_2\mp m_2+1)(j_2\pm m_2)} \\
&\qquad \times\langle j_1 j_2; m_1, m_2\mp 1|j_1 j_2; jm\rangle.
\end{aligned}$$

The Clebsch-Gordan coefficients are determined uniquely by

1. the recursion formulas.
2. the normalization condition

$$\sum_{m_1 m_2} |\langle j_1 j_2; m_1 m_2 | j_1 j_2; jm\rangle|^2 = 1.$$

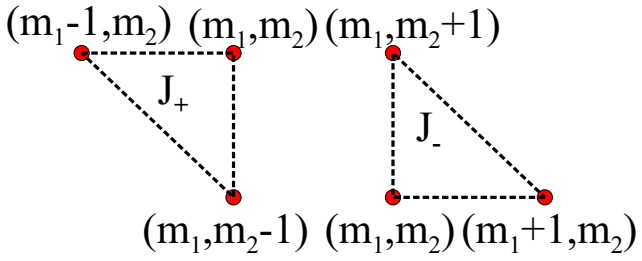
3. the sign conventions, for example

$$\langle j_1 j_2; j'm' | J_{1z} | j_1 j_2; jm\rangle \geq 0.$$

Note Due to the sign conventions the order of the coupling is essential:

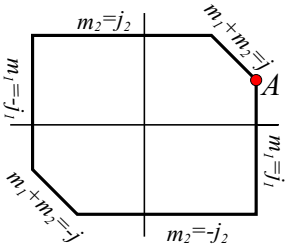
$$|j_1 j_2; jm\rangle = \pm |j_2 j_1; jm\rangle.$$

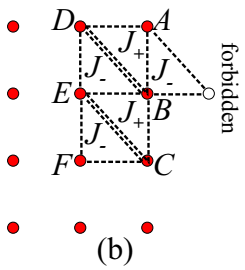
Graphical representation of recursion formulas



Recursion formula in $m_1 m_2$-plane
We fix j_1, j_2 and j. Then

$$|m_1| \leq j_1, \quad |m_2| \leq j_2, \quad |m_1 + m_2| \leq j.$$



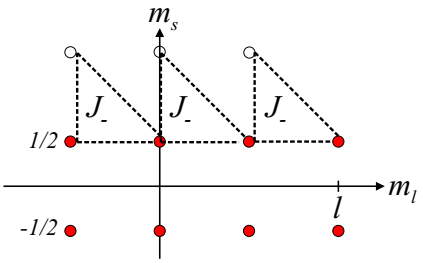


Using recursion formulas
We see that

1. every C-G coefficient depends on A,
2. the normalization condition determines the absolute value of A,
3. the sign is obtained from the sign conventions.

Example $\boldsymbol{L} + \boldsymbol{S}$-coupling.
Now

$$\begin{aligned} j_1 &= l = 0, 1, 2, \ldots \\ m_1 &= m_l = -l, -l+1, \ldots, l-1, l \\ j_2 &= s = \frac{1}{2} \\ m_2 &= m_s = \pm\frac{1}{2} \\ j &= \begin{cases} l \pm \frac{1}{2}, & \text{when } l > 0 \\ \frac{1}{2}, & \text{when } l = 0. \end{cases} \end{aligned}$$



Recursion when $j_1 = l$ and $j_2 = s = 1/2$
Using the selection rule

$$m_1 = m_l = m - \frac{1}{2}, \quad m_2 = m_s = \frac{1}{2}$$

and the shorthand notation the J_--recursion gives

$$\begin{aligned} &\sqrt{(l + \tfrac{1}{2} + m + 1)(l + \tfrac{1}{2} - m)}\langle m - \tfrac{1}{2}, \tfrac{1}{2} | l + \tfrac{1}{2}, m\rangle \\ &\quad = \sqrt{(l + m + \tfrac{1}{2})(l - m + \tfrac{1}{2})} \\ &\qquad \times \langle m + \tfrac{1}{2}, \tfrac{1}{2} | l + \tfrac{1}{2}, m + 1\rangle, \end{aligned}$$

or

$$\langle m - \tfrac{1}{2}, \tfrac{1}{2} | l + \tfrac{1}{2}, m\rangle = \sqrt{\frac{l + m + \frac{1}{2}}{l + m + \frac{3}{2}}} \langle m + \tfrac{1}{2}, \tfrac{1}{2} | l + \tfrac{1}{2}, m + 1\rangle.$$

Applying the same recursion repeatedly we have

$$\begin{aligned} &\langle m - \tfrac{1}{2}, \tfrac{1}{2} | l + \tfrac{1}{2}, m\rangle \\ &\quad = \sqrt{\frac{l + m + \frac{1}{2}}{l + m + \frac{3}{2}}} \sqrt{\frac{l + m + \frac{3}{2}}{l + m + \frac{5}{2}}} \langle m + \tfrac{3}{2}, \tfrac{1}{2} | l + \tfrac{1}{2}, m + 2\rangle \\ &\quad = \sqrt{\frac{l + m + \frac{1}{2}}{l + m + \frac{3}{2}}} \sqrt{\frac{l + m + \frac{3}{2}}{l + m + \frac{5}{2}}} \sqrt{\frac{l + m + \frac{5}{2}}{l + m + \frac{7}{2}}} \\ &\qquad \langle m + \tfrac{5}{2}, \tfrac{1}{2} | l + \tfrac{1}{2}, m + 3\rangle \\ &\qquad = \\ &\qquad \vdots \\ &\quad = \sqrt{\frac{l + m + \frac{1}{2}}{2l + 1}} \langle l, \tfrac{1}{2} | l + \tfrac{1}{2}, l + \tfrac{1}{2}\rangle. \end{aligned}$$

If $j = j_{\max} = j_1 + j_2$ and $m = m_{\max} = j_1 + j_2$ one must have

$$\begin{aligned} &|j_1 j_2; jm\rangle = \\ &\qquad \langle j_1 j_2; m_1 = j_1, m_2 = j_2 | j_1 j_2; jm\rangle |j_1 m_1\rangle |j_2 m_2\rangle. \end{aligned}$$

Now the normalization condition

$$|\langle j_1 j_2; m_1 = j_1, m_2 = j_2 | j_1 j_2; jm\rangle|^2 = 1$$

and the sign convention give

$$\langle j_1 j_2; m_1 = j_1, m_2 = j_2 | j_1 j_2; jm\rangle = 1.$$

Thus, in the case of the spin-orbit coupling,

$$\langle l, \tfrac{1}{2} | l + \tfrac{1}{2}, l + \tfrac{1}{2}\rangle = 1,$$

or

$$\langle m - \tfrac{1}{2}, \tfrac{1}{2} | l + \tfrac{1}{2}, m\rangle = \sqrt{\frac{l + m + \frac{1}{2}}{2l + 1}}.$$

With the help of the recursion relations, normalization condition and sign convention the rest of the C-G coefficients can be evaluated, too. We get

$$\begin{pmatrix} |j = l + \frac{1}{2}, m\rangle \\ |j = l - \frac{1}{2}, m\rangle \end{pmatrix} = \begin{pmatrix} \sqrt{\frac{l + m + \frac{1}{2}}{2l + 1}} & \sqrt{\frac{l - m + \frac{1}{2}}{2l + 1}} \\ -\sqrt{\frac{l - m + \frac{1}{2}}{2l + 1}} & \sqrt{\frac{l + m + \frac{1}{2}}{2l + 1}} \end{pmatrix} \begin{pmatrix} |m_l = m - \frac{1}{2}, m_s = \frac{1}{2}\rangle \\ |m_l = m + \frac{1}{2}, m_s = -\frac{1}{2}\rangle \end{pmatrix}.$$

Rotation matrices
If $\mathcal{D}^{(j_1)}(R)$ is a rotation matrix in the base $\{|j_1 m_1\rangle | m_1 = -j_1, \ldots, j_1\}$ and $\mathcal{D}^{(j_2)}(R)$ a rotation matrix in the base $\{|j_2 m_2\rangle | m_2 = -j_2, \ldots, j_2\}$, then $\mathcal{D}^{(j_1)}(R) \otimes \mathcal{D}^{(j_2)}(R)$ is a rotation matrix in the $(2j_1 + 1) \times (2j_2 + 1)$-dimensional base $\{|j_1, m_1\rangle \otimes |j_2, m_2\rangle\}$. Selecting suitable superpositions of the vectors $|j_1, m_1\rangle \otimes |j_2, m_2\rangle$ the matrix takes the form like

$$\mathcal{D}^{(j_1)}(R) \otimes \mathcal{D}^{(j_2)}(R) \longrightarrow \begin{pmatrix} \boxed{\mathcal{D}^{(j_1+j_2)}} & & & 0 \\ & \boxed{\mathcal{D}^{(j_1+j_2-1)}} & & \\ & & \ddots & \\ 0 & & & \boxed{\mathcal{D}^{(|j_1-j_2|)}} \end{pmatrix}.$$

One can thus write

$$\mathcal{D}^{(j_1)} \otimes \mathcal{D}^{(j_2)} = \mathcal{D}^{(j_1+j_2)} \oplus \mathcal{D}^{(j_1+j_2-1)} \oplus \cdots \oplus \mathcal{D}^{(|j_1-j_2|)}.$$

As a check we can calculate the dimensions:

$$\begin{aligned}(2j_1 + 1)(2j_2 + 1) = \\ 2(j_1 + j_2) + 1 + 2(j_1 + j_2 - 1) + 1 \\ + \cdots + 2|j_1 - j_2| + 1.\end{aligned}$$

The matrix elements of the rotation operator satisfy

$$\begin{aligned}&\langle j_1 j_2; m_1 m_2 | \mathcal{D}(R) | j_1 j_2; m_1' m_2'\rangle \\ &\quad = \langle j_1 m_1 | \mathcal{D}(R) | j_1 m_1'\rangle \langle j_2 m_2 | \mathcal{D}(R) | j_2 m_2'\rangle \\ &\quad = \mathcal{D}^{(j_1)}_{m_1 m_1'}(R) \mathcal{D}^{(j_2)}_{m_2 m_2'}(R).\end{aligned}$$

On the other hand we have

$$\begin{aligned}&\langle j_1 j_2; m_1 m_2 | \mathcal{D}(R) | j_1 j_2; m_1' m_2'\rangle \\ &\quad = \sum_{jm} \sum_{j'm'} \langle j_1 j_2; m_1 m_2 | j_1 j_2; jm\rangle \\ &\quad \times \langle j_1 j_2; jm | \mathcal{D}(R) | j_1 j_2; j'm'\rangle \\ &\quad \times \langle j_1 j_2; j'm' | j_1 j_2; m_1' m_2'\rangle \\ &\quad = \sum_{jm} \sum_{j'm'} \langle j_1 j_2; m_1 m_2 | j_1 j_2; jm\rangle \mathcal{D}^{(j)}_{mm'}(R) \delta_{jj'} \\ &\quad \times \langle j_1 j_2; m_1' m_2' | j_1 j_2; j'm'\rangle.\end{aligned}$$

We end up with the *Clebsch-Gordan series*

$$\begin{aligned}&\mathcal{D}^{(j_1)}_{m_1 m_1'}(R) \mathcal{D}^{(j_2)}_{m_2 m_2'}(R) = \\ &\quad \sum_j \sum_m \sum_{m'} \langle j_1 j_2; m_1 m_2 | j_1 j_2; jm\rangle \\ &\quad \times \langle j_1 j_2; m_1' m_2' | j_1 j_2; jm'\rangle \mathcal{D}^{(j)}_{mm'}(R).\end{aligned}$$

As an application we have

$$\begin{aligned}&\int d\Omega Y_l^{m*}(\theta, \phi) Y_{l_1}^{m_1}(\theta, \phi) Y_{l_2}^{m_2}(\theta, \phi) \\ &\quad = \sqrt{\frac{(2l_1 + 1)(2l_2 + 1)}{4\pi(2l + 1)}} \\ &\quad \times \langle l_1 l_2; 00 | l_1 l_2; l0\rangle \langle l_1 l_2; m_1 m_2 | l_1 l_2; lm\rangle.\end{aligned}$$

$3j$- $6j$- and $9j$-symbols

The Clebsch-Gordan coefficients obey certain symmetry relations, like

$$\begin{aligned}
&\langle j_1 j_2; m_1 m_2 | j_1 j_2; jm\rangle \\
&\quad = (-1)^{j_1+j_2-j}\langle j_2 j_1; m_2 m_1 | j_2 j_1; jm\rangle \\
&\langle j_1 j_2; m_1 m_2 | j_1 j_2; j_3 m_3\rangle \\
&\quad = (-1)^{j_2+m_2}\sqrt{\frac{2j_3+1}{2j_1+1}}\langle j_2 j_3; -m_2, m_3 | j_2 j_3; j_1 m_1\rangle \\
&\langle j_1 j_2; m_1 m_2 | j_1 j_2; j_3 m_3\rangle \\
&\quad = (-1)^{j_1-m_1}\sqrt{\frac{2j_3+1}{2j_2+1}}\langle j_3 j_1; m_3, -m_1 | j_3 j_1; j_2 m_2\rangle \\
&\langle j_1 j_2; m_1 m_2 | j_1 j_2; j_3 m_3\rangle \\
&\quad = (-1)^{j_1+j_2-j_3}\langle j_1 j_2; -m_1, -m_2 | j_1 j_2; j_3, -m_3\rangle.
\end{aligned}$$

Note The first relation shows that the coupling order is essential.

We define more symmetric $3j$*-symbols*:

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \equiv \frac{(-1)^{j_1-j_2-m_2}}{\sqrt{2j_3+1}}\langle j_1 j_2; m_1 m_2 | j_1 j_2; j_3, -m_3\rangle.$$

They satisfy

$$\begin{aligned}
&\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \\
&\quad = \begin{pmatrix} j_2 & j_3 & j_1 \\ m_2 & m_3 & m_1 \end{pmatrix} = \begin{pmatrix} j_3 & j_1 & j_2 \\ m_3 & m_1 & m_2 \end{pmatrix} \\
&(-1)^{j_1+j_2+j_3}\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \begin{pmatrix} j_2 & j_1 & j_3 \\ m_2 & m_1 & m_3 \end{pmatrix} \\
&\quad = \begin{pmatrix} j_1 & j_3 & j_2 \\ m_1 & m_3 & m_2 \end{pmatrix} = \begin{pmatrix} j_3 & j_2 & j_1 \\ m_3 & m_2 & m_1 \end{pmatrix} \\
&\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \\
&\quad = (-1)^{j_1+j_2+j_3}\begin{pmatrix} j_1 & j_2 & j_3 \\ -m_1 & -m_2 & -m_3 \end{pmatrix}.
\end{aligned}$$

As an application, we see that the coefficients

$$\begin{pmatrix} \frac{3}{2} & \frac{3}{2} & 2 \\ \frac{1}{2} & \frac{1}{2} & -1 \end{pmatrix}, \quad \begin{pmatrix} 2 & 2 & 3 \\ 1 & 1 & -2 \end{pmatrix}.$$

vanish.

On the other hand, the orthogonality properties are somewhat more complicated:

$$\sum_{j_3}\sum_{m_3}(2j_3+1)\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1' & m_2' & m_3 \end{pmatrix} = \delta_{m_1 m_1'}\delta_{m_2 m_2'}$$

and

$$\sum_{m_1}\sum_{m_2}\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}\begin{pmatrix} j_1 & j_2 & j_3' \\ m_1 & m_2 & m_3' \end{pmatrix} = \frac{\delta_{j_3 j_3'}\delta_{m_3 m_3'}\delta(j_1 j_2 j_3)}{\sqrt{2j_3+1}},$$

where

$$\delta(j_1 j_2 j_3) = \begin{cases} 1, & \text{when } |j_1 - j_2| \le j_3 \le j_1 + j_2 \\ 0, & \text{otherwise.} \end{cases}$$

$6j$-symbols

Let us couple three angular momenta, j_1, j_2 and j_3, to the angular momentum J. There are two ways:

1. first $j_1, j_2 \longrightarrow j_{12}$ and then $j_{12}, j_3 \longrightarrow J$.
2. first $j_2, j_3 \longrightarrow j_{23}$ and then $j_{23}, j_1 \longrightarrow J$.

Let's choose the first way. The quantum number j_{12} must satisfy the selection rules

$$\begin{aligned} |j_1 - j_2| &\le j_{12} \le j_1 + j_2 \\ |j_{12} - j_3| &\le J \le j_{12} + j_3. \end{aligned}$$

The states belonging to different j_{12} are independent so we must specify the intermediate state j_{12}. We use the notation

$$|(j_1 j_2) j_{12} j_3; JM\rangle.$$

Explicitely one has

$$\begin{aligned}
&|(j_1 j_2) j_{12} j_3; JM\rangle \\
&\quad = \sum_{m_{12}}\sum_{m_3}|j_1 j_2; j_{12} m_{12}\rangle|j_3 m_3\rangle \\
&\qquad \times\langle j_{12} j_3; m_{12} m_3 | j_{12} j_3; JM\rangle \\
&\quad = \sum_{m_1 m_2 m_3 m_{12}}|j_1 m_1\rangle|j_2 m_2\rangle|j_3 m_3\rangle \\
&\qquad \times\langle j_1 j_2; m_1 m_2 | j_1 j_2; j_{12} m_{12}\rangle \\
&\qquad \times\langle j_{12} j_3; m_{12} m_3 | j_{12} j_3; JM\rangle.
\end{aligned}$$

Correspondingly the angular momenta coupled in way 2 satisfy

$$\begin{aligned}
&|j_1 (j_2 j_3) j_{23}; JM\rangle \\
&\quad = \sum_{m_{23}}\sum_{m_1}|j_1 m_1\rangle|j_2 j_3; j_{23} m_{23}\rangle \\
&\qquad \times\langle j_1 j_{23}; m_1 m_{23} | j_1 j_{23}; JM\rangle \\
&\quad = \sum_{m_1 m_2 m_3 m_{23}}|j_1 m_1\rangle|j_2 m_2\rangle|j_3 m_3\rangle \\
&\qquad \times\langle j_2 j_3; m_2 m_3 | j_2 j_3; j_{23} m_{23}\rangle \\
&\qquad \times\langle j_1 j_{23}; m_1 m_{23} | j_1 j_{23}; JM\rangle.
\end{aligned}$$

Both bases are complete so there is a unitary transform between them:

$$\begin{aligned}
|j_1 (j_2 j_3) j_{23}; JM\rangle &= \sum_{j_{12}}|(j_1 j_2) j_{12} j_3; JM\rangle \\
&\times\langle (j_1 j_2) j_{12} j_3; JM | j_1 (j_2 j_3) j_{23}; JM\rangle.
\end{aligned}$$

In the transformation coefficients, *recoupling coefficients* it is not necessary to show the quantum number M, because

Theorem 1 *In the transformation*

$$|\alpha; jm\rangle = \sum_{\beta}|\beta; jm\rangle\langle\beta; jm|\alpha; jm\rangle$$

the coefficients $\langle\beta; jm|\alpha; jm\rangle$ do not depend on the quantum number m.

Proof: Let us suppose that $m < j$. Now

$$|\alpha; j, m+1\rangle = \sum_\beta |\beta; j, m+1\rangle\langle\beta; j, m+1|\alpha; j, m+1\rangle.$$

On the other hand

$$\begin{aligned} |\alpha; j, m+1\rangle &= \frac{J_+}{\hbar\sqrt{(j+m+1)(j-m)}}|\alpha; jm\rangle \\ &= \sum_\beta |\beta; j, m+1\rangle\langle\beta; jm|\alpha; jm\rangle, \end{aligned}$$

so

$$\langle\beta; j, m+1|\alpha; j, m+1\rangle = \langle\beta; j, m|\alpha; j, m\rangle \quad \blacksquare$$

The explicit expression for the recoupling coefficients will be

$$\begin{aligned} &\langle(j_1 j_2) j_{12} j_3; J|j_1(j_2 j_3) j_{23}; J\rangle \\ &\quad = \sum_{\substack{m_1 m_2 m_3 \\ m_{12} m_{23}}} \langle j_{12} j_3; JM|j_{12} j_3; m_{12} m_3\rangle \\ &\quad \times\langle j_1 j_2; j_{12} m_{12}|j_1 j_2; m_1 m_2\rangle \\ &\quad \times\langle j_2 j_3; m_2 m_3|j_2 j_3; j_{23} m_{23}\rangle \\ &\quad \times\langle j_1 j_{23}; m_1 m_{23}|j_1 j_{23}; JM\rangle. \end{aligned}$$

We define the more symmetric $6j$-*symbols*:

$$\begin{aligned} &\left\{ \begin{array}{ccc} j_1 & j_2 & j_{12} \\ j_3 & J & j_{23} \end{array} \right\} \\ &\quad \equiv \frac{(-1)^{j_1+j_2+j_3+J}}{\sqrt{(2j_{12}+1)(2j_{23}+1)}} \\ &\quad \times\langle(j_1 j_2) j_{12} j_3; J|j_1(j_2 j_3) j_{23}; J\rangle \\ &\quad = \frac{(-1)^{j_1+j_2+j_3+J}}{\sqrt{(2j_{12}+1)(2j_{23}+1)}} \\ &\quad \times \sum_{m_1 m_2} \langle j_1 j_2; m_1 m_2|j_1 j_2; j_{12}, m_1+m_2\rangle \\ &\quad \times\langle j_{12} j_3; m_1+m_2, M-m_1-m_2|j_{12} j_3; JM\rangle \\ &\quad \times\langle j_2 j_3; m_2, M-m_1-m_2|j_2 j_3; j_{23}, M-m_1\rangle \\ &\quad \times\langle j_1 j_{23}; m_1, M-m_1|j_1 j_{23}; JM\rangle. \end{aligned}$$

We can handle analogously the coupling of 4 angular momenta. Transformations from a coupling scheme to another are mediated by the $9j$-*symbols*:

$$\begin{aligned} &\left\{ \begin{array}{ccc} j_1 & j_2 & j_{12} \\ j_3 & j_4 & j_{34} \\ j_{13} & j_{24} & j \end{array} \right\} \\ &\quad \equiv \frac{\langle(j_1 j_2) j_{12}(j_3 j_4) j_{34}; j|(j_1 j_3) j_{13}(j_2 j_4) j_{24}; j\rangle}{\sqrt{(2j_{12}+1)(2j_{34}+1)(2j_{13}+1)(2j_{24}+1}}. \end{aligned}$$

Tensor operators

We have used the vector notation for three component operators for example to express the scalar product, like

$$\boldsymbol{p}\cdot\boldsymbol{x}' = p_x x' + p_y y' + p_z z'.$$

Classically a vector is a quantity that under rotations transforms like $\boldsymbol{V} \in \mathcal{R}^3$ (or $\in \mathcal{C}^3$), i.e. if $R \in \mathrm{O}(3)$, then

$$V_i' = \sum_{j=1}^{3} R_{ij} V_j.$$

In quantum mechanics $\boldsymbol{V}$ is a *vector operator* provided that $\langle \boldsymbol{V}\rangle \in \mathcal{C}^3$ is a vector:

$$\begin{aligned} {}_R\langle\alpha|V_i|\alpha\rangle_R &= \langle\alpha|\mathcal{D}^\dagger(R)V_i\mathcal{D}(R)|\alpha\rangle \\ &= \sum_{j=1}^{3} R_{ij}\langle\alpha|V_j|\alpha\rangle, \\ &\qquad \forall|\alpha\rangle \in \mathcal{H}, R \in \mathrm{O}(3). \end{aligned}$$

Thus we must have

$$\mathcal{D}^\dagger(R)V_i\mathcal{D}(R) = \sum_j R_{ij}V_j.$$

Thus the infinitesimal rotations

$$\mathcal{D}(\hat{\boldsymbol{n}}\epsilon) = 1 - \frac{i\epsilon\boldsymbol{J}\cdot\hat{\boldsymbol{n}}}{\hbar}$$

satisfy

$$\begin{aligned} &\left(1 + \frac{i\epsilon\boldsymbol{J}\cdot\hat{\boldsymbol{n}}}{\hbar}\right) V_i \left(1 + \frac{i\epsilon\boldsymbol{J}\cdot\hat{\boldsymbol{n}}}{\hbar}\right) \\ &\quad = V_i + \frac{i\epsilon}{\hbar}\left(\boldsymbol{J}\cdot\hat{\boldsymbol{n}}V_i - V_i\boldsymbol{J}\cdot\hat{\boldsymbol{n}}\right) + \mathcal{O}(\epsilon^2) \\ &\quad = \sum_j R_{ij}V_j \end{aligned}$$

or

$$V_i + \frac{\epsilon}{i\hbar}[V_i, \boldsymbol{J}\cdot\hat{\boldsymbol{n}}] = \sum_j R_{ij}(\hat{\boldsymbol{n}}\epsilon)V_j.$$

Substituting the explicit expressions for infinitesimal rotations, like

$$R(\hat{\boldsymbol{z}}\epsilon) = \begin{pmatrix} 1 - \frac{\epsilon^2}{2} & -\epsilon & 0 \\ \epsilon & 1 - \frac{\epsilon^2}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

we get

$$V_x + \frac{\epsilon}{i\hbar}[V_x, J_z] = V_x - \epsilon V_y + \mathcal{O}(\epsilon^3).$$

Handling similarly the other components we end up with

$$\boxed{[V_i, J_j] = i\hbar\epsilon_{ijk}V_k.}$$

Finite rotation

A finite rotation specified by Euler angles is accomplished by rotating around coordinate axises, so we have to consider such expressions as

$$\exp\left(\frac{iJ_j\phi}{\hbar}\right) V_i \exp\left(-\frac{iJ_j\phi}{\hbar}\right).$$

Applying the Baker-Hausdorff lemma

$$\begin{aligned} &e^{iG\lambda}Ae^{-iG\lambda} = \\ &\quad A + i\lambda[G,A] + \left(\frac{i^2\lambda^2}{2!}\right)[G,[G,A]] + \cdots \\ &\quad + \left(\frac{i^n\lambda^n}{n!}\right)[G,[G,\ldots[G,A]]\ldots] + \cdots \end{aligned}$$

we end up with the commutators

$$[J_j,[J_j,[\cdots[J_j,V_i]\cdots]]].$$

These will be evaluated in turn into operators V_i and V_k $(k \neq i,j)$.

A vector operator $(\boldsymbol{V})$ is *defined* so that it satisfies the commutation relation

$$[V_i, J_j] = i\hbar\epsilon_{ijk}V_k.$$

We can easily see that for example $\boldsymbol{p}$, $\boldsymbol{x}$ and $\boldsymbol{J}$ are vector operators.

In classical mechanics a quantity which under rotations transforms like

$$T_{\underbrace{ijk\ldots}_{n\text{ indeces}}} \longrightarrow \sum_{i'}\sum_{j'}\sum_{k'} \cdots R_{ii'}R_{jj'}R_{kk'}\cdots T_{i'j'k'\ldots},$$

is called a Cartesian tensor of the rank n.

Example The dyad product of the vectors $\boldsymbol{U}$ and $\boldsymbol{V}$

$$T_{ij} = U_iV_j$$

is a tensor of rank 2.

Cartesian tensors are reducible, for example the dyad product can be written as

$$\begin{aligned} U_iV_j &= \frac{\boldsymbol{U}\cdot\boldsymbol{V}}{3}\delta_{ij} + \frac{(U_iV_j - U_jV_i)}{2} \\ &\quad + \left(\frac{U_iV_j + U_jV_i}{2} - \frac{\boldsymbol{U}\cdot\boldsymbol{V}}{3}\delta_{ij}\right). \end{aligned}$$

We see that the terms transform under rotations differently:

- $\frac{\boldsymbol{U}\cdot\boldsymbol{V}}{3}\delta_{ij}$ is invariant. There is 1 term.
- $\frac{(U_iV_j - U_jV_i)}{2}$ retains its antisymmetry. There are 3 terms.
- $\left(\frac{U_iV_j + U_jV_i}{2} - \frac{\boldsymbol{U}\cdot\boldsymbol{V}}{3}\delta_{ij}\right)$ retains its symmetry and tracelessness. There are 5 terms.

We recognize that the number of terms checks and that the partition might have something to do with the angular momentum since the multiplicities correspond to the multiplicities of the angular momenta $l = 0, 1, 2$.

We define the *spherical tensor* $T_q^{(k)}$ of rank k so that the argument $\hat{\boldsymbol{n}}$ of the spherical function

$$Y_l^m(\hat{\boldsymbol{n}}) = \langle\hat{\boldsymbol{n}}|lm\rangle$$

is replaced by the vector $\boldsymbol{V}$:

$$T_q^{(k)} = Y_{l=k}^{m=q}(\boldsymbol{V}).$$

Example The spherical function Y_1:

$$\begin{aligned} Y_1^0 &= \sqrt{\frac{3}{4\pi}}\cos\theta = \sqrt{\frac{3}{4\pi}}\frac{z}{r} \mapsto T_0^{(1)} = \sqrt{\frac{3}{4\pi}}V_z \\ Y_1^{\pm 1} &= \mp\sqrt{\frac{3}{4\pi}}\frac{x \pm iy}{\sqrt{2}r} \mapsto T_{\pm 1}^{(1)} = \sqrt{\frac{3}{4\pi}}\left(\mp\frac{V_x \pm iV_y}{\sqrt{2}}\right). \end{aligned}$$

Similarly we could construct for example a spherical tensor of rank 2:

$$Y_2^{\pm 2} = \sqrt{\frac{15}{32\pi}}\frac{(x \pm iy)^2}{r^2} \mapsto T_{\pm 2}^{(2)} = \sqrt{\frac{15}{32\pi}}(V_x \pm iV_y)^2.$$

The tensors $T_q^{(k)}$ are irreducible, i.e. there does not exist any proper subset

$$\{T_{p_1}^{(k)}, T_{p_2}^{(k)}, \ldots\} \subset \{T_q^{(k)} | q = -k, \ldots, +k\},$$

which would remain invariant under rotations.

Transformation of spherical tensors
Under the rotation R an eigenstate of the direction transforms like

$$|\hat{\boldsymbol{n}}\rangle \longrightarrow |\hat{\boldsymbol{n}}'\rangle = \mathcal{D}(R)|\hat{\boldsymbol{n}}\rangle.$$

The state vectors $|lm\rangle$, on the other hand, transform under the rotation R^{-1} like

$$\mathcal{D}(R^{-1})|l,m\rangle = \sum_{m'} |l,m'\rangle \mathcal{D}^{(l)}_{m'm}(R^{-1}).$$

So we get

$$\begin{aligned} Y_l^m(\hat{\boldsymbol{n}}') &= \langle\hat{\boldsymbol{n}}'|lm\rangle = \langle\hat{\boldsymbol{n}}|\mathcal{D}^\dagger(R)|lm\rangle \\ &= \langle\hat{\boldsymbol{n}}|\mathcal{D}(R^{-1})|lm\rangle = \sum_{m'}\langle\hat{\boldsymbol{n}}||lm'\rangle\mathcal{D}^{(l)}_{m'm}(R^{-1}) \\ &= \sum_{m'} Y_l^{m'}(\hat{\boldsymbol{n}})\mathcal{D}^{(l)}_{m'm}(R^{-1}) \\ &= \sum_{m'} Y_l^{m'}(\hat{\boldsymbol{n}}){\mathcal{D}^{(l)}_{mm'}}^*(R). \end{aligned}$$

We define a tensor operator $Y_l^m(\boldsymbol{V})$ so that

$$\mathcal{D}^\dagger(R)Y_l^m(\boldsymbol{V})\mathcal{D}(R) = \sum_{m'} Y_l^{m'}(\boldsymbol{V})\mathcal{D}^{(l)*}_{mm'}(R).$$

Generalizing we define: $T_q^{(k)}$ is a $(2k+1)$-component spherical tensor of rank k if and only if

$$\mathcal{D}^\dagger(R)T_q^{(k)}\mathcal{D}(R) = \sum_{q'=-k}^{k} {\mathcal{D}^{(k)}_{qq'}}^*(R)T_{q'}^{(k)}$$

or equivalently

$$\boxed{\mathcal{D}(R)T_q^{(k)}\mathcal{D}^\dagger(R) = \textstyle\sum_{q'=-k}^{k}\mathcal{D}^{(k)}_{q'q}(R)T_{q'}^{(k)}.}$$

Under the infinitesimal rotations

$$\mathcal{D}(\hat{\boldsymbol{n}}\epsilon) = \left(1 - \frac{i\boldsymbol{J}\cdot\hat{\boldsymbol{n}}\epsilon}{\hbar}\right)$$

a spherical tensor behaves thus like

$$\begin{aligned} &\left(1 + \frac{i\boldsymbol{J}\cdot\hat{\boldsymbol{n}}\epsilon}{\hbar}\right)T_q^{(k)}\left(1 - \frac{i\boldsymbol{J}\cdot\hat{\boldsymbol{n}}\epsilon}{\hbar}\right) \\ &\quad= \sum_{q'=-k}^{k} T_{q'}^{(k)}\langle kq'|\left(1 + \frac{i\boldsymbol{J}\cdot\hat{\boldsymbol{n}}\epsilon}{\hbar}\right)|kq\rangle \\ &\quad= \sum_{q'=-k}^{k} T_{q'}^{(k)}\langle kq'|kq\rangle + \sum_{q'=-k}^{k} i\epsilon T_{q'}^{(k)}\langle kq'|\boldsymbol{J}\cdot\hat{\boldsymbol{n}}|kq\rangle, \end{aligned}$$

or

$$[\boldsymbol{J}\cdot\hat{\boldsymbol{n}}, T_q^{(k)}] = \sum_{q'} T_{q'}^{(k)}\langle kq'|\boldsymbol{J}\cdot\hat{\boldsymbol{n}}|kq\rangle.$$

Choosing $\hat{\boldsymbol{n}} = \hat{\boldsymbol{z}}$ and $\hat{\boldsymbol{x}} \pm i\hat{\boldsymbol{y}}$ we get

$$\boxed{[J_z, T_q^{(k)}] = \hbar q T_q^{(k)}}$$

and

$$\boxed{[J_\pm, T_q^{(k)}] = \hbar\sqrt{(k \mp q)(k \pm q + 1)}T_{q\pm 1}^{(k)}.}$$

Example Decomposition of the dyad product.
We form spherical tensors of rank 1 from the vector operators $\boldsymbol{U}$ and $\boldsymbol{V}$:

$$\begin{aligned} U_0 &= U_z, & V_0 &= V_z, \\ U_{\pm 1} &= \mp\frac{U_x \pm iU_y}{\sqrt{2}}, & V_{\pm 1} &= \mp\frac{V_x \pm iV_y}{\sqrt{2}}. \end{aligned}$$

Now

$$\begin{aligned} T_0^{(0)} &= -\frac{\boldsymbol{U}\cdot\boldsymbol{V}}{3} = \frac{U_{+1}V_{-1} + U_{-1}V_{+1} - U_0V_0}{3}, \\ T_q^{(1)} &= \frac{(\boldsymbol{U}\times\boldsymbol{V})_q}{i\sqrt{2}}, \\ T_{\pm 2}^{(2)} &= U_{\pm 1}V_{\pm 1}, \\ T_{\pm 1}^{(2)} &= \frac{U_{\pm 1}V_0 + U_0V_{\pm 1}}{\sqrt{2}}, \\ T_0^{(2)} &= \frac{U_{+1}V_{-1} + 2U_0V_0 + U_{-1}V_{+1}}{\sqrt{6}}. \end{aligned}$$

In general we have
Theorem 1 *Let $X_{q_1}^{(k_1)}$ and $Z_{q_2}^{(k_2)}$ be irreducible spherical tensors of rank k_1 and k_2. Then*

$$T_q^{(k)} = \sum_{q_1}\sum_{q_2}\langle k_1k_2; q_1q_2|k_1k_2; kq\rangle X_{q_1}^{(k_1)}Z_{q_q}^{(k_2)}$$

is a (irreducible) spherical tensor of rank k.
Proof: We show that $T_q^{(k)}$ transforms like

$$\mathcal{D}^\dagger(R)T_q^{(k)}\mathcal{D}(R) = \sum_{q'=-k}^{k} {\mathcal{D}^{(k)}_{qq'}}^*(R)T_{q'}^{(k)}.$$

Now

$$\begin{aligned}
&\mathcal{D}^\dagger(R)T_q^{(k)}\mathcal{D}(R)\\
&\quad=\sum_{q_1}\sum_{q_2}\langle k_1k_2;q_1q_2|k_1k_2;kq\rangle\\
&\quad\times\mathcal{D}^\dagger(R)X_{q_1}^{(k_1)}\mathcal{D}(R)\mathcal{D}^\dagger(R)Z_{q_2}^{(k_2)}\mathcal{D}(R)\\
&\quad=\sum_{q_1}\sum_{q_2}\sum_{q_1'}\sum_{q_2'}\langle k_1k_2;q_1q_2|k_1k_2;kq\rangle\\
&\quad\times X_{q_1'}^{(k_1)}\mathcal{D}_{q_1'q_1}^{(k_1)}(R^{-1})Z_{q_2'}^{(k_2)}\mathcal{D}_{q_2'q_2}^{(k_2)}(R^{-1})\\
&\quad=\sum_{k''}\sum_{q_1}\sum_{q_2}\sum_{q_1'}\sum_{q_2'}\sum_{q''}\sum_{q'}\langle k_1k_2;q_1q_2|k_1k_2;kq\rangle\\
&\quad\times\langle k_1k_2;q_1'q_2'|k_1k_2;k''q'\rangle\\
&\quad\times\langle k_1k_2;q_1q_2|k_1k_2;k''q''\rangle\mathcal{D}_{q'q''}^{(k'')}(R^{-1})X_{q_1'}^{(k_1)}Z_{q_2'}^{(k_2)},
\end{aligned}$$

where we have substituted the Clebsch-Gordan series expansion

$$\begin{aligned}
&\mathcal{D}_{m_1m_1'}^{(j_1)}(R)\mathcal{D}_{m_2m_2'}^{(j_2)}(R)=\\
&\qquad\sum_j\sum_m\sum_{m'}\langle j_1j_2;m_1m_2|j_1j_2;jm\rangle\\
&\qquad\times\langle j_1j_2;m_1'm_2'|j_1j_2;jm'\rangle\mathcal{D}_{mm'}^{(j)}(R)
\end{aligned}$$

Taking into account the orthogonality of the Clebsch-Gordan coefficients

$$\sum_{m_1m_2}\langle j_1j_2;m_1m_2|j_1j_2;jm\rangle\langle j_1j_2;m_1m_2|j_1j_2;j'm'\rangle=\delta_{jj'}\delta_{mm'}$$

we get

$$\begin{aligned}
&\mathcal{D}^\dagger(R)T_q^{(k)}\mathcal{D}(R)\\
&\quad=\sum_{k''}\sum_{q_1'}\sum_{q_2'}\sum_{q''}\sum_{q'}\delta_{kk''}\delta_{qq''}\langle k_1k_2;q_1'q_2'|k_1k_2;k''q'\rangle\\
&\quad\times\mathcal{D}_{q'q''}^{(k'')}(R^{-1})X_{q_1'}^{(k_1)}Z_{q_2'}^{(k_2)},
\end{aligned}$$

which can be rewritten as

$$\begin{aligned}
&\mathcal{D}^\dagger(R)T_q^{(k)}\mathcal{D}(R)\\
&\quad=\sum_{q'}\left(\sum_{q_1'q_2'}\langle k_1k_2;q_1'q_2'|k_1k_2;kq'\rangle X_{q_1'}^{(k_1)}Z_{q_2'}^{(k_2)}\right)\\
&\quad\times\mathcal{D}_{q'q}^{(k)}(R^{-1})\\
&\quad=\sum_{q'}T_{q'}^{(k)}\mathcal{D}_{q'q}^{(k)}(R^{-1})=\sum_{q'}\mathcal{D}_{qq'}^{(k)^*}(R)T_{q'}^{(k)}\quad\blacksquare
\end{aligned}$$

Matrix elements of tensor operators

Theorem 2 *The matrix elements of the tensor operator* $T_q^{(k)}$ *satisfy*

$$\langle\alpha',j'm'|T_q^{(k)}|\alpha,jm\rangle=0,$$

unless $m'=q+m$.

Proof: Due to the property

$$[J_z,T_q^{(k)}]=\hbar qT_q^{(k)}$$

we have

$$\begin{aligned}
&\langle\alpha',j'm'|[J_z,T_q^{(k)}]-\hbar qT_q^{(k)}|\alpha,jm\rangle\\
&\qquad=[(m'-m)\hbar-q\hbar]\times\langle\alpha',j'm'|T_q^{(k)}|\alpha,jm\rangle=0,
\end{aligned}$$

so

$$\langle\alpha',j'm'|T_q^{(k)}|\alpha,jm\rangle=0,$$

if $m'\neq q+m$ $\blacksquare$

Theorem 3 *(*Wigner-Eckardt's theorem*) The matrix elements of a tensor operator between eigenstates of the angular momentum satisfy the relation*

$$\langle\alpha',j'm'|T_q^{(k)}|\alpha,jm\rangle=\langle jk;mq|jk;j'm'\rangle\frac{\langle\alpha'j'\|T^{(k)}\|\alpha j\rangle}{\sqrt{2j+1}},$$

where the reduced matrix element $\langle\alpha'j'\|T^{(k)}\|\alpha j\rangle$ *depends neither on the quantum numbers* m, m' *nor on* q.

Proof: Since $T_q^{(k)}$ is a tensor operator it satisfies the condition

$$[J_\pm,T_q^{(k)}]=\hbar\sqrt{(k\mp q)(k\pm q+1)}T_{q\pm1}^{(k)},$$

so

$$\begin{aligned}
&\langle\alpha',j'm'|[J_\pm,T_q^{(k)}]|\alpha,jm\rangle\\
&\qquad=\hbar\sqrt{(k\mp q)(k\pm q+1)}\langle\alpha',j'm'|T_{q\pm1}^{(k)}|\alpha,jm\rangle.
\end{aligned}$$

Substituting the matrix elements of the ladder operators we get

$$\begin{aligned}
&\sqrt{(j'\pm m')(j'\mp m'+1)}\langle\alpha',j',m'\mp1|T_q^{(k)}|\alpha,jm\rangle\\
&\quad=\sqrt{(j\mp m)(j\pm m+1)}\langle\alpha',j',m'|T_q^{(k)}|\alpha,j,m\pm1\rangle\\
&\quad+\sqrt{(k\mp q)(k\pm q+1)}\langle\alpha',j',m'|T_{q\pm1}^{(k)}|\alpha,jm\rangle.
\end{aligned}$$

If we now substituted $j'\to j$, $m'\to m$, $j\to j_1$, $m\to m_1$, $k\to j_2$ and $q\to m_2$, we would note that the recursion formula above is exactly like the recursion formula for the Clebsch-Gordan coefficients,

$$\begin{aligned}
&\sqrt{(j\mp m)(j\pm m+1)}\langle j_1j_2;m_1m_2|j_1j_2;j,m\pm1\rangle\\
&\quad=\sqrt{(j_1\mp m_1+1)(j_1\pm m_1)}\\
&\qquad\times\langle j_1j_2;m_1\mp1,m_2|j_1j_2;jm\rangle\\
&\quad+\sqrt{(j_2\mp m_2+1)(j_2\pm m_2)}\\
&\qquad\times\langle j_1j_2;m_1,m_2\mp1|j_1j_2;jm\rangle.
\end{aligned}$$

Both recursions are of the form $\sum_j a_{ij}x_j=0$, or sets of linear homogenous simultaneous equations with the same coefficients a_{ij}. So we have two sets of equations

$$\sum_j a_{ij}x_j=0,\quad\sum_j a_{ij}y_j=0,$$

one for the matrix elements (x_i) of the tensor operator and the other for the Clebsch-Gordan coefficients (y_i). These sets of equations tell that

$$\frac{x_j}{x_k}=\frac{y_j}{y_k}\quad\forall j\text{ and }k\text{ fixed},$$

so $x_j = cy_j$ while c is a proportionality coefficient independent of the indeces j. Thus we see that

$$\begin{aligned}&\langle\alpha', j'm'|T_q^{(k)}|\alpha, jm\rangle\\ &\quad = (\text{ constant independent on } m,\ q \text{ and } m')\\ &\qquad \times\langle jk; mq|jk; j'm'\rangle.\end{aligned}$$

If we write the proportionality coefficient like

$$\frac{\langle\alpha' j'\|T^{(k)}\|\alpha j\rangle}{\sqrt{2j+1}}$$

we are through. ∎

According to the Wigner-Eckart theorem a matrix element of a tensor operator is a product of two factors, of which

- $\langle jk; mq|jk; j'm'\rangle$ depends only on the geometry, i.e. on the orientation of the system with respect to the z-axis.
- $\dfrac{\langle\alpha' j'\|T^{(k)}\|\alpha j\rangle}{\sqrt{2j+1}}$ depends on the dynamics of the system.

As a special case we have the *projection theorem*:

Theorem 4 *Let*

$$J_{\pm 1} = \mp\frac{1}{\sqrt{2}}(J_x \pm iJ_y) = \mp\frac{1}{\sqrt{2}}J_\pm, \quad J_0 = J_z$$

be the components of the tensor operator corresponding to the angular momentum. Then

$$\langle\alpha', jm'|V_q|\alpha, jm\rangle = \frac{\langle\alpha', jm|\boldsymbol{J}\cdot\boldsymbol{V}|\alpha, jm\rangle}{\hbar^2 j(j+1)}\langle jm'|J_q|jm\rangle.$$

Proof: Due to the expansions

$$\begin{aligned}T_0^{(0)} &= -\frac{\boldsymbol{U}\cdot\boldsymbol{V}}{3} = \frac{U_{+1}V_{-1} + U_{-1}V_{+1} - U_0V_0}{3},\\ T_q^{(1)} &= \frac{(\boldsymbol{U}\times\boldsymbol{V})_q}{i\sqrt{2}},\\ T_{\pm 2}^{(2)} &= U_{\pm 1}V_{\pm 1},\\ T_{\pm 1}^{(2)} &= \frac{U_{\pm 1}V_0 + U_0V_{\pm 1}}{\sqrt{2}},\\ T_0^{(2)} &= \frac{U_{+1}V_{-1} + 2U_0V_0 + U_{-1}V_{+1}}{\sqrt{6}}\end{aligned}$$

we can write

$$\begin{aligned}&\langle\alpha', jm|\boldsymbol{J}\cdot\boldsymbol{V}|\alpha, jm\rangle\\ &\quad = \langle\alpha', jm|(J_0V_0 - J_{+1}V_{-1} - J_{-1}V_{+1})\alpha, jm\rangle\\ &\quad = m\hbar\langle\alpha', jm|V_0|\alpha, jm\rangle\\ &\quad + \frac{\hbar}{\sqrt{2}}\sqrt{(j+m)(j-m+1)}\langle\alpha', j, m-1|V_{-1}|\alpha, jm\rangle\\ &\quad - \frac{\hbar}{\sqrt{2}}\sqrt{(j-m)(j+m+1)}\langle\alpha', j, m+1|V_{+1}|\alpha, jm\rangle\\ &\quad = c_{jm}\langle\alpha' j\|\boldsymbol{V}\|\alpha j\rangle,\end{aligned}$$

where, according to the Wigner-Eckart theorem the coefficient c_{jm} does not depend on α, α' or $\boldsymbol{V}$.

The coefficient c_{jm} does not depend either on the quantum number m, because $\boldsymbol{J}\cdot\boldsymbol{V}$ is a scalar operator, so we can write it briefly as c_j. Because c_j does not depend on the operator $\boldsymbol{V}$ the above equation is valid also when $\boldsymbol{V}\to\boldsymbol{J}$ and $\alpha'\to\alpha$, or

$$\langle\alpha, jm|\boldsymbol{J}^2|\alpha, jm\rangle = \hbar^2 j(j+1) = c_j\langle\alpha j\|\boldsymbol{J}\|\alpha j\rangle.$$

If we now apply the Wigner-Eckart theorem to the operators V_q and J_q we get

$$\frac{\langle\alpha', jm'|V_q|\alpha, jm\rangle}{\langle\alpha, jm'|J_q|\alpha, jm\rangle} = \frac{\langle\alpha' j\|\boldsymbol{V}\|\alpha j\rangle}{\langle\alpha j\|\boldsymbol{J}\|\alpha j\rangle}.$$

for the ratios of the matrix elements. On the other hand, the right hand side of this equation is

$$\frac{\langle\alpha', jm|\boldsymbol{J}\cdot\boldsymbol{V}|\alpha, jm\rangle}{\langle\alpha, jm|\boldsymbol{J}^2|\alpha, jm\rangle},$$

so

$$\langle\alpha', jm'|V_q|\alpha, jm\rangle = \frac{\langle\alpha', jm|\boldsymbol{J}\cdot\boldsymbol{V}|\alpha, jm\rangle}{\hbar^2 j(j+1)}\langle jm'|J_q|jm\rangle \quad ∎$$

Generalizing one can show that the reduced matrix elements of the irreducible product $T_q^{(k)}$ of two tensor operators, $X_{q_1}^{(k_1)}$ and $Z_{q_2}^{(k_2)}$, satisfy

$$\begin{aligned}&\langle\alpha' j'||T^{(k)}\|\alpha j\rangle\\ &\quad = \sqrt{2k+1}(-1)^{k+j+j'}\sum_{\alpha''}\sum_{j''}\begin{Bmatrix} k_1 & k_2 & k\\ j & j' & j''\end{Bmatrix}\\ &\qquad \times\langle\alpha' j'\|X^{(k_1)}\|\alpha'' j''\rangle\langle\alpha'' j''|Z^{(k_2)}\|\alpha j\rangle.\end{aligned}$$

Symmetry

Symmetries, constants of motion and degeneracies

Looking at the Lagrange equation of motion

$$\frac{d}{dt}\left(\frac{\partial \mathcal{L}}{\partial \dot{q}_i}\right) - \frac{\partial \mathcal{L}}{\partial q_i} = 0$$

of classical mechanics one can see that if the Lagrangian $\mathcal{L}(q_i, \dot{q}_i)$ is invariant under translations, i.e.

$$\mathcal{L}(q_i, \dot{q}_i) \longrightarrow \mathcal{L}(q_i + \delta q_i, \dot{q}_i) = \mathcal{L}(q_i, \dot{q}_i),$$

the momentum

$$p_i = \frac{\partial \mathcal{L}}{\partial \dot{q}_i}$$

is a conserved quantity, i.e.

$$\frac{dp_i}{dt} = \frac{d}{dt}\left(\frac{\partial \mathcal{L}}{\partial \dot{q}_i}\right) = 0.$$

Formulating classical mechanics using the Hamiltonian function $\mathcal{H}(q_i, p_i)$ the equations of motion take the forms

$$\begin{aligned} \dot{p}_i &= -\frac{\partial \mathcal{H}}{\partial q_i} \\ \dot{q}_i &= \frac{\partial \mathcal{H}}{\partial p_i}. \end{aligned}$$

Also looking at these one can see that if $\mathcal{H}$ is symmetric under the operation

$$q_i \longrightarrow q_i + \delta q_i$$

there exists a conserved quantity:

$$\dot{p}_i = 0.$$

In quantum mechanics operations of that kind (translations, rotations, ...) are associated with a unitary *symmetry operator*.
Let $\mathcal{S}$ be an arbitrary symmetry operator. We say that the Hamiltonian H is *symmetric*, if

$$[\mathcal{S}, H] = 0,$$

or due to the unitarity of the operator $\mathcal{S}$ equivalently

$$\mathcal{S}^\dagger H \mathcal{S} = H.$$

The matrix elements of the Hamiltonian are then invariant under that operation.
In the case of a continuum symmetry we can look at infinitesimal operations

$$\mathcal{S} = 1 - \frac{i\epsilon}{\hbar} G,$$

where the Hermitean operator G is the *generator* of that symmetry. From the condition

$$\mathcal{S}^\dagger H \mathcal{S} = H$$

it follows now

$$[G, H] = 0,$$

so according to the Heisenberg equation of motion

$$\frac{dA}{dt} = \frac{1}{i\hbar}[A, H]$$

we have

$$\frac{dG}{dt} = 0.$$

In the Heisenberg formalism the observable G is thus a constant of motion. if H is invariant for example under

- translations then the momentum is constant of motion.
- rotations then the angular momentum is a constant motion.

Let us suppose now that the Hamiltonian is symmetric under the operations $\mathcal{S}$ generated by G:

$$\begin{aligned} \mathcal{S}^\dagger H \mathcal{S} &= H \\ [\mathcal{S}, H] &= 0 \\ [G, H] &= 0. \end{aligned}$$

Let $|g'\rangle$ be the eigenstates of G, i.e.

$$G|g'\rangle = g'|g'\rangle$$

and let the system at the moment t_0 be in the eigenstate $|g'\rangle$ of G. Since the time evolution operator is a functional of the Hamiltonian only,

$$U = U[H],$$

so

$$[G, U] = 0.$$

At the moment t we then have

$$\begin{aligned} G|g', t_0; t\rangle &= GU(t_0, t)|g'\rangle = U(t_0, t)G|g'\rangle \\ &= g'|g', t_0; t\rangle, \end{aligned}$$

or an eigenstate associated with a particular eigenvalue of G remains always an eigenstate belonging to the same eigenvalue.
Let us consider now the energy eigenstates $|n\rangle$, i.e.

$$H|n\rangle = E_n|n\rangle.$$

When the Hamiltonian is symmetric under the operations $\mathcal{S}$ we have

$$H(\mathcal{S}|n\rangle = \mathcal{S}H|n\rangle = E_n\mathcal{S}|n\rangle.$$

If now

$$|n\rangle \neq \mathcal{S}|n\rangle,$$

then the energy states E_n are degenerate. Thus a symmetry is also usually associated with a degeneracy.
Let us suppose now that the symmetry operation $\mathcal{S}$ can be parametrized with a continuous quantity, say λ:

$$\mathcal{S} = \mathcal{S}(\lambda).$$

When the Hamiltonian is symmetric under these operations all states $\mathcal{S}(\lambda)|n\rangle$ have the same energy.
Example Rotations $\mathcal{D}(R)$.
If

$$[\mathcal{D}(R), H] = 0,$$

then

$$[\boldsymbol{J}, H] = 0, \quad [\boldsymbol{J}^2, H] = 0.$$

So there exist simultaneous eigenvectors $|n; jm\rangle$ of the operators H, $\boldsymbol{J}^2$ ja J_z. Now all rotated states

$$\mathcal{D}(R)|n; jm\rangle$$

belong to the same energy eigenvalue. We know that

$$\mathcal{D}(R)|n; jm\rangle = \sum_{m'} |n; jm'\rangle \mathcal{D}^{(j)}_{m'm}(R),$$

that is, every rotated state is a superposition of $(2j+1)$ linearly independent states. The degeneracy is thus $(2j+1)$-fold.
Example Atomic electron.
The potential acting on an electron is of form

$$U = V(r) + V_{LS}\boldsymbol{L} \cdot \boldsymbol{S}.$$

Now

$$[\boldsymbol{J}, H] = 0, \quad [\boldsymbol{J}^2, H] = 0,$$

where

$$\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}.$$

The energy levels are thus $(2j+1)$-foldly degenerated.
Let's set the atom in magnetic field parallel to the z-axis. The Hamiltonian is then appended by the term

$$Z = cS_z.$$

Now

$$[\boldsymbol{J}^2, S_z] \neq 0,$$

so the rotation symmetry is broken and the $(2j+1)$-fold degeneracy lifted.

Parity

The parity or space inversion operation converts a right handed coordinate system to left handed:

$$x \longrightarrow -x, y \longrightarrow -y, z \longrightarrow -z.$$

This is a case of a *non continuous* operation, i.e. the operation cannot be composed of infinitesimal operations. Thus the non continuous operations have no generator. We consider the parity operation, i.e. we let the parity operator π to act on vectors of a Hilbert space and keep the coordinate system fixed:

$$|\alpha\rangle \longrightarrow \pi|\alpha\rangle.$$

Like in all symmetry operations we require that π is unitary, i.e.

$$\pi^\dagger\pi = 1.$$

Furthermore we require:

$$\langle\alpha|\pi^\dagger \boldsymbol{x}\pi|\alpha\rangle = -\langle\alpha|\boldsymbol{x}|\alpha\rangle \ \forall|\alpha\rangle.$$

So we must have

$$\pi^\dagger \boldsymbol{x}\pi = -\boldsymbol{x},$$

or

$$\pi\boldsymbol{x} = -\boldsymbol{x}\pi.$$

The operators $\boldsymbol{x}$ ja π *anti*commute.
Let $|\boldsymbol{x}'\rangle$ be a position eigenstate, i.e.

$$\boldsymbol{x}|\boldsymbol{x}'\rangle = \boldsymbol{x}'|\boldsymbol{x}'\rangle.$$

Then

$$\boldsymbol{x}\pi|\boldsymbol{x}'\rangle = -\pi\boldsymbol{x}|\boldsymbol{x}'\rangle = (-\boldsymbol{x}')\pi|\boldsymbol{x}'\rangle,$$

and we must have

$$\pi|\boldsymbol{x}'\rangle = e^{i\varphi}|-\boldsymbol{x}'\rangle.$$

The phase is usually taken to be $\varphi = 0$, so

$$\pi|\boldsymbol{x}'\rangle = |-\boldsymbol{x}'\rangle.$$

Applying the parity operator again we get

$$\pi^2|\boldsymbol{x}'\rangle = |\boldsymbol{x}'\rangle$$

or

$$\pi^2 = 1.$$

We see that

- the eigenvalues of the operator π can be only ± 1,
- $\pi^{-1} = \pi^\dagger = \pi$.

Momentum and parity
We require that operations

- translation followed by space inversion
- space inversion followed by translation to the opposite direction

are equivalent:

$$\pi\mathcal{T}(d\boldsymbol{x}') = \mathcal{T}(-d\boldsymbol{x}')\pi.$$

Substituting

$$\mathcal{T}(d\boldsymbol{x}') = 1 - \frac{i}{\hbar}d\boldsymbol{x}'\cdot\boldsymbol{p},$$

we get the condition

$$\{\pi, \boldsymbol{p}\} = 0 \text{ or } \pi^\dagger\boldsymbol{p}\pi = -\boldsymbol{p},$$

or the momentum changes its sign under the parity operation.

Angular momentum and parity
In the case of the orbital angular momentum

$$\boldsymbol{L} = \boldsymbol{x}\times\boldsymbol{p}$$

one can easily evaluate

$$\begin{aligned}\pi^\dagger L\pi &= \pi^\dagger\boldsymbol{x}\times\boldsymbol{p}\pi = \pi^\dagger\boldsymbol{x}\pi\times\pi^\dagger\boldsymbol{p}\pi = (-\boldsymbol{x})\times(-\boldsymbol{p}) \\ &= \boldsymbol{L},\end{aligned}$$

so the parity and the angular momentum commute:

$$[\pi, \boldsymbol{L}] = 0.$$

In $\mathcal{R}^3$ the parity operator is the matrix

$$P = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix},$$

so quite obviously

$$PR = RP, \ \forall R \in \mathrm{O}(3).$$

We require that the corresponding operators of the Hilbert space satisfy the same condition, i.e.

$$\pi\mathcal{D}(R) = \mathcal{D}(R)\pi.$$

Looking at the infinitesimal rotation

$$\mathcal{D}(\epsilon\hat{\boldsymbol{n}}) = 1 - i\boldsymbol{J}\cdot\hat{\boldsymbol{n}}\epsilon/\hbar,$$

we see that

$$[\pi, \boldsymbol{J}] = 0 \text{ or } \pi^\dagger\boldsymbol{J}\pi = \boldsymbol{J},$$

which is equivalent to the transformation of the orbital angular momentum.
We see that under

- rotations $\boldsymbol{x}$ and $\boldsymbol{J}$ transform similarly, that is, like vectors or tensors of rank 1.
- space inversions $\boldsymbol{x}$ is odd and $\boldsymbol{J}$ even.

We say that under the parity operation

- odd vectors are *polar*,
- even vectors are *axial* or *pseudo*vectors.

Let us consider such scalar products as $\boldsymbol{p}\cdot\boldsymbol{x}$ and $\boldsymbol{S}\cdot\boldsymbol{x}$. One can easily see that under rotation these are invariant, scalars. Under the parity operation they transform like

$$\begin{aligned}\pi^\dagger \boldsymbol{p}\cdot\boldsymbol{x}\pi &= (-\boldsymbol{p})\cdot(-\boldsymbol{x}) = \boldsymbol{p}\cdot\boldsymbol{x}\\ \pi^\dagger \boldsymbol{S}\cdot\boldsymbol{x}\pi &= \boldsymbol{S}\cdot(-\boldsymbol{x}) = -\boldsymbol{S}\cdot\boldsymbol{x}.\end{aligned}$$

We say that quantities behaving under rotations like scalars, spherical tensors of rank 0, which under the parity operation are

- even, are (ordinary) *scalars*,
- odd, are *pseudoscalars*.

Wave functions and parity
Let ψ be the wave function of a spinles particle in the state $|\alpha\rangle$, i.e.

$$\psi(\boldsymbol{x}') = \langle \boldsymbol{x}'|\alpha\rangle.$$

Since the position eigenstates satisfy

$$\pi|\boldsymbol{x}'\rangle = |-\boldsymbol{x}'\rangle,$$

the wave function of the space inverted state is

$$\langle \boldsymbol{x}'|\pi|\alpha\rangle = \langle -\boldsymbol{x}'|\alpha\rangle = \psi(-\boldsymbol{x}').$$

Suppose that $|\alpha\rangle$ is a parity eigenstate, i.e.

$$\pi|\alpha\rangle = \pm|\alpha\rangle.$$

The corresponding wave function obeys the the relation

$$\psi(-\boldsymbol{x}') = \langle \boldsymbol{x}'|\pi|\alpha\rangle = \pm\langle \boldsymbol{x}'|\alpha\rangle = \pm\psi(\boldsymbol{x}'),$$

i.e. it is an even or odd function of its argument.
Note Not all physically relevant wave function have parity. For example,

$$[\boldsymbol{p},\pi] \neq 0,$$

so a momentum eigenstate is not an eigenstate of the parity. The wave function corresponding to an eigenstate of the momentum is the plane wave

$$\psi_{\boldsymbol{p}'}(\boldsymbol{x}') = e^{i\boldsymbol{p}'\cdot\boldsymbol{x}'/\hbar},$$

which is neither even nor odd.
Because

$$[\pi,\boldsymbol{L}] = 0,$$

the eigenstate $|\alpha, lm\rangle$ of the orbital angular momentum $(\boldsymbol{L}^2, L_z)$ is also an eigenstate of the parity. Now

$$R_\alpha(r)Y_l^m(\theta,\phi) = \langle \boldsymbol{x}'|\alpha, lm\rangle.$$

In spherical coordinates the transformation $\boldsymbol{x}' \longrightarrow -\boldsymbol{x}'$ maps to

$$\begin{aligned} r &\longrightarrow r\\ \theta &\longrightarrow \pi-\theta \quad (\cos\theta \longrightarrow -\cos\theta)\\ \phi &\longrightarrow \phi+\pi \quad (e^{im\phi} \longrightarrow (-1)^m e^{im\phi}).\end{aligned}$$

The explicit expression for spherical functions is

$$Y_l^m(\theta,\phi) = (-1)^m\sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}}P_l^m(\theta)e^{im\phi},$$

from which as a special case, $m=0$, we obtain

$$Y_l^0(\theta,\phi) = \sqrt{\frac{2l+1}{4\pi}}P_l(\cos\theta).$$

Depending on the degree l of the Legendre polynomial it is either even or odd:

$$P_l(-z) = (-1)^l P_l(z).$$

We see that

$$\langle \boldsymbol{x}'|\pi|\alpha, l0\rangle = (-1)^l\langle \boldsymbol{x}'|\alpha, l0\rangle,$$

so the state vectors obey

$$\pi|\alpha, l0\rangle = (-1)^l|\alpha, l0\rangle.$$

Now

$$[\pi, L_\pm] = 0$$

and

$$L_\pm^r|\alpha, l0\rangle \propto |\alpha, l, \pm r\rangle,$$

so the orbital angular momentum states satisfy the relation

$$\pi|\alpha, lm\rangle = (-1)^l|\alpha, lm\rangle.$$

Theorem 1 *If*

$$[H,\pi] = 0,$$

and $|n\rangle$ is an eigenstate of the Hamiltonian H belonging to the nondegenerate eigenvalue E_n, i.e.

$$H|n\rangle = E_n|n\rangle,$$

then $|n\rangle$ is also an eigenstate of the parity.
Proof: Using the property $\pi^2 = 1$ one can easily see that the state

$$\frac{1}{2}(1\pm\pi)|n\rangle$$

is a parity eigenstate belonging to the eigenvalue ±1. On the other hand, this is also an eigenstate of the Hamiltonia H with the energy E_n:

$$H(\frac{1}{2}(1\pm\pi)|n\rangle) = E_n\frac{1}{2}(1\pm\pi)|n\rangle.$$

Since we supposed the state $|n\rangle$ to be non degenerate the states $|n\rangle$ and $\frac{1}{2}(1\pm\pi)|n\rangle$ must be the same excluding a phase factor,

$$\frac{1}{2}(1\pm\pi)|n\rangle = e^{i\varphi}|n\rangle,$$

so the state $|n\rangle$ is a parity eigen state belonging to the eigenvalue ±1 ∎
Example The energy states of a one dimensional harmonic oscillator are non degenerate and the Hamiltonian even, so the wave functions are either even or odd.

Note The nondegeneracy condition is essential. For example, the Hamiltonian of a free particle, $H = \frac{p^2}{2m}$, is even but the energy states

$$H|\boldsymbol{p}'\rangle = \frac{p'^2}{2m}|\boldsymbol{p}'\rangle$$

are not eigenstates of the parity because

$$\pi|\boldsymbol{p}'\rangle = |-\boldsymbol{p}'\rangle.$$

The condition of the theorem is not valid because the states $|\boldsymbol{p}'\rangle$ and $|-\boldsymbol{p}'\rangle$ are degenerate. We can form parity eigenstates

$$1/\sqrt{2}(|\boldsymbol{p}'\rangle \pm |-\boldsymbol{p}'\rangle),$$

which are also degenerate energy (but not momentum) eigenstates. The corresponding wave functions

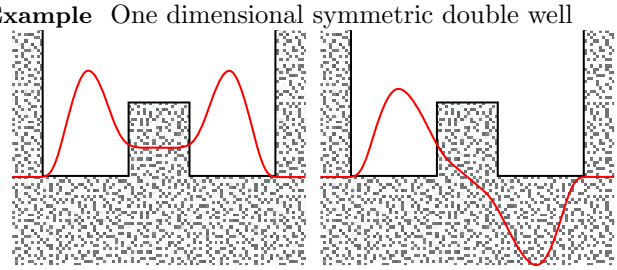
$$\psi_{\pm\boldsymbol{p}'}(\boldsymbol{x}') = \langle \boldsymbol{x}'| \pm \boldsymbol{p}'\rangle = e^{\pm i\boldsymbol{p}'\cdot\boldsymbol{x}'/\hbar}$$

are neither even nor odd, whereas

$$\begin{aligned}\langle \boldsymbol{x}'|(|\boldsymbol{p}'\rangle + |-\boldsymbol{p}'\rangle) &\propto \cos \boldsymbol{p}'\cdot\boldsymbol{x}'/\hbar \\ \langle \boldsymbol{x}'|(|\boldsymbol{p}'\rangle - |-\boldsymbol{p}'\rangle) &\propto \sin \boldsymbol{p}'\cdot\boldsymbol{x}'/\hbar\end{aligned}$$

are.

Example One dimensional symmetric double well



Symmetric ($\mathcal{S}$) Antisymmetric ($\mathcal{A}$)

The ground state is the symmetric state $|S\rangle$ and the first excited state the antisymmetric state $|A\rangle$:

$$\begin{aligned}H|S\rangle &= E_S|S\rangle \\ \pi|S\rangle &= |S\rangle \\ H|A\rangle &= E_A|S\rangle \\ \pi|A\rangle &= -|A\rangle,\end{aligned}$$

where $E_S < E_A$. When the potential barrier V between the wells increases the energy difference between the states decreases:

$$\lim_{V\to\infty}(E_A - E_S) \to 0.$$

We form the superpositions

$$\begin{aligned}|L\rangle &= \frac{1}{\sqrt{2}}(|S\rangle + |A\rangle) \\ |R\rangle &= \frac{1}{\sqrt{2}}(|S\rangle - |A\rangle),\end{aligned}$$

which are neither energy nor parity eigenstates.

Let us suppose that at the moment $t_0 = 0$ the state of the system is $|L\rangle$. At a later moment, t, the system is descibed by the state vector

$$\begin{aligned}&|L, t_0 = 0; t\rangle \\ &\quad = \frac{1}{\sqrt{2}}(e^{-iE_St/\hbar}|S\rangle + e^{-iE_At/\hbar}|A\rangle) \\ &\quad = \frac{1}{\sqrt{2}}e^{-iE_St/\hbar}(|S\rangle + e^{-i(E_A-E_S)t/\hbar}|A\rangle),\end{aligned}$$

because now the time evolution operator is simply

$$\mathcal{U}(t, t_0 = 0) = e^{-iHt/\hbar}.$$

At the moment $t = T/2 = 2\pi\hbar/2(E_A - E_S)$ the system is in the pure $|R\rangle$ state and at the moment $t = T$ again in its pure initial state $|L\rangle$. The system oscillates between the states $|L\rangle$ and $|R\rangle$ at the angular velocity

$$\omega = \frac{E_A - E_S}{\hbar}.$$

When $V \to \infty$, then $E_A \to E_S$. Then the states $|L\rangle$ and $|R\rangle$ are degenerate energy eigenstates but not parity eigenstates. A particle which is localized in one of the wells will remain there forever. Its wave function does not, however, obey the same symmetry as the Hamiltonian: we are dealing with a *broken symmetry.*

Selection rules

Suppose that the states $|\alpha\rangle$ and $|\beta\rangle$ are parity eigenstates:

$$\begin{aligned}\pi|\alpha\rangle &= \epsilon_\alpha|\alpha\rangle \\ \pi|\beta\rangle &= \epsilon_\beta|\beta\rangle,\end{aligned}$$

where ϵ_α and ϵ_β are the parities (± 1) of the states. Now

$$\langle\beta|\boldsymbol{x}|\alpha\rangle = \langle\beta|\pi^\dagger\pi\boldsymbol{x}\pi^\dagger\pi|\alpha\rangle = -\epsilon_\alpha\epsilon_\beta\langle\beta|\boldsymbol{x}|\alpha\rangle,$$

so

$$\langle\beta|\boldsymbol{x}|\alpha\rangle = 0 \text{ unless } \epsilon_\alpha = -\epsilon_\beta.$$

Example The intensity of the dipole transition is proportional to the matrix element of the operator $\boldsymbol{x}$ between the initial and final states. Dipole transitions are thus possible between states which have opposite parity.

Example Dipole moment.

If

$$[H, \pi] = 0,$$

then no non degenerate state has dipole moment:

$$\langle n|\boldsymbol{x}|n\rangle = 0.$$

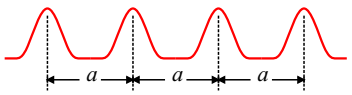
The same holds for any quantity if the corresponding operator o is odd:

$$\pi^\dagger o\pi = -o.$$

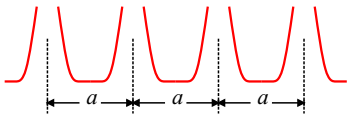
Lattice translations

We consider a particle in the one dimensional periodic potential

$$V(x \pm a) = V(x).$$



(a)



(b)

The Hamiltonian of the system is not in general invariant under translations

$$\tau^\dagger(l) x \tau(l) = x + l, \quad \tau(l)|x'\rangle = |x' + l\rangle.$$

However, when l is exactly equal to the period of the lattice a we have

$$\tau^\dagger(a) V(x) \tau(a) = V(x + a) = V(x).$$

Because the operator corresponding to the kinetic energy in the Hamiltonian is translationally invariant the whole Hamiltonian H satisfies the condition

$$\tau^\dagger(a) H \tau(a) = H,$$

which, due to the unitarity of the translation operator can be written as

$$[H, \tau(a)] = 0.$$

The operators H and $\tau(a)$ have thus common eigenstates.
Note The operator $\tau(a)$ is unitary and hence its eigenvalues need not be real.
Let us suppose that the potential barrier between the lattice points is infinitely high. Let $|n\rangle$ be the state localized in the lattice cell n, i.e.

$$\langle x'|n\rangle \neq 0 \text{ only if } x' \approx na.$$

Obviously $|n\rangle$ is a stationary state. Because all lattice cells are exactly alike we must have

$$H|n\rangle = E_0|n\rangle, \ \forall n.$$

Thus the system has countably infinite number of ground states $|n\rangle$, $n = -\infty, \ldots, \infty$.
Now

$$\tau(a)|n\rangle = |n + 1\rangle,$$

so the state $|n\rangle$ is not an eigenstate of the translation $\tau(a)$.
Let's try

$$|\theta\rangle \equiv \sum_{-\infty}^{\infty} e^{in\theta}|n\rangle,$$

where θ is a real parameter and

$$-\pi \leq \theta \leq \pi.$$

Obviously we have

$$H|\theta\rangle = E_0|\theta\rangle.$$

Furthermore we get

$$\begin{aligned} \tau(a)|\theta\rangle &= \sum_{n=-\infty}^{\infty} e^{in\theta}|n+1\rangle = \sum_{n=-\infty}^{\infty} e^{i(n-1)\theta}|n\rangle \\ &= e^{-i\theta}|\theta\rangle. \end{aligned}$$

Thus every state corresponding to a value of the continuous parameter θ has the same energy, i.e. the ground state of the system infinitely degenerate.
Let us suppose further that

- $|n\rangle$ is a state localized at the point n so that

$$\tau(a)|n\rangle = |n + 1\rangle,$$

- $\langle x'|n\rangle \neq 0$ (but small), when $|x' - na| > a$.

Due to the translation symmetry the diagonal elements of the Hamiltonian H in the base $\{|n\rangle\}$ are all equal to eachother:

$$\langle n|H|n\rangle = E_0.$$

Let us suppose now that

$$\langle n'|H|n\rangle \neq 0 \text{ only if } n' = n \text{ or } n' = n \pm 1.$$

We are dealing with the so called *tight binding approximation.*
When we define

$$\Delta = -\langle n \pm 1|H|n\rangle,$$

we can write

$$H|n\rangle = E_0|n\rangle - \Delta|n + 1\rangle - \Delta|n - 1\rangle,$$

where we have exploited the orthonormality of the basis $\{|n\rangle\}$. Thus the state $|n\rangle$ is not an energy eigen state.
Let us look again at the trial

$$|\theta\rangle = \sum_{n=-\infty}^{\infty} e^{in\theta}|n\rangle.$$

Like before we have

$$\tau(a)|\theta\rangle = e^{-i\theta}|\theta\rangle.$$

Furthermore

$$\begin{aligned} H \sum & e^{in\theta}|n\rangle \\ &= E_0 \sum e^{in\theta}|n\rangle - \Delta \sum e^{in\theta}|n+1\rangle \\ &\quad -\Delta \sum e^{in\theta}|n-1\rangle \\ &= E_0 \sum e^{in\theta}|n\rangle - \Delta \sum (e^{in\theta - i\theta} + e^{in\theta + i\theta})|n\rangle \\ &= (E_0 - 2\Delta \cos\theta) \sum e^{in\theta}|n\rangle. \end{aligned}$$

The earlier degeneracy will be lifted if $\Delta \neq 0$ and

$$E_0 - 2\Delta \leq E \leq E_0 + 2\Delta.$$

Bloch's theorem
Let us consider the wave function $\langle x'|\theta\rangle$. In the translated state $\tau(a)|\theta\rangle$ the wave function is

$$\langle x'|\tau(a)|\theta\rangle = \langle x' - a|\theta\rangle$$

when the operator $\tau(a)$ acts on left. When it acts on right we get

$$\langle x'|\tau(a)|\theta\rangle = e^{-i\theta}\langle x'|\theta\rangle,$$

so we have

$$\langle x' - a|\theta\rangle = \langle x'|\theta\rangle e^{-i\theta}.$$

This equation can be solved by substituting

$$\langle x'|\theta\rangle = e^{ikx'}u_k(x'),$$

when $\theta = ka$ and $u_k(x')$ is a periodic function with the period a.
We have derived a theorem known as the *Bloch theorem*:
Theorem 1 *The wave function of the eigenstate $|\theta\rangle$ of the translation operator $\tau(a)$ can be written as the procuct of the plane wave $e^{ikx'}$ and a function with the period a.*
Note When deriving the theorem we exploited only the fact that $|\theta\rangle$ an eigenstate of the operator $\tau(a)$ belonging to the eigenvalue $e^{i\theta}$. Thus it is valid for all periodic systems (whether the tight binding approximation holds or not)
With the help of the Bloch theorem the dispersion relation of the energy in the tight binding model can be written as

$$E(k) = E_0 - 2\Delta\cos ka,\ -\frac{\pi}{a} \le k \le \frac{\pi}{a}.$$

This continuum of the energies is known as the *Brillouin zone*.

Time reversal (reversal of motion)

The Newton equations of motion are invariant under the transformation $t \longrightarrow -t$: if $\boldsymbol{x}(t)$ is a solution of the equation

$$m\ddot{\boldsymbol{x}} = -\nabla V(\boldsymbol{x})$$

then also $\boldsymbol{x}(-t)$ is a solution.
At the moment $t = 0$ let there be a particle at the point $\boldsymbol{x}(t = 0)$ with the momentum $\boldsymbol{p}(t = 0)$. Then a particle at the same point but with the momentum $-\boldsymbol{p}(t = 0)$ follows the trajectory $\boldsymbol{x}(-t)$.
In the quantum mechanical Schrödinger equation

$$i\hbar\frac{\partial\psi}{\partial t} = \left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi,$$

due to the first derivative with respect to the time, $\psi(\boldsymbol{x}, -t)$ is not a solution eventhough $\psi(\boldsymbol{x}, t)$ were, but $\psi^*(\boldsymbol{x}, -t)$ is. In quantum mechanics the time reversal has obviously something to do with the complex conjugation. Let us consider the symmetry operation

$$|\alpha\rangle \longrightarrow |\tilde{\alpha}\rangle, \quad |\beta\rangle \longrightarrow |\tilde{\beta}\rangle.$$

We require that the absolute value of the scalar product is invariant under that operation:

$$|\langle\tilde{\beta}|\tilde{\alpha}\rangle| = |\langle\beta|\alpha\rangle|.$$

There are two possibilities to satisfy this condition:

1. $\langle\tilde{\beta}|\tilde{\alpha}\rangle = \langle\beta|\alpha\rangle$, so the corresponding symmetry operator is unitary, that is

   $$\langle\beta|\alpha\rangle \longrightarrow \langle\beta|U^\dagger U|\alpha\rangle = \langle\beta|\alpha\rangle.$$

   The symmetries treated earlier have obeyed this condition.

2. $\langle\tilde{\beta}|\tilde{\alpha}\rangle = \langle\beta|\alpha\rangle^* = \langle\alpha|\beta\rangle$, so the symmetry operator cannot be unitary.

We define the *antiunitary* operator θ so that

$$\begin{aligned}\langle\tilde{\beta}|\tilde{\alpha}\rangle &= \langle\alpha|\beta\rangle^* \\ \theta(c_1|\alpha\rangle + c_2|\beta\rangle) &= c_1^*\theta|\alpha\rangle + c_2^*\theta|\beta\rangle,\end{aligned}$$

where

$$|\alpha\rangle \longrightarrow |\tilde{\alpha}\rangle = \theta|\alpha\rangle, \quad |\beta\rangle \longrightarrow |\tilde{\beta}\rangle = \theta|\beta\rangle$$

If the operator satisfies only the last condition it is called *antilinear*.
We define the complex conjugation operator K so that

$$Kc|\alpha\rangle = c^*K|\alpha\rangle.$$

We present the state $|\alpha\rangle$ in the base $\{|a'\rangle\}$. The effect of the operator K is then

$$\begin{aligned}|\alpha\rangle &= \sum_{a'}|a'\rangle\langle a'|\alpha\rangle \xrightarrow{K} |\tilde{\alpha}\rangle = \sum_{a'}\langle a'|\alpha\rangle^* K|a'\rangle \\ &= \sum_{a'}\langle a'|\alpha\rangle^*|a'\rangle.\end{aligned}$$

The fact that the operator K does not change the base states can be justified like:
The state $|a'\rangle$ represented in the base $\{|a'\rangle\}$ maps to the column vector

$$|a'\rangle \mapsto \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \\ 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix},$$

which is unaffected by the complex conjugation.
Note The effect of the operator K depends thus on the choice of the basis states.
If U is a unitary operator then the operator $\theta = UK$ is antiunitary.
Proof: Firstly

$$\begin{aligned}\theta(c_1|\alpha\rangle + c_2|\beta\rangle) &= UK(c_1|\alpha\rangle + c_2|\beta\rangle) \\ &= (c_1^*UK|\alpha\rangle + c_2^*UK|\beta\rangle) \\ &= (c_1^*\theta|\alpha\rangle + c_2^*\theta|\beta\rangle),\end{aligned}$$

so θ is antiliniear. Secondly, expanding the states $|\alpha\rangle$ and $|\beta\rangle$ in a complete basis $\{|a'\rangle\}$ we get

$$\begin{aligned}|\alpha\rangle \xrightarrow{\theta} |\tilde{\alpha}\rangle &= \sum_{a'}\langle a'|\alpha\rangle^* UK|a'\rangle \\ &= \sum_{a'}\langle a'|\alpha\rangle^* U|a'\rangle \\ &= \sum_{a'}\langle\alpha|a'\rangle U|a'\rangle\end{aligned}$$

and

$$|\tilde{\beta}\rangle = \sum_{a'}\langle a'|\beta\rangle^* U|a'\rangle \leftrightarrow \langle\tilde{\beta}| = \sum_{a'}\langle a'|\beta\rangle\langle a'|U^\dagger.$$

Thus the scalar product is

$$\begin{aligned}\langle\tilde{\beta}|\tilde{\alpha}\rangle &= \sum_{a''}\sum_{a'}\langle a''|\beta\rangle\langle a''|U^\dagger U|a'\rangle\langle\alpha|a'\rangle \\ &= \sum_{a'}\langle\alpha|a'\rangle\langle a'|\beta\rangle = \langle\alpha|\beta\rangle \\ &= \langle\beta|\alpha\rangle^*.\end{aligned}$$

The operator θ is thus indeed antiunitary. ∎
Let Θ be the time reversal operator. We consider the transformation

$$|\alpha\rangle \longrightarrow \Theta|\alpha\rangle,$$

where $\Theta|\alpha\rangle$ is the time reversed (motion reversed) state. If $|\alpha\rangle$ is the momentum eigenstate $|\boldsymbol{p}'\rangle$, we should have

$$\Theta|\boldsymbol{p}'\rangle = e^{i\varphi}|-\boldsymbol{p}'\rangle.$$

Let the system be at the moment $t = 0$ in the state $|\alpha\rangle$. At a slightly later moment $t = \delta t$ it is in the state

$$|\alpha, t_0 = 0; t = \delta t\rangle = \left(1 - \frac{iH}{\hbar}\delta t\right)|\alpha\rangle.$$

We apply now, at the moment $t = 0$, the time reversal operator Θ and let the system evolve under the Hamiltonian H. Then at the moment δt the system is in the state

$$\left(1 - \frac{iH}{\hbar}\delta t\right)\Theta|\alpha\rangle.$$

If the motion of the system is invariant under time reversal this state should be the same as

$$\Theta|\alpha, t_0 = 0; -\delta t\rangle,$$

i.e. we first look at the state at the earlier moment $-\delta t$ and then reverse the direction of the momentum $\boldsymbol{p}$. Mathematically this condition can be expressed as

$$\left(1 - \frac{iH}{\hbar}\delta t\right)\Theta|\alpha\rangle = \Theta\left(1 - \frac{iH}{\hbar}(-\delta t)\right)|\alpha\rangle.$$

Thus we must have

$$-iH\Theta|\rangle = \Theta iH|\rangle,$$

where $|\rangle$ stands for an arbitrary state vector.
If Θ were linear we would obtain the anticommutator relation

$$H\Theta = -\Theta H.$$

If now $|n\rangle$ is an energy eigenstate corresponding to the eigenvalue E_n then, according to the anticommutation rule

$$H\Theta|n\rangle = -\Theta H|n\rangle = (-E_n)\Theta|n\rangle,$$

and the state $\Theta|n\rangle$ is an energy eigenstate corresponding to the eigenvalue $-E_n$. Thus most systems (those, whose energy spectrum is not bounded) would not have any ground state.
Thus the operator Θ must be antilinear, and, in order to be a symmetry operator, it must be antiunitary. Using the antilinearity for the right hand side of the condition

$$-iH\Theta|\rangle = \Theta iH|\rangle$$

we can write it as

$$\Theta iH|\rangle = -i\Theta H|\rangle.$$

So, we see that the operators commute:

$$\Theta H = H\Theta.$$

Note We have not defined the Hermitean conjugate of the antiunitary operator θ nor have we defined the meaning of the expression $\langle\beta|\theta$. That being, we let the time reversal operator Θ to operate always on the right and with the matrix element $\langle\beta|\Theta|\alpha\rangle$ we mean the expression $(\langle\beta|) \cdot (\Theta|\alpha\rangle)$.
Let $\otimes$ be an arbitrary linear operator. We define

$$|\gamma\rangle \equiv \otimes^\dagger|\beta\rangle,$$

so that

$$\langle\beta|\otimes = \langle\gamma|$$

and

$$\begin{aligned}\langle\beta| \otimes |\alpha\rangle &= \langle\gamma|\alpha\rangle = \langle\tilde{\alpha}|\tilde{\gamma}\rangle \\ &= \langle\tilde{\alpha}|\Theta \otimes^\dagger |\beta\rangle = \langle\tilde{\alpha}|\Theta \otimes^\dagger \Theta^{-1}\Theta|\beta\rangle \\ &= \langle\tilde{\alpha}|\Theta \otimes^\dagger \Theta^{-1}|\tilde{\beta}\rangle.\end{aligned}$$

In partcular, for a Hermitean observable A we have

$$\langle\beta|A|\alpha\rangle = \langle\tilde{\alpha}|\Theta A\Theta^{-1}|\tilde{\beta}\rangle.$$

We say that the observable A is even or odd under time reversal depending on wheter in the equation

$$\Theta A\Theta^{-1} = \pm A$$

the upper or the lower sign holds. This together with the equation

$$\langle\beta|A|\alpha\rangle = \langle\tilde{\alpha}|\Theta A\Theta^{-1}|\tilde{\beta}\rangle$$

imposes certain conditions on the phases of the matrix elements of the operator A between the time reversed states. Namely, they has to satisfy

$$\langle\beta|A|\alpha\rangle = \pm\langle\tilde{\beta}|A|\tilde{\alpha}\rangle^*.$$

In particular, the expectation value satisfies the condition

$$\langle\alpha|A|\alpha\rangle = \pm\langle\tilde{\alpha}|A|\tilde{\alpha}\rangle.$$

Example The expectation value of the momentum operator $\boldsymbol{p}$.
We require that

$$\langle\alpha|\boldsymbol{p}|\alpha\rangle = -\langle\tilde{\alpha}|\boldsymbol{p}|\tilde{\alpha}\rangle,$$

so $\boldsymbol{p}$ is odd, or

$$\Theta\boldsymbol{p}\Theta^{-1} = -\boldsymbol{p}.$$

The momentum eigenstates satisfy

$$\begin{aligned}\boldsymbol{p}\Theta|\boldsymbol{p}'\rangle &= -\Theta\boldsymbol{p}\Theta^{-1}\Theta|\boldsymbol{p}'\rangle \\ &= (-\boldsymbol{p}')\Theta|\boldsymbol{p}'\rangle,\end{aligned}$$

i.e. $\Theta|\boldsymbol{p}'\rangle$ is the momentum eigenstates correponding to the eigenvalue $-\boldsymbol{p}'$:

$$\Theta|\boldsymbol{p}'\rangle = e^{i\varphi}|-\boldsymbol{p}'\rangle.$$

Similarly we can derive for the position operator $\boldsymbol{x}$ the expressions

$$\begin{aligned}\Theta\boldsymbol{x}\Theta^{-1} &= \boldsymbol{x} \\ \Theta|\boldsymbol{x}'\rangle &= |\boldsymbol{x}'\rangle\end{aligned}$$

when we impose the physically sensible condition

$$\langle\alpha|\boldsymbol{x}|\alpha\rangle = \langle\tilde{\alpha}|\boldsymbol{x}|\tilde{\alpha}\rangle.$$

We consider the basic commutation relations

$$[x_i, p_j]|\rangle = i\hbar\delta_{ij}|\rangle.$$

Now

$$\Theta[x_i, p_j]\Theta^{-1}\Theta|\rangle = \Theta i\hbar\delta_{ij}|\rangle,$$

from which, using the antilinearity and the time reversal properties of the operators $\boldsymbol{x}$ and $\boldsymbol{p}$ we get

$$[x_i, (-p_j)]\Theta|\rangle = -i\hbar\delta_{ij}\Theta|\rangle.$$

We see thus that the commutation rule

$$[x_i, p_j]|\rangle = i\hbar\delta_{ij}|\rangle$$

remains invariant under the time reversal.
Correspondingly, the requirement of the invariance of the commutation rule

$$[J_i, J_j] = i\hbar\epsilon_{ijk}J_k$$

leads to the condition

$$\Theta\boldsymbol{J}\Theta^{-1} = -\boldsymbol{J}.$$

This agrees with transformation properties of the orbital angular momentum $\boldsymbol{x} \times \boldsymbol{p}$.

Wave functions
We expand the state $|\alpha\rangle$ with the help of position eigenstates:

$$|\alpha\rangle = \int d^3x' \, |\boldsymbol{x}'\rangle\langle\boldsymbol{x}'|\alpha\rangle.$$

Now

$$\begin{aligned}\Theta|\alpha\rangle &= \int d^3x' \, \Theta|\boldsymbol{x}'\rangle\langle\boldsymbol{x}'|\alpha\rangle^* \\ &= \int d^3x' \, |\boldsymbol{x}'\rangle\langle\boldsymbol{x}'|\alpha\rangle^*,\end{aligned}$$

so under the time reversal the wave function

$$\psi(\boldsymbol{x}') = \langle\boldsymbol{x}'|\alpha\rangle$$

transforms like

$$\psi(\boldsymbol{x}') \longrightarrow \psi^*(\boldsymbol{x}').$$

If in particular we have

$$\psi(\boldsymbol{x}') = R(r)Y_l^m(\theta, \phi),$$

we see that

$$Y_l^m(\theta, \phi) \longrightarrow Y_l^{m*}(\theta, \phi) = (-1)^m Y_l^{-m}(\theta, \phi).$$

Because Y_l^m is the wave function belonging to the state $|lm\rangle$ we must have

$$\Theta|lm\rangle = (-1)^m|l, -m\rangle.$$

The probability current corresponding to the wave function $R(r)Y_l^m$ seems to turn clockwise when looked at from the direction of the positive z-axis and $m > 0$. The probability current of the corresponding time reversed state on the other hand turns counterclockwise because m changes its sign under the operation.
The spinles particles obey
Theorem 1 *If the Hamiltonian H is invariant under the time reversal and the energy eigenstate $|n\rangle$ nondegenerate then the corresponding energy eigenfunction is real (or more generally a real function times a phase factor independent on the coordinate $\boldsymbol{x}'$).*

$$H\Theta|n\rangle = \Theta H|n\rangle = E_n\Theta|n\rangle,$$

so the states $|n\rangle$ and $\Theta|n\rangle$ have the same energy. Because the state $|n\rangle$ was supposed to be nondegenerate they must represent the same state. The wave function of the state $|n\rangle$ is $\langle\boldsymbol{x}'|n\rangle$ and the one of the state $\Theta|n\rangle$ correspondingly $\langle\boldsymbol{x}'|n\rangle^*$. These must be same (or more accurately, they can differ only by a phase factor which does not depend on the coordinate $\boldsymbol{x}'$), i.e.

$$\langle\boldsymbol{x}'|n\rangle = \langle\boldsymbol{x}'|n\rangle^* \quad \blacksquare$$

For example the wave function of a nondegenerate groundstate is always real.
For a spinles particle in the state $|\alpha\rangle$ we get

$$\begin{aligned}\Theta|\alpha\rangle &= \Theta\int d\boldsymbol{x}' \, \langle\boldsymbol{x}'|\alpha\rangle|\boldsymbol{x}'\rangle \\ &= \int d\boldsymbol{x}' \, \langle\boldsymbol{x}'|\alpha\rangle^*|\boldsymbol{x}'\rangle = K|\alpha\rangle,\end{aligned}$$

i.e. the time reversal is equivalent to the complex conjugation.
On the other hand, in the momentum space we have

$$\begin{aligned}\Theta|\alpha\rangle &= \int d^3p' \, |-\boldsymbol{p}'\rangle\langle\boldsymbol{p}'|\alpha\rangle^* \\ &= \int d^3p' \, |\boldsymbol{p}'\rangle\langle-\boldsymbol{p}'|\alpha\rangle^*,\end{aligned}$$

because

$$\Theta|\boldsymbol{p}'\rangle = |-\boldsymbol{p}'\rangle.$$

The momentum space wave function transform thus under time reversal like

$$\phi(\boldsymbol{p}') \longrightarrow \phi^*(-\boldsymbol{p}').$$

We consider a spin $\frac{1}{2}$ particle the spin of which is oriented along $\hat{\boldsymbol{n}}$. The corresponding state is obtained by rotating the state $|S_z;\uparrow\rangle$:

$$|\boldsymbol{n};\uparrow\rangle = e^{-iS_z\alpha/\hbar}e^{-iS_y\beta/\hbar}|S_z;\uparrow\rangle,$$

where α and β are the direction angles of the vector $\hat{\boldsymbol{n}}$.
Because

$$\Theta\boldsymbol{J}\Theta^{-1} = -\boldsymbol{J}.$$

we see that

$$\Theta|\boldsymbol{n};\uparrow\rangle = e^{-iS_z\alpha/\hbar}e^{-iS_y\beta/\hbar}\Theta|S_z;\uparrow\rangle.$$

Furthermore, due to the oddity of the angular momentum, it follows that

$$J_z\Theta|S_z;\uparrow\rangle = -\frac{\hbar}{2}\Theta|S_z;\uparrow\rangle,$$

so we must have

$$\Theta|S_z;\uparrow\rangle = \eta|S_z;\downarrow\rangle,$$

where η is an arbitrary phase factor. So we get

$$\Theta|\boldsymbol{n};\uparrow\rangle = \eta|\boldsymbol{n};\downarrow\rangle.$$

On the other hand we have

$$|\boldsymbol{n};\downarrow\rangle = e^{-i\alpha S_z/\hbar}e^{-i(\pi+\beta)S_y/\hbar}|S_z;\uparrow\rangle,$$

so

$$\begin{aligned}\eta|\boldsymbol{n};\downarrow\rangle &= \Theta|\boldsymbol{n};\uparrow\rangle = e^{-iS_z\alpha/\hbar}e^{-iS_y\beta/\hbar}\Theta|S_z;\uparrow\rangle \\ &= \eta e^{-i\alpha S_z/\hbar}e^{-i(\pi+\beta)S_y/\hbar}|S_z;\uparrow\rangle.\end{aligned}$$

Writing

$$\Theta = UK,\ U \text{ unitary}$$

and recalling that the complex conjugation K has no effect on the base states we see that

$$\Theta = \eta e^{-i\pi S_y/\hbar}K = -i\eta\left(\frac{2S_y}{\hbar}\right)K.$$

Now

$$\begin{aligned}e^{-i\pi S_y/\hbar}|S_z;\uparrow\rangle &= +|S_z;\downarrow\rangle \\ e^{-i\pi S_y/\hbar}|S_z;\downarrow\rangle &= -|S_z;\uparrow\rangle,\end{aligned}$$

so the effect of the time reversal on a general spin $\frac{1}{2}$ state is

$$\Theta(c_\uparrow|S_z;\uparrow\rangle + c_\downarrow|S_z;\downarrow\rangle) = +\eta c_\uparrow^*|S_z;\downarrow\rangle - \eta c_\downarrow^*|S_z;\uparrow\rangle.$$

Applying the operator Θ once again we get

$$\begin{aligned}&\Theta^2(c_\uparrow|S_z;\uparrow\rangle + c_\downarrow|S_z;\downarrow\rangle) \\ &\quad = -|\eta|^2c_\uparrow|S_z;\uparrow\rangle - |\eta|^2c_\downarrow|S_z;\downarrow\rangle \\ &\quad = -(c_\uparrow|S_z;\uparrow\rangle + c_\downarrow|S_z;\downarrow\rangle),\end{aligned}$$

i.e. for an arbitrary spin orientation we have

$$\Theta^2 = -1.$$

From the relation

$$\Theta|lm\rangle = (-1)^m|l,-m\rangle$$

we see that for spinles particles we have

$$\Theta^2 = 1.$$

In general, one can show that

$$\begin{aligned}\Theta^2|j \text{ half integer}\rangle &= -|j \text{ half integer}\rangle \\ \Theta^2|j \text{ integer}\rangle &= +|j \text{ integer}\rangle.\end{aligned}$$

Generally we can write

$$\Theta = \eta e^{-i\pi J_y/\hbar}K.$$

Now

$$e^{-2i\pi J_y/\hbar}|jm\rangle = (-1)^{2j}|jm\rangle,$$

so

$$\begin{aligned}\Theta^2|jm\rangle &= \Theta\left(\eta e^{-i\pi J_y/\hbar}|jm\rangle\right) \\ &= |\eta|^2e^{-2i\pi J_y/\hbar}|jm\rangle \\ &= (-1)^{2j}|jm\rangle.\end{aligned}$$

Thus we must have

$$\Theta^2 = (-1)^{2j}.$$

Often one chooses

$$\Theta|jm\rangle = i^{2m}|j,-m\rangle.$$

Spherical tensors

Let us suppose that the operator A is either even or odd, i.e.

$$\Theta A\Theta^{(-1)} = \pm A.$$

We saw that then we have

$$\langle\alpha|A|\alpha\rangle = \pm\langle\tilde{\alpha}|A|\tilde{\alpha}\rangle.$$

In an eigenstate of the angular momentum we have thus

$$\langle\alpha,jm|A|\alpha,jm\rangle = \pm\langle\alpha,j,-m|A|\alpha,j,-m\rangle.$$

Let now A be a component of a Hermitian spherical tensor:

$$A = T_q^{(k)}.$$

According to the Wigner-Eckart theorem it is sufficient to consider only the component $q = 0$.
We define $T^{(k)}$ to be even/odd under the time reversal if

$$\Theta T_{q=0}^{(k)}\Theta^{-1} = \pm T_{q=0}^{(k)}.$$

Then we have

$$\langle\alpha,jm|T_0^{(k)}|\alpha,jm\rangle = \pm\langle\alpha,j,-m|T_0^{(k)}|\alpha,j,-m\rangle.$$

The state $|\alpha,j,-m\rangle$ is obtained by rotating the state $|\alpha,jm\rangle$:

$$\mathcal{D}(0,\pi,0)|\alpha,jm\rangle = e^{i\varphi}|\alpha,j,-m\rangle.$$

On the other hand, due to the definition of the spherical tensor

$$\mathcal{D}^\dagger(R)T_q^{(k)}\mathcal{D}(R) = \sum_{q'=-k}^{k}\mathcal{D}_{qq'}^{(k)^*}(R)T_{q'}^{(k)},$$

we get

$$\mathcal{D}^\dagger(0,\pi,0)T_0^{(k)}\mathcal{D}(0,\pi,0) = \sum_q \mathcal{D}_{0q}^{(k)}(0,\pi,0)T_q^{(k)}.$$

Now

$$\mathcal{D}_{00}^{(k)}(0,\pi,0) = P_k(\cos\pi) = (-1)^k,$$

so we have

$$\begin{aligned}&\mathcal{D}^\dagger(0,\pi,0)T_0^{(k)}\mathcal{D}(0,\pi,0) \\ &\quad = (-1)^kT_0^{(k)} + (q \neq 0 \text{ components}).\end{aligned}$$

Furthermore

$$\langle\alpha,jm|T_{q\neq0}^{(k)}|\alpha,jm\rangle = 0,$$

since the m selection rule would require $m = m + q$. So we get

$$\begin{aligned}&\langle \alpha, jm|T_0^{(k)}|\alpha, jm\rangle \\ &\quad = \pm\langle \alpha, jm|\mathcal{D}^\dagger(0,\pi,0)T_0^{(k)}\mathcal{D}(0,\pi,0)|\alpha, jm\rangle \\ &\quad = \pm(-1)^k\langle \alpha, jm|T_0^{(k)}|\alpha, jm\rangle.\end{aligned}$$

Note Unlike under other symmetries the invariance of the Hamiltonian under the time reversal

$$[\Theta, H] = 0,$$

does not lead to any conservation laws. This is due to the fact that the time evolution operator is not invariant:

$$\Theta U(t, t_0) \neq U(t, t_0)\Theta.$$

Time reversal and degeneracy
Let us suppose that

$$[\Theta, H] = 0.$$

Then the energy eigenstates obey

$$\begin{aligned}H|n\rangle &= E_n|n\rangle \\ H\Theta|n\rangle &= E_n\Theta|n\rangle.\end{aligned}$$

If we now had

$$\Theta|n\rangle = e^{i\delta}|n\rangle,$$

then, reapplying the time reversal we would obtain

$$\Theta^2|n\rangle = e^{-i\delta}\Theta|n\rangle = |n\rangle,$$

or

$$\Theta^2 = 1.$$

This is, however, impossible if the system j is half integer, because then $\Theta^2 = -1$. In systems of this kind $|n\rangle$ and $\Theta|n\rangle$ are degenerate.
Example Electon in electromagnetic field
If a particle is influenced by an external static electric field

$$V(\boldsymbol{x}) = e\phi(\boldsymbol{x}),$$

then clearly the Hamiltonian

$$H = \frac{\boldsymbol{p}^2}{2m} + V(\boldsymbol{x})$$

is invariant under the time reversal:

$$[\Theta, H] = 0.$$

If now there are odd number of electrons in the system the total j is half integer. Thus, in a system of this kind there is at least twofold degeneracy, so called *Kramers' degeneracy*.
In the magnetic field

$$\boldsymbol{B} = \nabla \times \boldsymbol{A}$$

the Hamiltonian of an electron contains such terms as

$$\boldsymbol{S} \cdot \boldsymbol{B}, \quad \boldsymbol{p} \cdot \boldsymbol{A} + \boldsymbol{A} \cdot \boldsymbol{p}.$$

The magnetic field $\boldsymbol{B}$ is external, independent on the system, so

$$[\Theta, \boldsymbol{B}] = 0 \text{ ja } [\Theta, \boldsymbol{A}] = 0.$$

On the other hand, $\boldsymbol{S}$ and $\boldsymbol{p}$ are odd, or

$$\Theta\boldsymbol{S}\Theta^{-1} = -\boldsymbol{S} \text{ ja } \Theta\boldsymbol{p}\Theta^{-1} = -\boldsymbol{p},$$

so

$$[\Theta, H] \neq 0.$$

We say that magnetic field breaks the time reversal symmetry and lifts the Kramers degeneracy.

Perturbation theory

Stationary perturbation methods

Let us suppose that

- we have solved completely the problem

$$H_0|n^{(0)}\rangle = E_n^{(0)}|n^{(0)}\rangle.$$

  The basis $\{|n^{(0)}\rangle\}$ is now complete.

- the states $|n^{(0)}\rangle$ are non degenerate.

- we want to solve the problem

$$(H_0 + \lambda V)|n\rangle_\lambda = E_n^{(\lambda)}|n\rangle_\lambda.$$

  Usualy the index λ is dropped off.

When we denote

$$\Delta_n \equiv E_n - E_n^{(0)},$$

the eigenvalue equation to be solved takes the form

$$(E_n^{(0)} - H_0)|n\rangle = (\lambda V - \Delta_n)|n\rangle.$$

Note Because the expression $(E_n^{(0)} - H_0)^{-1}|n^{(0)}\rangle$ is undefined the operator $(E_n^{(0)} - H_0)^{-1}$ is not well defined. So, in the equation above we cannot invert the operator $(E_n^{(0)} - H_0)$.

Now

$$\langle n^{(0)}|\lambda V - \Delta_n|n\rangle = \langle n^{(0)}|E_n^{(0)} - H_0|n\rangle,$$

so in the state $(\lambda V - \Delta_n)|n\rangle$ there is no component along the state $|n^{(0)}\rangle$.

We define a projection operator as

$$\phi_n = 1 - |n^{(0)}\rangle\langle n^{(0)}| = \sum_{k\neq n} |k^{(0)}\rangle\langle k^{(0)}|.$$

Now

$$\frac{1}{E_n^{(0)} - H_0}\phi_n = \sum_{k\neq n} \frac{1}{E_n^{(0)} - E_k^{(0)}}|k^{(0)}\rangle\langle k^{(0)}|$$

and

$$(\lambda V - \Delta_n)|n\rangle = \phi_n(\lambda V - \Delta_n)|n\rangle.$$

Since in the limit $\lambda \to 0$ we must have

$$|n\rangle \to |n^{(0)}\rangle,$$

the formal solution is of the form

$$|n\rangle = c_n(\lambda)|n^{(0)}\rangle + \frac{1}{E_n^{(0)} - H_0}\phi_n(\lambda V - \Delta_n)|n\rangle,$$

where

$$\lim_{\lambda\to 0} c_n(\lambda) = 1$$

and

$$c_n(\lambda) = \langle n^{(0)}|n\rangle.$$

Diverting from the normal procedure we normalize

$$\langle n^{(0)}|n\rangle = c_n(\lambda) = 1.$$

We write

$$\begin{aligned} |n\rangle &= |n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \cdots \\ \Delta_n &= \lambda\Delta_n^{(1)} + \lambda^2\Delta_n^{(2)} + \cdots. \end{aligned}$$

Because

$$\langle n^{(0)}|\lambda V - \Delta_n|n\rangle = 0,$$

we have, on the other hand

$$\Delta_n = \lambda\langle n^{(0)}|V|n\rangle.$$

Thus we get

$$\begin{aligned} &\lambda\Delta_n^{(1)} + \lambda^2\Delta_n^{(2)} + \cdots \\ &\quad = \lambda\langle n^{(0)}|V|n^{(0)}\rangle + \lambda^2\langle n^{(0)}|V|n^{(1)}\rangle + \cdots. \end{aligned}$$

Equalizing the coefficients of the powers of the parameter λ we get

$$\begin{aligned} \mathcal{O}(\lambda^1): &\quad \Delta_n^{(1)} &&= \langle n^{(0)}|V|n^{(0)}\rangle \\ \mathcal{O}(\lambda^2): &\quad \Delta_n^{(2)} &&= \langle n^{(0)}|V|n^{(1)}\rangle \\ &\quad \vdots &&\quad \vdots \\ \mathcal{O}(\lambda^N): &\quad \Delta_n^{(N)} &&= \langle n^{(0)}|V|n^{(N-1)}\rangle \\ &\quad \vdots &&\quad \vdots \end{aligned}.$$

We substitute into the expression

$$|n\rangle = |n^{(0)}\rangle + \frac{\phi_n}{E_n^{(0)} - H_0}(\lambda V - \Delta_n)|n\rangle$$

for the state vector the power series of the state vector and the energy correction and we get

$$\begin{aligned} &|n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \cdots \\ &\quad = |n^{(0)}\rangle + \frac{\phi_n}{E_n^{(0)} - H_0}(\lambda V - \lambda\Delta_n^{(1)} - \lambda^2\Delta_n^{(2)} - \cdots) \\ &\quad\quad \times(|n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \cdots). \end{aligned}$$

Equalizing the coefficients of the linear λ-terms we get in the first order

$$\begin{aligned} \mathcal{O}(\lambda):\ &|n^{(1)}\rangle \\ &= \frac{\phi_n}{E_n^{(0)} - H_0}V|n^{(0)}\rangle - \frac{\Delta_n^{(1)}}{E_n^{(0)} - H_0}\phi_n|n^{(0)}\rangle \\ &= \frac{\phi_n}{E_n^{(0)} - H_0}V|n^{(0)}\rangle, \end{aligned}$$

because

$$\phi_n\Delta_n^{(1)}|n^{(0)}\rangle = 0.$$

We substitute $|n^{(1)}\rangle$ into the expression

$$\Delta_n^{(2)} = \langle n^{(0)}|V|n^{(1)}\rangle,$$

so

$$\Delta_n^{(2)} = \langle n^{(0)}|V\frac{\phi_n}{E_n^{(0)} - H_0}V|n^{(0)}\rangle.$$

We substitute this further into the power series of the state vectors and we get for the coeffients of λ^2 the condition

$$\mathcal{O}(\lambda^2): \ |n^{(2)}\rangle = \frac{\phi_n}{E_n^{(0)} - H_0} V \frac{\phi_n}{E_n^{(0)} - H_0} V |n^{(0)}\rangle - \frac{\phi_n}{E_n^{(0)} - H_0} \langle n^{(0)}|V|n^{(0)}\rangle \frac{\phi_n}{E_n^{(0)} - H_0} V |n^{(0)}\rangle.$$

Likewise we could continue to higher powers of the parameter λ. This method is known as the *Rayleigh-Schrödinger perturbation theory.*
The explicit expression for the second order energy correction will be

$$\begin{aligned}\Delta_n^{(2)} &= \langle n^{(0)}|V \frac{\phi_n}{E_n^{(0)} - H_0} V |n^{(0)}\rangle \\ &= \sum_{k,l} \langle n^{(0)}|V|k^{(0)}\rangle\langle k^{(0)}| \frac{\phi_n}{E_n^{(0)} - H_0} |l^{(0)}\rangle\langle l^{(0)}|V|n^{(0)}\rangle \\ &= \sum_{k,l\neq n} V_{nk} \frac{\langle k^{(0)}|l^{(0)}\rangle}{E_n^{(0)} - E_l^{(0)}} V_{ln} \\ &= \sum_{k\neq n} \frac{|V_{nk}|^2}{E_n^{(0)} - E_k^{(0)}}.\end{aligned}$$

Thus, up to the second order we have

$$\begin{aligned}\Delta_n &\equiv E_n - E_n^{(0)} \\ &= \lambda V_{nn} + \lambda^2 \sum_{k\neq n} \frac{|V_{nk}|^2}{E_n^{(0)} - E_k^{(0)}} + \cdots.\end{aligned}$$

Correspondingly, up to the second order the state vector is

$$|n\rangle = |n^{(0)}\rangle + \lambda \sum_{k\neq n} |k^{(0)}\rangle \frac{V_{kn}}{E_n^{(0)} - E_k^{(0)}} + \lambda^2 \sum_{k\neq n} |k^{(0)}\rangle \left(\sum_{l\neq n} \frac{V_{kl}V_{ln}}{(E_n^{(0)} - E_k^{(0)})(E_n^{(0)} - E_l^{(0)})} - \frac{V_{nn}V_{kn}}{(E_n^{(0)} - E_k^{(0)})^2} \right) + \cdots.$$

We see that the perturbation *mixes* in also other states (than $|n^{(0)}\rangle$).
We see that

- in the 1st order we need only the matrix element V_{nn}.
- in the 2nd order the energy levels i and j repel each other. Namely, if $E_i^{(0)} < E_j^{(0)}$, then the contributions of one of these states to the energy corrections of the other are

$$\begin{aligned}\Delta_i^{(2)} &= \frac{|V_{ij}|^2}{E_i^{(0)} - E_j^{(0)}} < 0 \\ \Delta_j^{(2)} &= \frac{|V_{ij}|^2}{E_j^{(0)} - E_i^{(0)}} > 0\end{aligned}$$

  and the energy levels move apart from each other.

Perturbation expansions converge if $|V_{ij}/(E_i^{(0)} - E_j^{(0)})|$ is "small". In general, no exact convergence criterion is known.
The state $|n\rangle$ is not normalized. We define the normalized state

$$|n\rangle_N = Z_n^{1/2} |n\rangle,$$

so that

$$\langle n^{(0)}|n\rangle_N = Z_n^{1/2} \langle n^{(0)}|n\rangle = Z_n^{1/2}.$$

Thus the normalization factor Z_n is the probablility for the perturbed state to be in the unperturbed state.
The normalization condition

$${}_N\langle n|n\rangle_N = Z_n \langle n|n\rangle = 1$$

gives us

$$\begin{aligned}Z_n^{-1} &= \langle n|n\rangle = (\langle n^{(0)}| + \lambda\langle n^{(1)}| + \lambda^2\langle n^{(2)}| + \cdots) \\ &\quad \times (|n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \cdots) \\ &= 1 + \lambda^2 \langle n^{(1)}|n^{(1)}\rangle + \mathcal{O}(\lambda^3) \\ &= 1 + \lambda^2 \sum_{k\neq n} \frac{|V_{kn}|^2}{(E_n^{(0)} - E_k^{(0)})^2} + \mathcal{O}(\lambda^3).\end{aligned}$$

Up to the order λ^2 the probability for the perturbed state to lie in the unperturbed state is thus

$$Z_n \approx 1 - \lambda^2 \sum_{k\neq n} \frac{|V_{kn}|^2}{(E_n^{(0)} - E_k^{(0)})^2}.$$

The latter term can be interpreted as the probability for the "leakage" of the system from the state $|n^{(0)}\rangle$ to other states.
Example The quadratic Stark effect.
We consider hydrogen like atoms, i.e. atoms with one electron outside a closed shell, under external uniform electric field parallel to the positive z-axis. Now

$$H_0 = \frac{\boldsymbol{p}^2}{2m} + V_0(r) \text{ and } V = -e|\boldsymbol{E}|z.$$

We suppose that the eigenstates of H_0 are non degenerate (not valid for hydrogen). The energy shift due to the external field is

$$\Delta_k = -e|\boldsymbol{E}|z_{kk} + e^2|\boldsymbol{E}|^2 \sum_{j\neq k} \frac{|z_{kj}|^2}{E_k^{(0)} - E_j^{(0)}} + \cdots,$$

where

$$z_{kj} = \langle k^{(0)}|z|j^{(0)}\rangle.$$

Since we assumed the states $|k^{(0)}\rangle$ to be non degenerate they are eigenstates of the parity. So, according to the parity selection rule the matrix element of z_{kk} vanishes. Indeces k and j are collective indeces standing for the quantum number triplet (n, l, m). According to the Wigner-Eckart theorem we have

$$\begin{aligned}z_{kj} &= \langle n', l'm'|z|n, lm\rangle \\ &= \langle l1; m0|l1; l'm'\rangle \frac{\langle n'l'\|T^{(1)}\|nl\rangle}{\sqrt{2l+1}},\end{aligned}$$

where we have written the operator z as the spherical tensor

$$T_0^{(1)} = z.$$

In order to satisfy $z_{kj} \neq 0$ we must have

- $m' = m$ and
- $l' = l-1, l, l+1$. From these $l' = l$ is not suitable due to the parity selection rule.

So we get

$$\langle n', l'm'|z|n, lm\rangle = 0 \text{ unless } \left\{ \begin{array}{l} l' = l \pm 1 \\ m' = m \end{array} \right. .$$

We define the polarizability α so that

$$\Delta = -\frac{1}{2}\alpha |\boldsymbol{E}|^2.$$

As a special case we consider the ground state $|0^{(0)}\rangle = |1, 00\rangle$ of hydrogen atom which is non degenerate when we ignore the spin. The perturbation expansion gives

$$\alpha = -2e^2 \sum_{k\neq 0}^{\infty} \frac{|\langle k^{(0)}|z|1, 00\rangle|^2}{E_0^{(0)} - E_k^{(0)}},$$

where the summing must be extended also over the continuum states.
Let us suppose that

$$E_0^{(0)} - E_k^{(0)} \approx \text{constant},$$

so that

$$\begin{aligned} \sum_{k\neq 0} |\langle k^{(0)}|z|1, 00\rangle|^2 &= \sum_{\text{all } k\text{'s}} |\langle k^{(0)}|z|1, 00\rangle|^2 \\ &= \langle 1, 00|z^2|1, 00\rangle. \end{aligned}$$

In the spherically symmetric ground state we obviously have

$$\langle z^2\rangle = \langle x^2\rangle = \langle y^2\rangle = \frac{1}{3}\langle r^2\rangle.$$

Using the explicit wave functions we get

$$\langle z^2\rangle = a_0^2.$$

Now

$$-E_0^{(0)} + E_k^{(0)} \geq -E_0^{(0)} + E_1^{(0)} = \frac{e^2}{2a_0}\left[1 - \frac{1}{4}\right],$$

so

$$\alpha < 2e^2 a_0^2 \frac{8a_0}{3e^2} = \frac{16a_0^3}{3} \approx 5.3a_0^3.$$

The exact summation gives

$$\alpha = \frac{9a_0^3}{2} = 4.5a_0^3.$$

Degeneracy
Let's suppose that the energy state $E_D^{(0)}$ is g-foldly degenerated:

$$H_0|m^{(0)}\rangle = E_D^{(0)}|m^{(0)}\rangle, \ \forall |m^{(0)}\rangle \in D, \ \dim D = g.$$

We want to solve the problem

$$(H_0 + \lambda V)|l\rangle = E_l|l\rangle$$

with the boundary condition

$$\lim_{\lambda\to 0}|l\rangle \to \sum_{m\in D}\langle m^{(0)}|l^{(0)}\rangle|m^{(0)}\rangle,$$

i.e. we are looking for corrections to the degenerated states. With the help of the energy correction we have to solve

$$(E_D^{(0)} - H_0)|l\rangle = (\lambda V - \Delta_l)|l\rangle.$$

We write again

$$\begin{aligned} |l\rangle &= |l^{(0)}\rangle + \lambda|l^{(1)}\rangle + \lambda^2|l^{(2)}\rangle + \cdots \\ \Delta_l &= \lambda\Delta_l^{(1)} + \lambda^2\Delta_l^{(2)} + \cdots, \end{aligned}$$

so we get

$$\begin{aligned} &(E_D^{(0)} - H_0)(|l^{(0)}\rangle + \lambda|l^{(1)}\rangle + \lambda^2|l^{(2)}\rangle + \cdots) \\ &\quad = (\lambda V - \lambda\Delta_l^{(1)} - \lambda^2\Delta_l^{(2)} - \cdots) \\ &\qquad \times(|l^{(0)}\rangle + \lambda|l^{(1)}\rangle + \lambda^2|l^{(2)}\rangle + \cdots). \end{aligned}$$

Equalizing the coefficients of the powers of λ we get in the first order

$$\begin{aligned} &(E_D^{(0)} - H_0)|l^{(1)}\rangle \\ &\quad = (V - \Delta_l^{(1)})|l^{(0)}\rangle \\ &\quad = (V - \Delta_l^{(1)})\left[\sum_{m\in D}|m^{(0)}\rangle\langle m^{(0)}|l^{(0)}\rangle\right]. \end{aligned}$$

Taking the scalar product with the vector $\langle m'^{(0)}|$ and recalling that

$$\langle m'^{(0)}|(E_D^{(0)} - H_0) = 0,$$

we end up with the simultaneous eigenvalue equations

$$\sum_m V_{m'm}\langle m^{(0)}|l^{(0)}\rangle = \Delta_l^{(1)}\langle m'^{(0)}|l^{(0)}\rangle.$$

The energy corrections $\Delta_l^{(1)}$ are obtained as eigenvalues. From the equation

$$(E_D^{(0)} - H_0)|l^{(1)}\rangle = (\lambda V - \Delta_l)|l^{(0)}\rangle$$

we also see that

$$\langle m^{(0)}|V - \Delta_l^{(1)}|l^{(0)}\rangle = 0 \ \forall |m^{(0)}\rangle \in D.$$

Thus the vector $(V - \Delta_l^{(1)})|l^{(0)}\rangle$ has no components in the subspace D. Defining a projection operator as

$$\phi_D = 1 - \sum_{m\in D}^{g}|m^{(0)}\rangle\langle m^{(0)}| = \sum_{k\notin D}|k^{(0)}\rangle\langle k^{(0)}|$$

we can write

$$(V - \Delta_l^{(1)})|l^{(0)}\rangle = \phi_D(V - \Delta_l^{(1)})|l^{(0)}\rangle = \phi_D V|l^{(0)}\rangle.$$

We get the equation

$$(E_D^{(0)} - H_0)|l^{(1)}\rangle = \phi_D(\lambda V - \Delta_l)|l^{(0)}\rangle,$$

where now the operator $(E_D^{(0)} - H_0)$ can be inverted:

$$\begin{aligned} |l^{(1)}\rangle &= \frac{\phi_D}{E_D^{(0)} - H_0} V|l^{(0)}\rangle \\ &= \sum_{k\notin D} \frac{|k^{(0)}\rangle V_{kl}}{E_D^{(0)} - E_k^{(0)}}. \end{aligned}$$

When we again normalize

$$\langle l^{(0)}|l\rangle = 1,$$

we get from the equation

$$(E_D^{(0)} - H_0)|l\rangle = (\lambda V - \Delta_l)|l\rangle$$

for the energy shift

$$\Delta_l = \lambda\langle l^{(0)}|V|l\rangle.$$

We substitute the power series and get

$$\begin{aligned} &\lambda\langle l^{(0)}|V(|l^{(0)}\rangle + \lambda|l^{(1)}\rangle + \lambda^2|l^{(2)}\rangle + \cdots) \\ &= \lambda\Delta_l^{(1)} + \lambda^2\Delta_l^{(2)} + \cdots. \end{aligned}$$

The second order energy correction is now

$$\begin{aligned} \Delta_l^{(2)} &= \langle l^{(0)}|V|l^{(1)}\rangle = \langle l^{(0)}|V\frac{\phi_D}{E_D^{(0)} - H_0}V|l^{(0)}\rangle \\ &= \sum_{k\notin D} \frac{|V_{kl}|^2}{E_D^{(0)} - E_k^{(0)}}. \end{aligned}$$

Thus the perturbation calculation in a degenerate system proceeds as follows:

1° Identify the degenerated eigenstates. We suppose that their count is g. Construct the $g \times g$-perturbation matrix V.

2° Diagonalize the perturbation matrix.

3° The resulting eigenvalues are first order corrections for the energy shifts. The corresponding eigenvectors are those zeroth order eigenvectors to which the corrected eigenvectors approach when $\lambda \to 0$.

4° Evaluate higher order corrections using non degenerate perturbation methods but omit in the summations all contributions coming from the degenerated state vectors of the space D.

Example The Stark efect in the hydrogen atom.
The hydrogen 2s ($n = 2, l = 0, m = 0$) and 2p ($n = 2, l = 1, m = -1, 0, 1$) states are degenerate. Their energy is

$$E_D^{(0)} = -e^2/8a_0.$$

We put the atom in external electric field parallel to the z-axis:

$$V = -ez|\boldsymbol{E}|.$$

Now z is the $q = 0$ component of a spherical tensor:

$$z = T_0^{(1)}.$$

According to the parity selection rule the operator V now has nonzero matrix elements only between states with $l = 0$ and $l = 1$, and due to the m-selection rule all states must have the same m:

$$V = \begin{array}{c} \\ 2s \\ 2p,0 \\ 2p,1 \\ 2p,-1 \end{array} \begin{array}{c} \begin{array}{cccc} 2s & 2p,0 & 2p,1 & 2p,-1 \end{array} \\ \begin{pmatrix} 0 & \times & 0 & 0 \\ \times & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \end{array}.$$

The nonzero matrix elements are

$$\langle 2s|V|2p, m = 0\rangle = \langle 2p, m = 0|V|2s\rangle = 3ea_0|\boldsymbol{E}|.$$

The eigenvalues of the perturbation matrix are

$$\Delta_\pm^{(1)} = \pm 3ea_0|\boldsymbol{E}|$$

and the eigenvectors

$$|\pm\rangle = \frac{1}{\sqrt{2}}(|2s, m = 0\rangle \pm |2p, m = 0\rangle).$$

Note The energy shift is a linear function of the electric field. The states $|\pm\rangle$ are not parity eigenstates so it is perfectly possible that they have permanent electric dipole moment $\langle z\rangle \neq 0$.

Nearly degenerated states
Let the states $m \in D$ to be almost degenerate. We write

$$V = V_1 + V_2,$$

where

$$\begin{aligned} V_1 &= \sum_{m\in D}\sum_{m'\in D} |m^{(0)}\rangle\langle m^{(0)}|V|m'^{(0)}\rangle\langle m'^{(0)}| \\ V_2 &= V - V_1. \end{aligned}$$

We proceed so that

1. we diagonalize the Hamiltonian $H_0 + V_1$ exactly in the basis $\{|m^{(0)}\rangle\}$ and
2. handle the term V_2 like in an ordinary non degenerate perturbation theory. This is possible since

$$\langle m'^{(0)}|V_2|m^{(0)}\rangle = 0 \quad \forall m, m' \in D.$$

Example Weak periodic potential.
Now

$$H_0 = \frac{p^2}{2m}$$

and for the perturbation

$$V(x) = V(x + a).$$

We denote the unperturbed eigenstates by the wave vector:

$$H_0|k\rangle = \frac{\hbar^2 k^2}{2m}|k\rangle,$$

so that

$$E_k^{(0)} = \frac{\hbar^2 k^2}{2m}.$$

We impose the periodic boundary conditions

$$\langle x'|k\rangle = \psi_k(x') = \langle x' + L|k\rangle = \psi_k(x' + L),$$

for the wave function and get

$$\psi_k(x') = \frac{1}{\sqrt{L}} e^{ikx'},\ k = \frac{2\pi}{L} n, n \in I.$$

Because the potential V is periodic it can be represented as the Fourier series

$$V(x) = \sum_{n=-\infty}^{\infty} e^{inKx} V_n,$$

where

$$K = 2\pi/a$$

is the *reciprocal lattice vector*. The only nonzero matrix elements are now

$$\langle k + nK|V|k\rangle = V_n,$$

because

$$\begin{aligned} \langle k'|V|k\rangle &= \frac{1}{L}\sum_n V_n \int dx' e^{-ik'x'} e^{inKx'} e^{inkx'} \\ &= \sum_n V_n \delta_{k+nK,k'}. \end{aligned}$$

So the potential couples states

$$|k\rangle, |k + K\rangle, \ldots, |k + nK\rangle, \ldots.$$

The corresponding energy denominators are

$$E_k^{(0)} - E_{k+nK}^{(0)}.$$

In general

$$E_k^{(0)} \neq E_{k+nK}^{(0)}$$

except when

$$k \approx -\frac{nK}{2}.$$

We suppose that the condition

$$k \neq -\frac{nK}{2}$$

holds safely. The first order state vectors are then

$$|k^{(1)}\rangle = |k\rangle + \sum_{n\neq 0} |k + nK\rangle \frac{V_n}{E_k^{(0)} - E_{k+nK}^{(0)}},$$

and the wave functions

$$\psi_k^{(1)}(x') = \frac{1}{\sqrt{L}} e^{ikx'} + \sum_{n\neq 0} \frac{1}{\sqrt{L}} e^{i(k+nK)x'} \frac{V_n}{E_k^{(0)} - E_{k+nK}^{(0)}}.$$

Correspondingly the energy up to the second order is

$$E_k^{(2)} = E_k^{(0)} + V_0 + \sum_{n\neq 0} \frac{|V_n|^2}{E_k^{(0)} - E_{k+nK}^{(0)}}.$$

Let us suppose now that

$$k \approx -\frac{nK}{2}.$$

We diagonalize the Hamiltonian in the basis

$$\{|k\rangle, |k + nK\rangle\},$$

i.e. we diagonalize the matrix

$$\begin{array}{c} \\ |k\rangle \\ |k+nK\rangle \end{array} \begin{array}{c} \begin{array}{cc} |k\rangle & |k+nK\rangle \end{array} \\ \begin{pmatrix} E_k^{(0)} + V_0 & V_n^* \\ V_n & E_k^{(0)} + V_0 \end{pmatrix} \end{array}.$$

Its eigenvalues are

$$\begin{aligned} E_{k\pm} = V_0 &+ \frac{E_k^{(0)} + E_{k+nK}^{(0)}}{2} \\ &\pm \sqrt{\left(\frac{E_k^{(0)} - E_{k+nK}^{(0)}}{2}\right)^2 + |V_n|^2}. \end{aligned}$$

When $|E_k^{(0)} - E_{k+nK}^{(0)}| \gg |V_n|$, it reduces to two solutions

$$\begin{aligned} E_{k+} &= E_k^{(0)} + V_0 \\ E_{k-} &= E_{k+nK}^{(0)} + V_0, \end{aligned}$$

which are first order corrected energies. In the limiting case we get

$$\lim_{k\to -nK/2} E_{k\pm} = E_{nK/2}^{(0)} + V_0 \pm |V_n|.$$

Brillouin-Wigner perturbation theory

We start with the Schrödinger equation

$$(E_n - H_0)|n\rangle = \lambda V|n\rangle,$$

and take on both sides the scalar product with the state $|m^{(0)}\rangle$, and get

$$(E_n - E_m^{(0)})\langle m^{(0)}|n\rangle = \lambda \langle m^{(0)}|V|n\rangle.$$

We correct the state $|n^{(0)}\rangle$. We write the corrected state $|n\rangle$ in the form

$$\begin{aligned} |n\rangle &= \sum_m |m^{(0)}\rangle\langle m^{(0)}|n\rangle = |n^{(0)}\rangle\langle n^{(0)}|n\rangle + \phi_n|n\rangle \\ &= |n^{(0)}\rangle + \sum_{m\neq n} |m^{(0)}\rangle\langle m^{(0)}|n\rangle, \end{aligned}$$

which has been normalized, like before,

$$\langle n^{(0)}|n\rangle = 1.$$

We substitute into this the scalar products

$$\langle m^{(0)}|n\rangle = \frac{\lambda\langle m^{(0)}|V|n\rangle}{E_n - E_m^{(0)}},$$

and end up with the fundamental equation of the *Brillouin-Wigner method*

$$|n\rangle = |n^{(0)}\rangle + \sum_{m\neq n} |m^{(0)}\rangle \frac{\lambda}{E_n - E_m^{(0)}} \langle m^{(0)}|V|n\rangle.$$

Iteration gives us the series

$$\begin{aligned}
|n\rangle = |n^{(0)}\rangle &+ \lambda \sum_{m\neq n} |m^{(0)}\rangle \frac{1}{E_n - E_m^{(0)}} \langle m^{(0)}|V|n^{(0)}\rangle \\
&+ \lambda^2 \sum_{m\neq n} \sum_{l\neq n} |l^{(0)}\rangle \frac{1}{E_n - E_l^{(0)}} \langle l^{(0)}|V|m^{(0)}\rangle \\
&\quad \times \frac{1}{E_n - E_m^{(0)}} \langle m^{(0)}|V|n^{(0)}\rangle \\
&+ \lambda^3 \sum_{m\neq n} \sum_{l\neq n} \sum_{k\neq n} |k^{(0)}\rangle \frac{1}{E_n - E_k^{(0)}} \langle k^{(0)}|V|l^{(0)}\rangle \\
&\quad \times \frac{1}{E_n - E_l^{(0)}} \langle l^{(0)}|V|m^{(0)}\rangle \frac{1}{E_n - E_m^{(0)}} \langle m^{(0)}|V|n^{(0)}\rangle \\
&+ \cdots.
\end{aligned}$$

Note This is not a power series of the parameter λ because the energy denominators

$$E_n - E_m^{(0)} = E_n^{(0)} - E_m^{(0)} + \Delta_n$$

depend also on the parameter λ according to the equation

$$\Delta_n = \lambda\Delta_n^{(1)} + \lambda^2\Delta_n^{(2)} + \cdots$$

Time dependent potentials

We have solved the problem

$$H_0|n\rangle = E_n|n\rangle$$

completely and want to solve the eigenstates of the Hamiltonian

$$H = H_0 + V(t).$$

Since the Hamiltonian depends on time we have

$$\mathcal{U} \neq e^{-iHt/\hbar},$$

so a system in a stationary state $|i\rangle$ can in the course of time get components also in other stationary states.

Pictures of the time evolution

At the moment $t = 0$ let the system be in the state

$$|\alpha\rangle = \sum_n c_n(0)|n\rangle$$

and at the moment t in the state

$$|\alpha, t_0 = 0; t\rangle = \sum_n c_n(t)e^{-iE_nt/\hbar}|n\rangle.$$

Note The time dependence of the coefficients $c_n(t)$ is due only to the potential $V(t)$. The effect of the Hamiltonian H_0 is in the phase factors $e^{-iE_nt/\hbar}$.

Schrödinger's picture

The evolution of the state vectors is governed by the time evolution operator:

$$|\alpha, t_0 = 0; t\rangle_S = \mathcal{U}(t)|\alpha, t_0 = 0\rangle.$$

Heisenberg's picture

The state vectors remain constant, i.e.

$$|\alpha, t_0 = 0, t\rangle_H = |\alpha, t_0 = 0\rangle.$$

On the other hand, the operators depend on time. We can go from the time independent operators of the Schrödinger picture to the operators of the Heisenberg picture via the transformation

$$A_H(t) = \mathcal{U}^\dagger(t)A_S\mathcal{U}(t).$$

If the Hamiltonian does not depend on time then

$$H_H(t) = \mathcal{U}^\dagger(t)H\mathcal{U}(t) = H$$

and

$$\frac{dA_H}{dt} = \frac{1}{i\hbar}[A_H, H_H] = \frac{1}{i\hbar}[A_H, H].$$

Interaction picture

The state vectors depend on time as

$$|\alpha, t_0; t\rangle_I \equiv e^{iH_0t/\hbar}|\alpha, t_0; t\rangle_S.$$

At the moment $t = 0$ we have obviously

$$|\rangle_S = |\rangle_I = |\rangle_H.$$

The interaction picture observables A_I are defined so that

$$A_I \equiv e^{iH_0t/\hbar}A_Se^{-iH_0t/\hbar}.$$

In particular we have

$$V_I = e^{iH_0t/\hbar}Ve^{-iH_0t/\hbar}.$$

We see that the equation governing the time dpendence of the interaction picture state vectors is

$$\begin{aligned} &i\hbar\frac{\partial}{\partial t}|\alpha, t_0; t\rangle_I \\ &\quad = i\hbar\frac{\partial}{\partial t}\left(e^{iH_0t/\hbar}|\alpha, t_0; t\rangle_S\right) \\ &\quad = -H_0e^{iH_0t/\hbar}|\alpha, t_0; t\rangle_S \\ &\qquad +e^{iH_0t/\hbar}(H_0 + V)|\alpha, t_0; t\rangle_S \\ &\quad = e^{iH_0t/\hbar}Ve^{-iH_0t/\hbar}e^{iH_0t/\hbar}|\alpha, t_0; t\rangle_S, \end{aligned}$$

so

$$i\hbar\frac{\partial}{\partial t}|\alpha, t_0; t\rangle_I = V_I|\alpha, t_0; t\rangle_I.$$

If now A_S does not depend on time we can derive

$$\frac{dA_I}{dt} = \frac{1}{i\hbar}[A_I, H_0],$$

which in turn resembles the Heisenberg equation of motion provided that in the latter we substitute for the total Hamiltonian H the stationary operator H_0.

We expand state vectors in the base $\{|n\rangle\}$:

$$|\alpha, t_0; t\rangle_I = \sum_n c_n(t)|n\rangle.$$

If now $t_0 = 0$ so multiplying the previous expansion

$$|\alpha, t_0 = 0; t\rangle = \sum_n c_n(t)e^{-iE_nt/\hbar}|n\rangle$$

on both sides by the operator $e^{-iH_0t/\hbar}$ we get

$$|\alpha, t_0 = 0; t\rangle_I = \sum_n c_n(t)|n\rangle,$$

i.e. the coefficients c_n are equal. We just derived the equation

$$i\hbar\frac{\partial}{\partial t}|\alpha, t_0; t\rangle_I = V_I|\alpha, t_0; t\rangle_I.$$

From this we get

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\langle n|\alpha, t_0; t\rangle_I &= \langle n|V_I|\alpha, t_0; t\rangle_I \\ &= \sum_m \langle n|V_I|m\rangle\langle m|\alpha, t_0; t\rangle_I. \end{aligned}$$

The matrix elements of the operator V_I are

$$\begin{aligned} \langle n|V_I|m\rangle &= \langle n|e^{iH_0t/\hbar}Ve^{-iH_0t/\hbar}|m\rangle \\ &= V_{nm}(t)e^{i(E_n-E_m)t/\hbar} \end{aligned}$$

.

Because we furthermore have

$$c_n(t) = \langle n|\alpha, t_0; t\rangle_I,$$

we can write the equation governing the time dependence of the superposition coefficients as

$$i\hbar\frac{d}{dt}c_n(t) = \sum_m V_{nm}e^{i\omega_{nm}t}c_m(t),$$

where

$$\omega_{nm} \equiv \frac{E_n - E_m}{\hbar} = -\omega_{mn}.$$

This system of differential equations can be written explicitely in the matrix form

$$i\hbar\begin{pmatrix}\dot{c}_1\\ \dot{c}_2\\ \dot{c}_3\\ \vdots\end{pmatrix} = \begin{pmatrix} V_{11} & V_{12}e^{i\omega_{12}t} & \cdots\\ V_{21}e^{i\omega_{21}t} & V_{22} & \cdots\\ & & V_{33} \quad \cdots\\ \vdots & \vdots & \ddots\end{pmatrix}\begin{pmatrix}c_1\\ c_2\\ c_3\\ \vdots\end{pmatrix}.$$

Example Two state systems.
Suppose that

$$H_0 = E_1|1\rangle\langle 1| + E_2|2\rangle\langle 2| \quad (E_1 < E_2)$$

and that the time dependent potential is like

$$V(t) = \gamma e^{i\omega t}|1\rangle\langle 2| + \gamma e^{-i\omega t}|2\rangle\langle 1|.$$

The matrix elements V_{nm} are now

$$\begin{aligned} V_{12} &= V_{21}^* &&= \gamma e^{i\omega t}\\ V_{11} &= V_{22} &&= 0,\end{aligned}$$

so transitions between the states $|1\rangle$ and $|2\rangle$ are possible. The system of differential equations to be solved is

$$\begin{aligned} i\hbar\dot{c}_1 &= \gamma e^{i\omega t}e^{i\omega_{12}t}c_2\\ i\hbar\dot{c}_2 &= \gamma e^{-i\omega t}e^{i\omega_{21}t}c_1,\end{aligned}$$

where

$$\omega_{21} = -\omega_{12} = \frac{E_2 - E_1}{\hbar}.$$

We can see that the solution satisfying the initial conditions

$$c_1(0) = 1, \quad c_2(0) = 0$$

is

$$\begin{aligned} |c_2(t)|^2 &= \frac{\gamma^2/\hbar^2}{\gamma^2/\hbar^2 + (\omega-\omega_{21})^2/4}\\ &\quad \times \sin^2\left\{\left[\frac{\gamma^2}{\hbar^2} + \frac{(\omega-\omega_{21})^2}{4}\right]^{1/2}t\right\}\\ |c_1(t)|^2 &= 1 - |c_2(t)|^2.\end{aligned}$$

The system oscillates between the states $|1\rangle$ and $|2\rangle$ with the angular velocity

$$\Omega = \sqrt{\left(\frac{\gamma^2}{\hbar^2}\right) + \frac{(\omega-\omega_{21})^2}{4}}.$$

The amplitude of the oscillations is at its maximum, i.e. we are in a resonance, when

$$\omega \approx \omega_{21} = \frac{E_2 - E_1}{\hbar}.$$

Example Spin magnetic resonance.
We put a spin $\frac{1}{2}$ particle into

- time independent magnetic field parallel to the z axis,
- time dependent magnetic field rotating in the xy plane,

i.e.

$$\boldsymbol{B} = B_0\hat{\boldsymbol{z}} + B_1(\hat{\boldsymbol{x}}\cos\omega t + \hat{\boldsymbol{y}}\sin\omega t)$$

when the fields B_0 and B_1 are constant. Since the magnetic moment of the electron is

$$\boldsymbol{\mu} = \frac{e}{m_e c}\boldsymbol{S},$$

the Hamiltonian is the sum of the terms

$$\begin{aligned} H_0 &= -\left(\frac{e\hbar B_0}{2m_e c}\right)(|S_z;\uparrow\rangle\langle S_z;\uparrow| - |S_z;\downarrow\rangle\langle S_z;\downarrow|)\\ V(t) &= -\left(\frac{e\hbar B_1}{2m_e c}\right)\\ &\quad \times\big[\cos\omega t(|S_z;\uparrow\rangle\langle S_z;\downarrow| + |S_z;\downarrow\rangle\langle S_z;\uparrow|)\\ &\quad + \sin\omega t(-i|S_z;\uparrow\rangle\langle S_z;\downarrow| + i|S_z;\downarrow\rangle\langle S_z;\uparrow|)\big].\end{aligned}$$

If $e < 0$, then

$$E_2 = E_\uparrow = \frac{|e|\hbar B_0}{2m_e c} > E_1 = E_\downarrow = -\frac{|e|\hbar B_0}{2m_e c}.$$

We can thus identify in the above treated two stated system the quantities:

$$\begin{aligned} |S_z;\uparrow\rangle &\mapsto |2\rangle \quad \text{(higher state)}\\ |S_z;\downarrow\rangle &\mapsto |1\rangle \quad \text{(lower state)}\\ \frac{|e|B_0}{m_e c} &\mapsto \omega_{21}\\ -\frac{e\hbar B_1}{2m_e c} &\mapsto \gamma, \quad \omega \mapsto \omega.\end{aligned}$$

Comparing with our earlier discussion on the spin precession we see that

- if $B_1 = 0$ and $B_0 \neq 0$, the the expectation value $\langle S_{x,y}\rangle$ rotates in the course of time counterclockwise but the probabilities $|c_1|^2$ and $|c_2|^2$ remain still constant.
- if $B_1 \neq 0$, the the coefficients $|c_1|^2$ and $|c_2|^2$ are functions of time.

When the resonance condition

$$\omega \approx \omega_{21}$$

holds the probability for the spin flips

$$|S_z;\uparrow\rangle \longleftrightarrow |S_z;\downarrow\rangle$$

is very high.
Because experimental production of rotating magnetic fields is difficult it is common to use a field oscillating for example along the x axis. This can be divided into components rotating counterclockwise and clockwise:

$$\begin{aligned} & 2B_1\hat{\boldsymbol{x}}\cos\omega t \\ & \quad = B_1(\hat{\boldsymbol{x}}\cos\omega t + \hat{\boldsymbol{y}}\sin\omega t) \\ & \qquad + B_1(\hat{\boldsymbol{x}}\cos\omega t - \hat{\boldsymbol{y}}\sin\omega t). \end{aligned}$$

In experiments one usually has

$$\frac{B_1}{B_0} \ll 1,$$

so

$$\frac{\gamma}{\hbar} = \frac{|e|B_1}{4m_e c} = \frac{|e|B_0}{m_e c}\,\frac{B_1}{4B_0} = \omega_{21}\frac{B_1}{4B_0} \ll \omega_{21}.$$

If now the component rotating counterclockwise triggers the resonance condition

$$\omega \approx \omega_{21},$$

the the transition probability due to this component is

$$\begin{aligned} |c_R(t)|^2 &= \frac{\gamma^2/\hbar^2}{\gamma^2/\hbar^2 + (\omega-\omega_{21})^2/4} \\ &\qquad \times \sin^2\left\{\left[\frac{\gamma^2}{\hbar^2} + \frac{(\omega-\omega_{21})^2}{4}\right]^{1/2} t\right\} \\ &\approx \sin^2\left(\frac{\gamma}{\hbar}t\right). \end{aligned}$$

The clockwise rotating component,

$$\omega = -\omega_{21},$$

contributes

$$\begin{aligned} |c_L(t)|^2 &\approx \frac{\gamma^2/\hbar^2}{\gamma^2/\hbar^2 + \omega_{21}^2} \\ &\qquad \times \sin^2\left\{\left[\frac{\gamma^2}{\hbar^2} + \omega_{21}^2\right]^{1/2} t\right\} \\ &\ll |c_R(t)|^2. \end{aligned}$$

Time dependent perturbation theory

In the interaction picture the time evolution operator is determined by the equation

$$|\alpha, t_0; t\rangle_I = \mathcal{U}_I(t, t_0)|\alpha, t_0; t_0\rangle_I.$$

Since the time evolution of the state vectors is governed by the equation

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}|\alpha, t_0; t\rangle_I &= V_I|\alpha, t_0; t\rangle_I \\ &= V_I\mathcal{U}_I(t, t_0)|\alpha, t_0; t_0\rangle_I, \end{aligned}$$

we see that

$$i\hbar\frac{\partial\mathcal{U}_{\mathcal{I}}(t, t_0)}{\partial t}|\alpha, t_0; t_0\rangle_I = V_I\mathcal{U}_I(t, t_0)|\alpha, t_0; t_0\rangle_I.$$

The interaction picture time evolution operator satisfies thus the equation

$$i\hbar\frac{d}{dt}\mathcal{U}_I(t, t_0) = V_I(t)\mathcal{U}_I(t, t_0).$$

As the initial condition we have obviously

$$\mathcal{U}_I(t, t_0)\big|_{t=t_0} = 1.$$

Integration gives

$$\mathcal{U}_I(t, t_0) = 1 - \frac{i}{\hbar}\int_{t_0}^{t} V_I(t')\mathcal{U}_I(t', t_0)\, dt'.$$

By iteration we end up with Dyson's series

$$\begin{aligned} &\mathcal{U}_I(t, t_0) \\ &= 1 - \frac{i}{\hbar}\int_{t_0}^{t} V_I(t')\left[1 - \frac{i}{\hbar}\int_{t_0}^{t'} V_I(t'')\mathcal{U}_I(t'')\, dt''\right] dt' \\ &= 1 - \frac{i}{\hbar}\int_{t_0}^{t} dt'\, V_I(t') \\ &\quad + \left(-\frac{i}{\hbar}\right)^2\int_{t_0}^{t} dt'\int_{t_0}^{t'} dt''\, V_I(t')V_I(t'') \\ &\quad + \cdots + \left(-\frac{i}{\hbar}\right)^n\int_{t_0}^{t} dt'\int_{t_0}^{t'} dt''\cdots \\ &\quad \times\int_{t_0}^{t^{(n-1)}} dt^{(n)} V_I(t')V_I(t'')\cdots V_I(t^{(n)}) \\ &\quad + \cdots. \end{aligned}$$

Let us suppose again that we have solved the problem

$$H_0|n\rangle = E_n|n\rangle$$

completely. Let the initial state of the system be $|i\rangle$ at the moment $t = t_0 = 0$, i.e.

$$|\alpha, t_0 = 0; t = 0\rangle_I = |i\rangle.$$

At the moment t this has evolved to the state

$$\begin{aligned} |i, t_0 = 0; t\rangle_I &= \mathcal{U}_I(t, 0)|i\rangle \\ &= \sum_n |n\rangle\langle n|\mathcal{U}_I(t, 0)|i\rangle. \end{aligned}$$

Here

$$\langle n|\mathcal{U}_I(t, 0)|i\rangle = c_n(t)$$

is the same as the superposition coefficient we used before. From the relation binding the interaction and Schrödinger picture state vectors we get

$$\begin{aligned} |\alpha, t_0; t\rangle_I &= e^{iH_0t/\hbar}|\alpha, t_0; t\rangle_S \\ &= e^{iH_0t/\hbar}\mathcal{U}(t, t_0)|\alpha, t_0; t_0\rangle_S \\ &= e^{iH_0t/\hbar}\mathcal{U}(t, t_0)e^{-iH_0t_0/\hbar}|\alpha, t_0; t_0\rangle_I, \end{aligned}$$

so the time evolution operators of these pictures are obtained with the help of the formula

$$\mathcal{U}_I(t, t_0) = e^{iH_0t/\hbar}\mathcal{U}(t, t_0)e^{-iH_0t_0/\hbar}.$$

The matrix elements of the operator $\mathcal{U}_I(t, t_0)$ can now be calculated from the relation

$$\langle n|\mathcal{U}_I(t, t_0)|i\rangle = e^{i(E_nt - E_it_0)/\hbar}\langle n|\mathcal{U}(t, t_0)|i\rangle.$$

We see that

- the matrix element $\langle n|\mathcal{U}_I(t, t_0)|i\rangle$ is not quite the transition amplitude $\langle n|\mathcal{U}(t, t_0)|i\rangle$,
- the transition probabilities satisfy

$$|\langle n|\mathcal{U}_I(t, t_0)|i\rangle|^2 = |\langle n|\mathcal{U}(t, t_0)|i\rangle|^2.$$

Note If the states $|a'\rangle$ and $|b'\rangle$ are not eigenstates of H_0 then

$$|\langle b'|\mathcal{U}_I(t, t_0)|a'\rangle|^2 \neq |\langle b'|\mathcal{U}(t, t_0)|a'\rangle|^2.$$

In this case the matrix elements are evaluated by expanding the states $|a'\rangle$ and $|b'\rangle$ in the base $\{|n\rangle\}$ formed by the eigenstates of H_0.
Let us suppose now that at the moment $t = t_0$ the system is in the eigenstate $|i\rangle$ of H_0. This state vector can always be multiplied by an arbitrary phase factor, so the Schrödinger picture state vector $|i, t_0; t_0\rangle_S$ can be chosen as

$$|i, t_0; t_0\rangle_S = e^{-iE_it_0/\hbar}|i\rangle.$$

Then in the interaction picture we have

$$|i, t_0; t_0\rangle_I = |i\rangle.$$

At the moment t this has evolved to the state

$$|i, t_0; t\rangle_I = \mathcal{U}_I(t, t_0)|i\rangle = \sum_n c_n(t)|n\rangle,$$

so

$$c_n(t) = \langle n|\mathcal{U}_I(t, t_0)|i\rangle,$$

as we already noted.
Now

1. substitute the Dyson series into this
2. expand the coefficient as a power series of the perturbation

$$c_n(t) = c_n^{(0)}(t) + c_n^{(1)}(t) + c_n^{(2)}(t) + \cdots,$$

3. equalize the terms $c_n^{(k)}$ with the perturbation terms of the order k,

4. denote
$$e^{i(E_n-E_i)t/\hbar} = e^{i\omega_{ni}t}.$$

We get

$$\begin{aligned}
c_n^{(0)}(t) &= \delta_{ni} \\
c_n^{(1)}(t) &= -\frac{i}{\hbar}\int_{t_0}^{t} \langle n|V_I(t')|i\rangle\, dt' \\
&= -\frac{i}{\hbar}\int_{t_0}^{t} e^{i\omega_{ni}t'} V_{ni}(t')\, dt' \\
c_n^{(2)}(t) &= \left(-\frac{i}{\hbar}\right)^2 \sum_m \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt''\, e^{i\omega_{nm}t'} V_{nm}(t') \\
&\quad \times e^{i\omega_{mi}t''} V_{mi}(t'').
\end{aligned}$$

The probability for the transition from the state $|i\rangle$ to the state $|n\rangle$ can be written as

$$\Pr(i \to n) = |c_n(t)|^2 = |c_n^{(1)}(t) + c_n^{(2)}(t) + \cdots|^2.$$

Fermi's golden rule
Consider the constant perturbation

$$V(t) = \begin{cases} 0, & \text{when } t < 0 \\ V \quad \text{(time independent)} & \text{when } t \geq 0. \end{cases}$$

switched on at the moment $t = 0$. At the moment $t = 0$ let the system be in the pure state $|i\rangle$. Now

$$\begin{aligned}
c_n^{(0)} &= c_n^{(0)}(0) = \delta_{in} \\
c_n^{(1)} &= -\frac{i}{\hbar} V_{ni} \int_0^t e^{i\omega_{ni}t'}\, dt' \\
&= \frac{V_{ni}}{E_n - E_i}(1 - e^{i\omega_{ni}t}).
\end{aligned}$$

The transition probability to the state $|n\rangle$ is thus

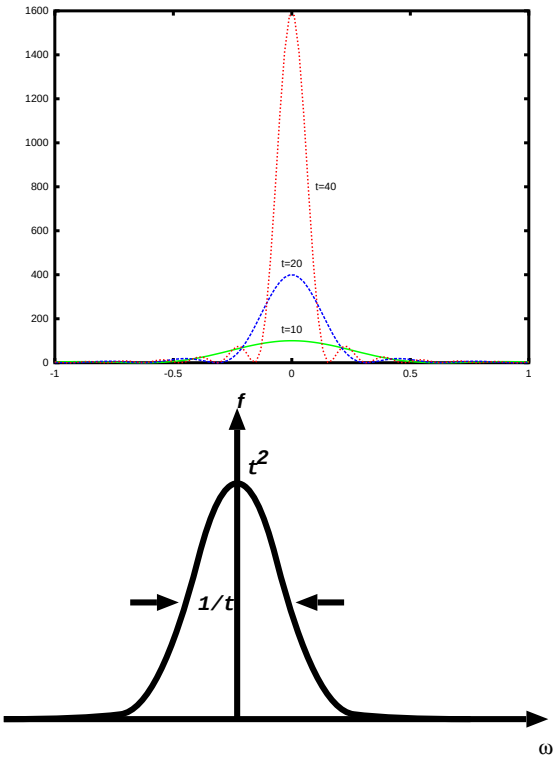
$$\begin{aligned}
|c_n^{(1)}|^2 &= \frac{|V_{ni}|^2}{|E_n - E_i|^2}(2 - 2\cos\omega_{ni}t) \\
&= \frac{4|V_{ni}|^2}{|E_n - E_i|^2} \sin^2\left[\frac{(E_n - E_i)t}{2\hbar}\right].
\end{aligned}$$

The quantity
$$\omega \equiv \frac{E_n - E_i}{\hbar}$$
is almost continuous because usually the E_n states form almost a continuum. The transition probability is now

$$|c_n^{(1)}|^2 = \frac{|V_{ni}|^2}{\hbar^2} f(\omega),$$

where

$$f(\omega) = \frac{4\sin^2 \omega t/2}{\omega^2}.$$



When t is large then $|c_n(t)|^2 \neq 0$ only if

$$t \approx \frac{2\pi}{\omega} = \frac{2\pi\hbar}{|E_n - E_i|}.$$

If now Δt is the time the perturbation has been on then transitions are possible only if

$$\Delta t \Delta E \approx \hbar.$$

Note If the energy is conserved exactly, i.e.

$$E_n = E_i,$$

then

$$|c_n^{(1)}(t)|^2 = \frac{1}{\hbar^2}|V_{ni}|^2 t^2.$$

The transition probability is proportional to the square of the on-time of the perturbation (and not linearly proportional to the time).
In general we are interested in transitions in which the initial state $|i\rangle$ is fixed but the final state $|n\rangle$ can be any state satisfying the energy conservation rule

$$E_n \approx E_i$$

The total probability for such a transition is now

$$\begin{aligned}
&\Pr(i \to f) \\
&= \sum_{\substack{n \\ E_n \approx E_i}} |c_n^{(1)}(t)|^2 \\
&= \int dE_n\, \rho(E_n) |c_n^{(1)}|^2 \\
&= 4\int \sin^2\left[\frac{(E_n - E_i)t}{2\hbar}\right] \frac{|V_{ni}|^2}{|E_n - E_i|^2} \rho(E_n)\, dE_n.
\end{aligned}$$

Here $\rho(E)$ is the density of states, i.e.

$$\rho(E)dE = \text{the number of states between}(E, E+dE).$$

Because

$$\lim_{t\to\infty} \frac{1}{\pi}\frac{\sin^2 xt}{tx^2} = \delta(x),$$

we get

$$\begin{aligned}\lim_{t\to\infty} \frac{1}{(E_n-E_i)^2}\sin^2\frac{E_n-E_i}{2\hbar}t &= \frac{\pi t}{4\hbar^2}\delta\left(\frac{E_n-E_i}{2\hbar}\right)\\ &= \frac{\pi t}{2\hbar}\delta(E_n-E_i).\end{aligned}$$

The transition probability is thus

$$\lim_{t\to\infty}\Pr(i\to f) = \left(\frac{2\pi}{\hbar}\right)\overline{|V_{ni}|^2}\rho(E_n)t\Big|_{E_n\approx E_i},$$

where $\overline{|V_{ni}|^2}$ is the average of the term $|V_{ni}|^2$.
Note The total transition probability depends linearly on time t.
The transition rate w is defined to be the transition probability per unit time. We end up with the Fermi golden rule

$$\begin{aligned}w_{i\to f} &= \frac{d}{dt}\left(\sum_n |c_n^{(1)}(t)|^2\right)\\ &= \left(\frac{2\pi}{\hbar}\right)\overline{|V_{ni}|^2}\rho(E_n)\Big|_{E_n\approx E_i}.\end{aligned}$$

Quite often this is also written as

$$w_{i\to n} = \left(\frac{2\pi}{\hbar}\right)|V_{ni}|^2\delta(E_n-E_i),$$

but then one implicitely assumes that it will be integrated in the expression $\int dE_n\,\rho(E_n)w_{i\to n}\cdots$.

Second order corrections
In the second order we got

$$\begin{aligned}c_n^{(2)}(t) &= \left(-\frac{i}{\hbar}\right)^2\sum_m\int_{t_0}^t dt'\int_{t_0}^{t'}dt''\,e^{i\omega_{nm}t'}V_{nm}(t')\\ &\quad\times e^{i\omega_{mi}t''}V_{mi}(t''),\end{aligned}$$

so in the case of the potential

$$V(t) = \begin{cases} 0, & \text{when } t<0\\ V \quad \text{(time independent)} & \text{when } t\geq 0.\end{cases}$$

we have

$$\begin{aligned}c_n^{(2)} &= \left(-\frac{i}{\hbar}\right)^2\sum_m V_{nm}V_{mi}\int_0^t dt'\,e^{i\omega_{nm}t'}\int_0^{t'}dt''\,e^{i\omega_{mi}t''}\\ &= \frac{i}{\hbar}\sum_m\frac{V_{nm}V_{mi}}{E_m-E_i}\int_0^t(e^{i\omega_{ni}t'}-e^{i\omega_{nm}t'})dt'.\end{aligned}$$

Above

- the term $e^{i\omega_{ni}t'}$ is same as in the coefficient $c_n^{(1)}$, so it contributes only if $E_n\approx E_i$ when $t\to\infty$.
- if E_m in the term $e^{i\omega_{nm}t'}$ differs from E_n and at the same time from E_i it oscillates rapidly and contributes nothing.

So we can write

$$w_{i\to f} = \frac{2\pi}{\hbar}\overline{\left|V_{ni}+\sum_m\frac{V_{nm}V_{mi}}{E_i-E_m}\right|^2}\rho(E_n)\Big|_{E_n\approx E_i}.$$

In the second order the term $V_{nm}V_{mi}$ can be thougth to describe *virtual transitions*

$$|i\rangle\longrightarrow|m\rangle\longrightarrow|n\rangle.$$

Harmonic perturbations
Consider the potential

$$V(t) = \mathcal{V}e^{i\omega t}+\mathcal{V}^\dagger e^{-i\omega t},$$

which is again assumed to be switched on at the moment $t=0$. When $t<0$, the system is supposed to be in the state $|i\rangle$. The first order term is now

$$\begin{aligned}c_n^{(1)} &= -\frac{i}{\hbar}\int_0^t\left(\mathcal{V}_{ni}e^{i\omega t'}+\mathcal{V}_{ni}^\dagger e^{-i\omega t'}\right)e^{i\omega_{ni}t'}\,dt'\\ &= \frac{1}{\hbar}\left[\frac{1-e^{i(\omega+\omega_{ni})t}}{\omega+\omega_{ni}}\mathcal{V}_{ni}+\frac{1-e^{i(\omega-\omega_{ni})t}}{-\omega+\omega_{ni}}\mathcal{V}_{ni}^\dagger\right].\end{aligned}$$

This is of the same form as in the case of our earlier step potential, provided that we substitute

$$\omega_{ni} = \frac{E_n-E_i}{\hbar}\longrightarrow\omega_{ni}\pm\omega.$$

When $t\to\infty$, $|c_n^{(1)}|^2$ is thus non zero only if

$$\begin{aligned}\omega_{ni}+\omega\approx 0 \quad &\text{or} \quad E_n\approx E_i-\hbar\omega\\ \omega_{ni}-\omega\approx 0 \quad &\text{or} \quad E_n\approx E_i+\hbar\omega.\end{aligned}$$

Obviously, if the first term is important the second one does not contribute and vice versa. The energy of a quantum mechanical system is not conserved in these transitions but the "external" potential either gives (*absorption*) or takes (*stimulated emission*) energy to/from the system. Analogically to the constant potential the transition rate will be

$$w_{i\to n} = \frac{2\pi}{\hbar}|\mathcal{V}_{ni}|^2\delta(E_n-E_i\pm\hbar\omega).$$

Energgy shifts and line widths

Evolution of the initial state
We consider the case where the initial and final states are the same. We switch the interaction on slowly:

$$V(t) = e^{\eta t} V.$$

Here $\eta \to 0$ at the end.
We suppose that in the far past, $t = -\infty$, the system has been in the state $|i\rangle$.
Check
If $n \neq i$, then the perturbation theory gives

$$\begin{aligned} c_n^{(0)}(t) &= 0 \\ c_n^{(1)}(t) &= -\frac{i}{\hbar} V_{ni} \lim_{t_0 \to -\infty} \int_{t_0}^{t} e^{\eta t'} e^{i\omega_{ni} t'} \, dt' \\ &= -\frac{i}{\hbar} V_{ni} \frac{e^{\eta t + i\omega_{ni} t}}{\eta + i\omega_{ni}}. \end{aligned}$$

Up to the lowest non vanishing order the transition probability is

$$|c_n(t)|^2 \approx \frac{|V_{ni}|^2}{\hbar^2} \left(\frac{e^{2\eta t}}{\eta^2 + \omega_{ni}^2} \right)$$

and the transition rate correspondingly

$$\frac{d}{dt}|c_n(t)|^2 \approx \frac{2|V_{ni}|^2}{\hbar^2} \left(\frac{\eta e^{2\eta t}}{\eta^2 + \omega_{ni}^2} \right).$$

Now

$$\lim_{\eta \to 0} \frac{\eta}{\eta^2 + \omega_{ni}^2} = \pi \delta(\omega_{ni}) = \pi \hbar \delta(E_n - E_i),$$

so in the limit $\eta \to 0$ we get the Fermi golden rule

$$w_{i \to n} \approx \left(\frac{2\pi}{\hbar} \right) |V_{ni}|^2 \delta(E_n - E_i).$$

This is equivalent with our previous result.
Let now $n = i$. We get

$$\begin{aligned} c_i^{(0)} &= 1 \\ c_i^{(1)} &= -\frac{i}{\hbar} V_{ii} \lim_{t_0 \to -\infty} \int_{t_0}^{t} e^{\eta t'} \, dt' = -\frac{i}{\hbar \eta} V_{ii} e^{\eta t} \end{aligned}$$

$$\begin{aligned} c_i^{(2)} &= \left(-\frac{i}{\hbar} \right)^2 \sum_m |V_{mi}|^2 \\ &\quad \times \lim_{t_0 \to -\infty} \int_{t_0}^{t} dt' \, e^{i\omega_{im} t' + \eta t'} \int_{t_0}^{t'} dt'' e^{i\omega_{mi} t'' + \eta t''} \\ &= \left(-\frac{i}{\hbar} \right)^2 \sum_m |V_{mi}|^2 \\ &\quad \times \lim_{t_0 \to -\infty} \int_{t_0}^{t} dt' \, e^{i\omega_{im} t' + \eta t'} \frac{e^{i\omega_{mi} t' + \eta t'}}{i(\omega_{mi} - i\eta)} \\ &= \left(-\frac{i}{\hbar} \right)^2 |V_{ii}|^2 \frac{e^{2\eta t}}{2\eta^2} \\ &\quad + \left(-\frac{i}{\hbar} \right) \sum_{m \neq i} \frac{|V_{mi}|^2 e^{2\eta t}}{2\eta(E_i - E_m + i\hbar\eta)}. \end{aligned}$$

Thus, up to the second order the coefficient c_i is

$$\begin{aligned} c_i(t) &\approx 1 - \frac{i}{\hbar \eta} V_{ii} e^{\eta t} + \left(-\frac{i}{\hbar} \right)^2 |V_{ii}|^2 \frac{e^{2\eta t}}{2\eta^2} \\ &\quad + \left(-\frac{i}{\hbar} \right) \sum_{m \neq i} \frac{|V_{mi}|^2 e^{2\eta t}}{2\eta(E_i - E_m + i\hbar\eta)}. \end{aligned}$$

For the logarithmic time derivative of the coefficient c_i up to the second order in the perturbation V we get

$$\begin{aligned} \frac{\dot{c}_i}{c_i} &\approx -\frac{i}{\hbar} \frac{V_{ii} - \frac{i}{\hbar} \frac{|V_{ii}|^2}{\eta} + \sum_{m \neq i} \frac{|V_{mi}|^2}{(E_i - E_m + i\hbar\eta)}}{1 - \frac{i}{\hbar} \frac{V_{ii}}{\eta}} \\ &\approx \frac{-i}{\hbar} V_{ii} + \left(\frac{-i}{\hbar} \right) \sum_{m \neq i} \frac{|V_{mi}|^2}{E_i - E_m + i\hbar\eta}, \end{aligned}$$

where we have already set $e^{\eta t} \to 1$.
Note We cannot set in the denominator $\eta = 0$, because the states E_m can form nearly a continuum in the vicinity of E_i.
The logarithmic derivative is thus time independent, i.e. of form

$$\frac{\dot{c}_i(t)}{c_i(t)} = -\frac{i}{\hbar} \Delta_i.$$

The solution satisfying the initial condition $c_i(0) = 1$ is

$$c_i(t) = e^{-i\Delta_i t/\hbar}.$$

Note Δ_i is not necessarily real.
We interprete this so that the state $|i\rangle$ evolves gradually like

$$|i\rangle \longrightarrow c_i(t)|i\rangle = e^{-i\Delta_i t/\hbar}|i\rangle.$$

In the Schrödinger picture the latter contains also a phase factor, or

$$e^{-i\Delta_i t/\hbar}|i\rangle \mapsto e^{-i\Delta_i t/\hbar - iE_i t/\hbar}|i\rangle.$$

Due to the perturbation the energy levels shift like

$$E_i \longrightarrow E_i + \Delta_i.$$

We expand now Δ_i as the power series in the perturbation:

$$\Delta_i = \Delta_i^{(1)} + \Delta_i^{(2)} + \cdots.$$

Comparing with our previous expression

$$\Delta_i = V_{ii} + \sum_{m \neq i} \frac{|V_{mi}|^2}{E_i - E_m + i\hbar\eta},$$

we see that in the first order we have

$$\Delta_i^{(1)} = V_{ii}.$$

This is equivalent with the time independent perturbation theory.

Because the energies E_m for almost a continuum we can in the second order term

$$\sum_{m\neq i} \frac{|V_{mi}|^2}{E_i - E_m + i\hbar\eta}$$

replace the summation with the integration. To handle the limit $\eta \to 0$ we recall from the function theory that

$$\lim_{\epsilon\to 0+} \int_{-\infty}^{\infty} \frac{f(z)}{z+i\epsilon} dz = \wp \int_{-\infty}^{\infty} \frac{f(z)}{z} dz - i\pi f(0),$$

where $\wp$ stands for the principal value integral. A common shorthand notation for this is

$$\lim_{\epsilon\to 0} \frac{1}{x+i\epsilon} = \wp \frac{1}{x} - i\pi\delta(x).$$

Thus we get

$$\begin{aligned} \mathrm{Re}(\Delta_i^{(2)}) &= \wp \sum_{m\neq i} \frac{|V_{mi}|^2}{E_i - E_m} \\ \mathrm{Im}(\Delta_i^{(2)}) &= -\pi \sum_{m\neq i} |V_{mi}|^2 \delta(E_i - E_m). \end{aligned}$$

The right hand side of the latter equation is familiar from the Fermi golden rule, so we can write

$$\sum_{m\neq i} w_{i\to m} = \frac{2\pi}{\hbar} \sum_{m\neq i} |V_{mi}|^2 \delta(E_i - E_m) = -\frac{2}{\hbar} \mathrm{Im}\left[\Delta_i^{(2)}\right].$$

The coefficient $c_i(t)$ can be written with the help of the energy shift as

$$c_i(t) = e^{-(i/\hbar)[\mathrm{Re}(\Delta_i)t] + (1/\hbar)[\mathrm{Im}(\Delta_i)t]}.$$

We define

$$\frac{\Gamma_i}{\hbar} \equiv -\frac{2}{\hbar} \mathrm{Im}(\Delta_i).$$

Then

$$|c_i(t)|^2 = e^{2\mathrm{Im}(\Delta_i)t/\hbar} = e^{-\Gamma_i t/\hbar}.$$

Thus the quantity Γ_i tells us at which rate the state $|i\rangle$ disappears. The quantity

$$\tau_i = \frac{\hbar}{\Gamma_i}$$

is thus the average life time of the state $|i\rangle$.
In the Schrödinger picture the time evolution is

$$c_i(t) e^{-iE_i t/\hbar} = \frac{\hbar}{2\pi} \int f(E) e^{-iEt/\hbar} dE,$$

where the energy spectrum

$$f(E) = \int e^{-i[E_i + \mathrm{Re}(\Delta_i)]t/\hbar - \Gamma_i t/2\hbar} e^{iEt/\hbar}\, dt$$

is the Fourier transform of the coefficient $c_i(t)e^{-iE_i t/\hbar}$.
Now

$$|f(E)|^2 \propto \frac{1}{\{E - [E_i + \mathrm{Re}(\Delta_i)]\}^2 + \Gamma_i^2/4},$$

so Γ_i —or excluding the factor -2, the imaginary part of the energy shift— is the width of the decay line and the real part of the energy shift what is usually called the energy shift.
In the case of harmonic perturbations we can repeat the same derivation provided that we substitute

$$E_m - E_i \mapsto E_m - E_i \pm \hbar\omega.$$

Radiation and matter

We handle the interaction of radiation and matter *semiclassically*:

- the radiation field classically,
- the matter quantum mechanically,
- OK, if there is large number of photons in the volume $\approx \lambda^3$,
- in the case of the spontaneous emission we impose a fictive field equivalent with the quantum theory.

The vector potential $\boldsymbol{A}$ of the classical radiation field can always be chosen to satisfy the transverse condition: $\nabla \cdot \boldsymbol{A} = 0$. The electric and magnetic field are obtained from the vector potential as

$$\begin{aligned} \boldsymbol{E} &= -\frac{1}{c}\frac{\partial}{\partial t}\boldsymbol{A} \\ \boldsymbol{B} &= \nabla \times \boldsymbol{A}. \end{aligned}$$

The energy flux —energy/unit area/unit time— is

$$c\mathcal{U} = \frac{c}{2}\left(\frac{E_{\max}^2}{8\pi} + \frac{B_{\max}^2}{8\pi}\right).$$

For a monochromatic plane wave we have

$$\boldsymbol{A} = A_0\hat{\boldsymbol{\epsilon}}\left[e^{i(\omega/c)\hat{\boldsymbol{n}}\cdot\boldsymbol{x}-i\omega t} + e^{-i(\omega/c)\hat{\boldsymbol{n}}\cdot\boldsymbol{x}+i\omega t}\right],$$

where $\hat{\boldsymbol{n}}$ and $\hat{\boldsymbol{\epsilon}}$ are the directions of the propagation and polarization of the plane wave. Due to the transverse condition

$$\nabla \cdot \boldsymbol{A} = 0$$

we have $\hat{\boldsymbol{\epsilon}} \perp \hat{\boldsymbol{n}}$. The energy flux is then

$$c\mathcal{U} = \frac{1}{2\pi}\frac{\omega^2}{c}|A_0|^2.$$

A particle in the radiation field has the mechanical momentum

$$\begin{aligned} \left(\boldsymbol{p} - \frac{e}{c}\boldsymbol{A}\right)^2 &= \boldsymbol{p}^2 - \frac{e}{c}\boldsymbol{p}\cdot\boldsymbol{A} - \frac{e}{c}\boldsymbol{A}\cdot\boldsymbol{p} + \frac{e^2}{c^2}\boldsymbol{A}^2 \\ &= \boldsymbol{p}^2 - 2\frac{e}{c}\boldsymbol{A}\cdot\boldsymbol{p} + \frac{e^2}{c^2}\boldsymbol{A}^2, \end{aligned}$$

since due to the transvers condition

$$\boldsymbol{p}\cdot\boldsymbol{A} = \boldsymbol{A}\cdot\boldsymbol{p}.$$

The Hamiltonian of an electron in the field is now

$$\begin{aligned} H &= \frac{1}{2m_e}\left(\boldsymbol{p} - \frac{e}{c}\boldsymbol{A}\right)^2 + e\phi(\boldsymbol{x}) \\ &\approx \frac{\boldsymbol{p}^2}{2m_e} + e\phi(\boldsymbol{x}) - \frac{e}{m_e c}\boldsymbol{A}\cdot\boldsymbol{p}, \end{aligned}$$

when we drop off the term $|\boldsymbol{A}|^2$. Now

$$\begin{aligned} &-\left(\frac{e}{m_e c}\right)\boldsymbol{A}\cdot\boldsymbol{p} \\ &\quad = -\left(\frac{e}{m_e c}\right)A_0\hat{\boldsymbol{\epsilon}}\cdot\boldsymbol{p} \\ &\qquad \times\left[e^{i(\omega/c)\hat{\boldsymbol{n}}\cdot\boldsymbol{x}-i\omega t} + e^{-i(\omega/c)\hat{\boldsymbol{n}}\cdot\boldsymbol{x}+i\omega t}\right]. \end{aligned}$$

Earlier we saw that in the case of the harmonic potential

$$V(t) = \mathcal{V}e^{i\omega t} + \mathcal{V}^\dagger e^{-i\omega t}$$

transitions are possible if

$$\begin{aligned} \omega_{ni} + \omega \approx 0 \quad &\text{or} \quad E_n \approx E_i - \hbar\omega \\ \omega_{ni} - \omega \approx 0 \quad &\text{or} \quad E_n \approx E_i + \hbar\omega, \end{aligned}$$

or

$$\begin{aligned} e^{i\omega t} &\longleftrightarrow \text{stimulated emission} \\ e^{-i\omega t} &\longleftrightarrow \text{absorption.} \end{aligned}$$

Absorption

In the case of the radiation field,

$$\mathcal{V}_{ni}^\dagger = -\frac{eA_0}{m_e c}\left(e^{i(\omega/c)\hat{\boldsymbol{n}}\cdot\boldsymbol{x}}\hat{\boldsymbol{\epsilon}}\cdot\boldsymbol{p}\right)_{ni}$$

is the matrix element corresponding to the absorption. The transition rate is then

$$\begin{aligned} w_{i\to n} &= \frac{2\pi}{\hbar}\frac{e^2}{m_e^2 c^2}|A_0|^2|\langle n|e^{i(\omega/c)\hat{\boldsymbol{n}}\cdot\boldsymbol{x}}\hat{\boldsymbol{\epsilon}}\cdot\boldsymbol{p}|i\rangle|^2 \\ &\quad \times\delta(E_n - E_i - \hbar\omega). \end{aligned}$$

We should note that

- if the final states $|n\rangle$ form a continuum we integrate weighing with the state density $\rho(E_n)$.
- if the final states $|n\rangle$ are discrete they, nevertheless, are not ground states so that their energy cannot be extremely accurate.
- collisions can broaden the energy levels.
- the incoming radiation is not usually completely monochromatic.

So we write the δ-function as

$$\delta(\omega - \omega_{ni}) = \lim_{\gamma\to 0}\left(\frac{\gamma}{2\pi}\right)\frac{1}{\left[(\omega-\omega_{ni})^2 + \gamma^2/4\right]}.$$

We define the absorption cross section:

$$\sigma_{\text{abs}} = \frac{\text{(energy/unit time) absorbed by the atom } (i\to n)}{\text{energy flux of the radiation field}}.$$

Since in every absorption process the atom absorbs the energy $\hbar\omega$, we have

$$\begin{aligned} \sigma_{\text{abs}} &= \frac{\hbar\omega w_{i\to n}}{\frac{1}{2\pi}\frac{\omega^2}{c}A_0^2} \\ &= \frac{\hbar\omega\frac{2\pi}{\hbar}\frac{e^2}{m_e^2c^2}|A_0|^2|\langle n|e^{i(\omega/c)\hat{\boldsymbol{n}}\cdot\boldsymbol{x}}\hat{\boldsymbol{\epsilon}}\cdot\boldsymbol{p}|i\rangle|^2}{\frac{1}{2\pi}\frac{\omega^2}{c}|A_0|^2} \\ &\quad \times\delta(E_n - E_i - \hbar\omega) \\ &= \frac{4\pi^2\hbar}{m_e^2\omega}\left(\frac{e^2}{\hbar c}\right)|\langle n|e^{i(\omega/c)\hat{\boldsymbol{n}}\cdot\boldsymbol{x}}\hat{\boldsymbol{\epsilon}}\cdot\boldsymbol{p}|i\rangle|^2 \\ &\quad \times\delta(E_n - E_i - \hbar\omega). \end{aligned}$$

Here $e^2/\hbar c$ is the fine structure constant $\alpha \approx 1/137$.
In order the absorption to be possible the energy quantum $\hbar\omega$ of the radiation must be of the order of the energy level spacing:

$$\hbar\omega \approx \frac{Ze^2}{(a_0/Z)} \approx \frac{Ze^2}{R_{\text{atom}}},$$

when Z is the atomic number. Now

$$\frac{c}{\omega} = \frac{\lambda}{2\pi} \approx \frac{c\hbar R_{\text{atom}}}{Ze^2} \approx \frac{137R_{\text{atom}}}{Z}$$

or

$$\frac{R_{\text{atom}}}{\lambda} \approx \frac{Z}{2\pi 137} \ll 1.$$

We expand the exponential function in the expression for the cross section as the power series

$$e^{i(\omega/c)\hat{\boldsymbol{n}}\cdot\boldsymbol{x}} = 1 + i\frac{\omega}{c}\hat{\boldsymbol{n}}\cdot\boldsymbol{x} + \cdots.$$

Now

$$\frac{\omega}{c}\langle\hat{\boldsymbol{n}}\cdot\boldsymbol{x}\rangle \approx \frac{\omega}{c}R_{\text{atom}} \approx \frac{Z}{137R_{\text{atom}}}\,R_{\text{atom}} = \frac{Z}{137},$$

so it is usually enough if we keep only the term 1. We have then the so called *electric dipole approximation*. Thus in the electric dipole approximation

$$\langle n|e^{i(\omega/c)\hat{\boldsymbol{n}}\cdot\boldsymbol{x}}\hat{\boldsymbol{\epsilon}}\cdot\boldsymbol{p}|i\rangle \longrightarrow \hat{\boldsymbol{\epsilon}}\cdot\langle n|\boldsymbol{p}|i\rangle.$$

We choose

$$\hat{\boldsymbol{\epsilon}} \parallel \hat{\boldsymbol{x}} \text{ and } \hat{\boldsymbol{n}} \parallel \hat{\boldsymbol{z}}.$$

Let the states $|n\rangle$ be the solutions of the problem

$$H_0|n\rangle = E_n|n\rangle,\ H_0 = \frac{\boldsymbol{p}^2}{2m_e} + e\phi(\boldsymbol{x})$$

Because

$$[x, H_0] = \frac{i\hbar p_x}{m_e},$$

we have

$$\begin{aligned}\langle n|p_x|i\rangle &= \frac{m_e}{i\hbar}\langle n|[x,H_0]|i\rangle \\ &= im_e\omega_{ni}\langle n|x|i\rangle.\end{aligned}$$

Since x is a superposition of the spherical tensors $T^{(1)}_{\pm1}$ we get the selection rules

$$\begin{aligned}m' - m &= \pm 1 \\ |j' - j| &= 0, 1.\end{aligned}$$

If we had

- $\hat{\boldsymbol{\epsilon}} \parallel \hat{\boldsymbol{y}}$, the same selection rules were valid.
- $\hat{\boldsymbol{\epsilon}} \parallel \hat{\boldsymbol{z}}$, we should have $m' = m$, because $z = T^{(1)}_0$.

In the dipole approximation the absorption cross section is

$$\sigma_{\text{abs}} = 4\pi^2\alpha\omega_{ni}|\langle n|x|i\rangle|^2\delta(\omega - \omega_{ni}).$$

Integration gives

$$\int \sigma_{\text{abs}}(\omega)\,d\omega = \sum_n 4\pi^2\alpha\omega_{ni}|\langle n|x|i\rangle|^2.$$

The oscillator strength is defined as follows:

$$f_{ni} \equiv \frac{2m_e\omega_{ni}}{\hbar}|\langle n|x|i\rangle|^2.$$

One can show that it satisfies so called *Thomas-Reiche-Kuhn's sum rule*:

$$\sum_n f_{ni} = 1.$$

We see that

$$\int \sigma_{\text{abs}}(\omega)\,d\omega = \frac{4\pi^2\alpha\hbar}{2m_e} = 2\pi^2 c\left(\frac{e^2}{m_e c^2}\right).$$

This is known as the oscillator sum rule of classical electrodynamics.

Photoelectric effect
The initial state $|i\rangle$ is atomic but the final state $|n\rangle$ is in the continuum formed by the plane waves $|\boldsymbol{k}_f\rangle$. In the absorption cross section we have now to weigh the function $\delta(\omega_{ni} - \omega)$ with the final state density $\rho(E_n)$:

$$\begin{aligned}\sigma_{\text{abs}} &= \frac{4\pi^2\hbar}{m_e^2\omega}\alpha|\langle n|e^{i(\omega/c)\hat{\boldsymbol{n}}\cdot\boldsymbol{x}}\hat{\boldsymbol{\epsilon}}\cdot\boldsymbol{p}|i\rangle|^2 \\ &\quad\times\rho(E_n)\delta(E_n - E_i - \hbar\omega).\end{aligned}$$

Under the periodic boundary conditions in the L-sided cube we have

$$\langle\boldsymbol{x}'|\boldsymbol{k}_f\rangle = \frac{e^{i\boldsymbol{k}_f\cdot\boldsymbol{x}'}}{L^{3/2}},$$

where

$$k_i = \frac{2\pi n_i}{L},\ n_i = 0, \pm1, \pm2, \ldots.$$

When $L \to \infty$, the variable n, defined via the relation

$$n^2 = n_x^2 + n_y^2 + n_z^2,$$

can be considered continuous. Then the volume in the solid angle $d\Omega$ bounded by the surfaces $n' = n$ and $n' = n + dn$ is $n^2\,dn\,d\Omega$.
The final state energy is

$$E = \frac{\hbar^2 k_f^2}{2m_e} = \frac{\hbar^2}{2m_e}\frac{n^2(2\pi)^2}{L^2}.$$

The number of states with the wave vector $\boldsymbol{k}_f$ in the interval $(E, E + dE)$ and in the solid angle is

$$\begin{aligned}n^2\,d\Omega\frac{dn}{dE}\,dE &= \left(\frac{L}{2\pi}\right)^3(\boldsymbol{k}_f^2)\,\frac{dk_f}{dE}\,d\Omega\,dE \\ &= \left(\frac{L}{2\pi}\right)^3\frac{m_e}{\hbar^2}k_f\,dE\,d\Omega.\end{aligned}$$

The differential cross section is now

$$\frac{d\sigma}{d\Omega} = \frac{4\pi^2\alpha\hbar}{m_e^2\omega}|\langle\boldsymbol{k}_f|e^{i(\omega/c)\hat{\boldsymbol{n}}\cdot\boldsymbol{x}}\hat{\boldsymbol{\epsilon}}\cdot\boldsymbol{p}|i\rangle|^2\frac{m_e k_f L^3}{\hbar^2(2\pi)^3}.$$

Example Emission of an electron from the innermost shell.
The wave function of the initial state is approximately like the one of the hydrogen ground state provided we substitute $a_0 \longrightarrow a_0/Z$:

$$\langle \boldsymbol{x}'|i\rangle \approx \left(\frac{Z}{a_0}\right)^{3/2} e^{-iZr/a_0}.$$

The matrix element is now

$$\begin{aligned}
&\langle \boldsymbol{k}_f|e^{i(\omega/c)\hat{\boldsymbol{n}}\cdot\boldsymbol{x}}\hat{\boldsymbol{\epsilon}}\cdot\boldsymbol{p}|i\rangle \\
&\quad = \hat{\boldsymbol{\epsilon}}\cdot\int d^3x' \frac{e^{-i\boldsymbol{k}_f\cdot\boldsymbol{x}'}}{L^{3/2}} e^{i(\omega/c)\hat{\boldsymbol{n}}\cdot\boldsymbol{x}'} \\
&\qquad \times(-i\hbar\nabla)\left[e^{-Zr/a_0}\left(\frac{Z}{a_0}\right)^{3/2}\right].
\end{aligned}$$

Integrating by parts and noting that due to the transversal condition $\hat{\boldsymbol{\epsilon}}\cdot\hat{\boldsymbol{n}} = 0$ we have

$$\hat{\boldsymbol{\epsilon}}\cdot\left[\nabla e^{i(\omega/c)\hat{\boldsymbol{n}}\cdot\boldsymbol{x}'}\right] = 0.$$

We get

$$\begin{aligned}
&\langle \boldsymbol{k}_f|e^{i(\omega/c)\hat{\boldsymbol{n}}\cdot\boldsymbol{x}}\hat{\boldsymbol{\epsilon}}\cdot\boldsymbol{p}|i\rangle \\
&\quad = \frac{\hbar\hat{\boldsymbol{\epsilon}}\cdot\boldsymbol{k}_f}{L^{3/2}}\int d^3x' e^{i(\boldsymbol{k}_f - \frac{\omega}{c}\hat{\boldsymbol{n}})\cdot\boldsymbol{x}'}\psi_{\text{atom}}(\boldsymbol{x}').
\end{aligned}$$

Thus the matrix element is proportional to the Fourier transform of the atomic wave function with the respect of the variable

$$\boldsymbol{q} = \boldsymbol{k}_f - \left(\frac{\omega}{c}\right)\hat{\boldsymbol{n}}.$$

As the final result we can write the differential cross section as

$$\frac{d\sigma}{d\Omega} = 32e^2k_f\frac{(\hat{\boldsymbol{\epsilon}}\cdot\boldsymbol{k}_f)^2}{m_e c\omega}\frac{Z^5}{a_0^5}\frac{1}{\left[(Z/a_0)^2 + q^2\right]^4}.$$

If now $\hat{\boldsymbol{\epsilon}} \parallel \hat{\boldsymbol{x}}$ and $\hat{\boldsymbol{n}} \parallel \hat{\boldsymbol{z}}$, the differential cross section can be written using the polar angle θ, the azimuthal angle ϕ and the relations

$$\begin{aligned}
\boldsymbol{k}_f &= k_f(\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta) \\
(\hat{\boldsymbol{\epsilon}}\cdot\boldsymbol{k}_f)^2 &= k_f^2\sin^2\theta\cos^2\phi \\
q^2 &= k_f^2 - 2k_f\frac{\omega}{c}\cos\theta + \left(\frac{\omega}{c}\right)^2.
\end{aligned}$$

Relativistic quantum mechanics

Classical fields

We suppose that the Lagrange function

$$L = L(q_i, \dot{q}_i) = T - V$$

of classical mechanics does not depend explicitely on time. From the Hamilton variation principle

$$\delta \int_{t_1}^{t_2} L(q_i, \dot{q}_i)\, dt = 0, \quad \delta q_i(t)\big|_{t=t_{1,2}} = 0$$

one can derive the equations of motion

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right) - \frac{\partial L}{\partial q_i} = 0.$$

The Hamiltonian function of the Hamiltonian mechanics is

$$H = \sum_i p_i \dot{q}_i - L,$$

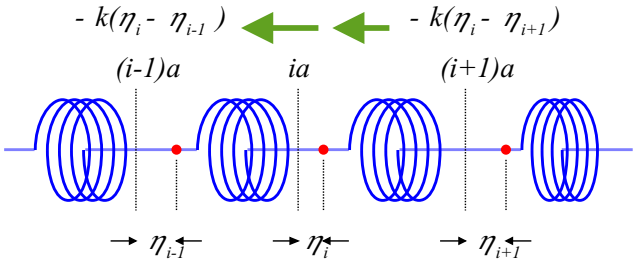
where the canonically conjugated momentum p_i of q_i is

$$p_i = \frac{\partial L}{\partial \dot{q}_i}.$$

The equations of motion are now

$$\begin{aligned} \dot{q}_i &= \frac{\partial H}{\partial p_i} \\ \dot{p}_i &= -\frac{\partial H}{\partial q_i}. \end{aligned}$$

Many body system



We consider N identical particles coupled to eachother by identical parallel springs. The Lagrangian of the system is

$$\begin{aligned} L &= T - V \\ &= \frac{1}{2}\sum_i^N \left[m\dot{\eta}_i^2 - k(\eta_{i+1} - \eta_i)^2\right], \end{aligned}$$

when η_i is the deviation of the particle i from its equilibrium position ia.
We write this as

$$\begin{aligned} L &= \frac{1}{2}\sum_i^N \left[m\dot{\eta}_i^2 - k(\eta_{i+1} - \eta_i)^2\right] \\ &= \sum_i^N a\frac{1}{2}\left[\frac{m}{a}\dot{\eta}_i^2 - ka\left(\frac{\eta_{i+1} - \eta_i}{a}\right)^2\right] \\ &= \sum_i^N a\mathcal{L}_i. \end{aligned}$$

Here $\mathcal{L}_i$ is the linear Lagrangian density.
We go to continuum by substituting the limits

$$\begin{aligned} a &\to dx \\ \frac{m}{a} &\to \mu = \text{linear mass density} \\ \frac{\eta_{i+1} - \eta_i}{a} &\to \frac{\partial \eta}{\partial x} \\ ka &\to Y = \text{Young's modulus.} \end{aligned}$$

Now

$$L = \int \mathcal{L}\, dx,$$

where

$$\mathcal{L} = \frac{1}{2}\left[\mu\dot{\eta}^2 - Y\left(\frac{\partial \eta}{\partial x}\right)^2\right].$$

In the continuous case the Hamiltonian variation principle takes the form

$$\begin{aligned} &\delta \int_{t_1}^{t_2} L\, dt \\ &= \delta \int_{t_1}^{t_2} dt \int dx\, \mathcal{L}\left(\eta, \dot{\eta}, \frac{\partial \eta}{\partial x}\right) \\ &= \int dt \int dx \left\{\frac{\partial \mathcal{L}}{\partial \eta}\delta\eta + \frac{\partial \mathcal{L}}{\partial(\partial\eta/\partial x)}\delta\left(\frac{\partial \eta}{\partial x}\right)\right. \\ &\quad \left. + \frac{\partial \mathcal{L}}{\partial(\partial\eta/\partial t)}\delta\left(\frac{\partial \eta}{\partial t}\right)\right\} \\ &= \int dt \int dx \left\{\frac{\partial \mathcal{L}}{\partial \eta} + \frac{\partial \mathcal{L}}{\partial(\partial\eta/\partial x)}\frac{\partial}{\partial x}(\delta\eta)\right. \\ &\quad \left. + \frac{\partial \mathcal{L}}{\partial(\partial\eta/\partial t)}\frac{\partial}{\partial t}(\delta\eta)\right\} \\ &= \int dt \int dx \left\{\frac{\partial \mathcal{L}}{\partial \eta} - \frac{\partial}{\partial x}\left(\frac{\partial \mathcal{L}}{\partial(\partial\eta/\partial x)}\right)\right. \\ &\quad \left. - \frac{\partial}{\partial t}\left(\frac{\partial \mathcal{L}}{\partial(\partial\eta/\partial t)}\right)\right\}\delta\eta. \end{aligned}$$

To get the variation to vanish for all $\delta\eta$ one must satisfy the Euler-Lagrange equation

$$\frac{\partial}{\partial x}\frac{\partial \mathcal{L}}{\partial(\partial\eta/\partial x)} + \frac{\partial}{\partial t}\frac{\partial \mathcal{L}}{\partial(\partial\eta/\partial t)} - \frac{\partial \mathcal{L}}{\partial \eta} = 0.$$

When

$$\mathcal{L} = \frac{1}{2}\left[\mu\dot{\eta}^2 - Y\left(\frac{\partial \eta}{\partial x}\right)^2\right],$$

then

$$\begin{aligned} \frac{\partial \mathcal{L}}{\partial \eta} &= 0 \\ \frac{\partial}{\partial x}\frac{\partial \mathcal{L}}{\partial(\partial\eta/\partial x)} &= -Y\frac{\partial}{\partial x}\frac{\partial \eta}{\partial x} = -Y\frac{\partial^2 \eta}{\partial x^2} \\ \frac{\partial}{\partial t}\frac{\partial \mathcal{L}}{\partial(\partial\eta/\partial t)} &= \mu\frac{\partial^2 \eta}{\partial t^2}. \end{aligned}$$

Substituting into the Euler-Lagrange equation we get

$$Y\frac{\partial^2 \eta}{\partial x^2} - \mu\frac{\partial^2 \eta}{\partial t^2} = 0,$$

which describes a wave progating in one dimension with the velocity $\sqrt{Y/\mu}$.
We define the canonically conjugated momentum

$$\pi = \frac{\partial \mathcal{L}}{\partial \dot{\eta}}$$

and the Hamiltonian density

$$\mathcal{H} = \dot{\eta}\pi - \mathcal{L}.$$

Now

$$\pi = \mu\dot{\eta},$$

so

$$\begin{aligned} \mathcal{H} &= \mu\dot{\eta}^2 - \frac{1}{2}\left[\mu\dot{\eta}^2 - Y\left(\frac{\partial\eta}{\partial x}\right)^2\right] \\ &= \frac{1}{2}\mu\dot{\eta}^2 + \frac{1}{2}Y\left(\frac{\partial\eta}{\partial x}\right)^2. \end{aligned}$$

The Lagrangian formalism generalizes easily to three dimensions. The Euler-Lagrange equation takes then the form

$$\sum_{k=1}^{3} \frac{\partial}{\partial x_k}\frac{\partial \mathcal{L}}{\partial(\partial\phi/\partial x_k)} + \frac{\partial}{\partial t}\frac{\partial \mathcal{L}}{\partial(\partial\phi/\partial t)} - \frac{\partial \mathcal{L}}{\partial \phi} = 0.$$

Covariant formulation
We employ the metrics where the components of a four-vector b_μ are

$$b_\mu = (b_1, b_2, b_3, b_4) = (\boldsymbol{b}, ib_0).$$

In particular the coordinate four-vector is

$$x_\mu = (x_1, x_2, x_3, x_4) = (\boldsymbol{x}, ict).$$

Under Lorentz transformations the coordinate vector transforms according to the equation

$$x'_\mu = a_{\mu\nu}x_\nu.$$

The coefficients of the Lorentz transformation satisfy the orthogonality condition

$$a_{\mu\nu}a_{\mu\lambda} = \delta_{\nu\lambda}, \quad (a^{-1})_{\mu\nu} = a_{\nu\mu},$$

so that

$$x_\mu = (a^{-1})_{\mu\nu}x'_\nu = a_{\nu\mu}x'_\nu.$$

We define the *four-vector* so that under Lorentz transformations it transforms like x_μ.
Now

$$\frac{\partial}{\partial x'_\mu} = \frac{\partial x_\nu}{\partial x'_\mu}\frac{\partial}{\partial x_\nu} = a_{\mu\nu}\frac{\partial}{\partial x_\nu},$$

so the four-gradient $\partial/\partial x_\mu$ is a four-vector.
The scalar product of the four-vectors b and c,

$$\begin{aligned} b \cdot c &= b_\mu c_\mu = \sum_{j=1}^{3} b_j c_j + b_4 c_4 \\ &= \boldsymbol{b}\cdot\boldsymbol{c} - b_0 c_0, \end{aligned}$$

is invariant under Lorentz transformations.
Using the four-vector notation the Euler-Lagrange equation can be written into the compact form

$$\frac{\partial}{\partial x_\mu}\left[\frac{\partial \mathcal{L}}{\partial(\partial\phi/\partial x_\mu)}\right] - \frac{\partial \mathcal{L}}{\partial \phi} = 0.$$

We see that the field equation derived from the Lagrangian density $\mathcal{L}$ is covariant provided that the Lagrangian density $\mathcal{L}$ itself is relativistically scalar (invariant under Lorentz transformations).

Klein-Gordon's equation

We consider the scalar field $\phi(x)$ which, according to its definition, behaves under Lorentz transformation like

$$\phi'(x') = \phi(x).$$

Now

$$\mathcal{L} = \mathcal{L}(\phi, \partial\phi/\partial x_\mu).$$

Since we want

- the Lagrangian density to be invariant under Lorentz transformations
- a linear wave equation,

the Lagrangian density can contain only the terms

$$\phi^2 \text{ and } \frac{\partial\phi}{\partial x_\mu}\frac{\partial\phi}{\partial x_\mu}.$$

One possible form for the Lagrangian density is

$$\mathcal{L} = -\frac{1}{2}\left(\frac{\partial\phi}{\partial x_\mu}\frac{\partial\phi}{\partial x_\mu} + \mu^2\phi^2\right).$$

Substituting this into the Euler-Lagrange equation

$$\frac{\partial}{\partial x_\mu}\left[\frac{\partial\mathcal{L}}{\partial(\partial\phi/\partial x_\mu)}\right] - \frac{\partial\mathcal{L}}{\partial\phi} = 0,$$

we get

$$-\frac{\partial}{\partial x_\mu}\left(\frac{\partial\phi}{\partial x_\mu}\right) + \mu^2\phi = 0.$$

If we employ the notation

$$\Box = \nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2},$$

we end up with the *Klein-Gordon* equation

$$\Box\phi - \mu^2\phi = 0.$$

Heuristic derivation

We substitute into the relativistic energy-momentum relation

$$E^2 - |\boldsymbol{p}|^2c^2 = m^2c^4$$

the operators

$$E \mapsto i\hbar\frac{\partial}{\partial t}, \quad p_k \mapsto -i\hbar\frac{\partial}{\partial x_k},$$

and get

$$\left(-\frac{\partial^2}{c^2\partial t^2} + \nabla^2 - \frac{m^2c^2}{\hbar^2}\right)\phi = 0.$$

When we set

$$\mu = \frac{mc}{\hbar}, \ [\mu] = \frac{1}{\text{length}},$$

we end up with the Klein-Gordon equation.

There are no sources in the Lagrangian density

$$\mathcal{L} = -\frac{1}{2}\left(\frac{\partial\phi}{\partial x_\mu}\frac{\partial\phi}{\partial x_\mu} + \mu^2\phi^2\right)$$

so the solution describes a free field. We include the term

$$\mathcal{L}_{\text{int}} = -\phi\rho,$$

where ρ is the (usually position dependent) density of the source. The field equation is now

$$\Box\phi - \mu^2\phi = \rho.$$

When we choose

$$\rho = G\delta(\boldsymbol{x})$$

and seek for a stationary solution we end up with the equation

$$(\nabla^2 - \mu^2)\phi = G\delta(\boldsymbol{x}).$$

We substitute ϕ using its Fourier transform

$$\phi(\boldsymbol{x}) = \frac{1}{(2\pi)^{2/3}}\int d^3k e^{i\boldsymbol{k}\cdot\boldsymbol{x}}\tilde{\phi}(\boldsymbol{k}),$$

where

$$\tilde{\phi}(\boldsymbol{k}) = \frac{1}{(2\pi)^{3/2}}\int d^3x\, e^{-i\boldsymbol{k}\cdot\boldsymbol{x}}\phi(\boldsymbol{x}).$$

We end up with the algebraic equation

$$(-\boldsymbol{k}^2 - \mu^2)\tilde{\phi}(\boldsymbol{k}) = \frac{G}{(2\pi)^{3/2}}$$

of the Fourier components. Its solution is

$$\tilde{\phi}(\boldsymbol{k}) = -\frac{G}{(2\pi)^{2/3}}\frac{1}{k^2 + \mu^2}.$$

Taking the Fourier transform we get the solution

$$\phi(\boldsymbol{x}) = -\frac{G}{4\pi}\frac{e^{-\mu r}}{r},$$

known as the *Yukawa potential*. Let's suppose that the meson field of a nucleon at the point $\boldsymbol{x}_1$ satisfies the equations

$$(\nabla_2^2 - \mu^2)\phi = G\delta(\boldsymbol{x}_1 - \boldsymbol{x}_2).$$

Its solution is thus the Yukawa potential.

$$\phi(\boldsymbol{x}_2) = -\frac{G}{4\pi}\frac{e^{-\mu|\boldsymbol{x}_2 - \boldsymbol{x}_1|}}{|\boldsymbol{x}_2 - \boldsymbol{x}_1|}.$$

Because the Hamiltonian density was

$$\mathcal{H} = \dot{\eta}\pi - \mathcal{L},$$

the Hamiltonian density of the interaction is

$$\mathcal{H}_{\text{int}} = -\mathcal{L}_{\text{int}}$$

and the total interaction Hamiltonian

$$H_{\text{int}} = \int \mathcal{H}_{\text{int}}\, d^3x = \int \phi\rho\, d^3x.$$

We see that the interaction energy of nucleons located at the points $\boldsymbol{x}_1$ and $\boldsymbol{x}_2$ is

$$H_{\text{int}}^{(1,2)} = -\frac{G}{4\pi}\frac{e^{-\mu|\boldsymbol{x}_2 - \boldsymbol{x}_1|}}{|\boldsymbol{x}_2 - \boldsymbol{x}_1|}.$$

Note Unlike in the Coulomb case, this interaction is atractive and short ranged.
In the reality there are 3 mesons (π^+, π^0, π^-), with different charges but with (almost) equal masses, consistent with the thory. We expand our theory so that we consider two real fields, ϕ_1 and ϕ_2, for two particles with equal masses. From these we construct the complex fields

$$\begin{aligned} \phi &= \frac{\phi_1 + i\phi_2}{\sqrt{2}} \\ \phi^* &= \frac{\phi_1 - i\phi_2}{\sqrt{2}}. \end{aligned}$$

The Lagrangian density for the free fields can be written using either the complex or real fields:

$$\begin{aligned} \mathcal{L} &= -\frac{1}{2}\left(\frac{\partial\phi_1}{\partial x_\mu}\frac{\partial\phi_1}{\partial x_\mu} + \mu^2\phi_1^2\right) - \frac{1}{2}\left(\frac{\partial\phi_2}{\partial x_\mu}\frac{\partial\phi_2}{\partial x_\mu} + \mu^2\phi_2^2\right) \\ &= -\left(\frac{\partial\phi^*}{\partial x_\mu}\frac{\partial\phi}{\partial x_\mu} + \mu^2\phi^*\phi\right). \end{aligned}$$

Considering the fields ϕ and ϕ^* independent we get two Euler-Lagrange equations

$$\begin{aligned} \frac{\partial}{\partial x_\mu}\frac{\partial\mathcal{L}}{\partial(\partial\phi/\partial x_\mu)} - \frac{\partial\mathcal{L}}{\partial\phi} &= 0 \\ \frac{\partial}{\partial x_\mu}\frac{\partial\mathcal{L}}{\partial(\partial\phi^*/\partial x_\mu)} - \frac{\partial\mathcal{L}}{\partial\phi^*} &= 0, \end{aligned}$$

which can be further written as two Klein-Gordon equations

$$\begin{aligned} \Box\phi^* - \mu^2\phi^* &= 0 \\ \Box\phi - \mu^2\phi &= 0. \end{aligned}$$

We define the *first order gauge transformation* so that the fields transform under it like

$$\begin{aligned} \phi' &= e^{i\lambda}\phi \\ \phi^{*\prime} &= e^{-i\lambda}\phi^*, \end{aligned}$$

when λ is a real parameter. Let λ be now an arbitrary, infinitesimally small, number. Then

$$\begin{aligned} \delta\phi &= i\lambda\phi \\ \delta\phi^* &= -i\lambda\phi^*. \end{aligned}$$

The Lagrangian density transforms then as

$$\begin{aligned} \delta\mathcal{L} &= \left[\frac{\partial\mathcal{L}}{\partial\phi}\delta\phi + \frac{\partial\mathcal{L}}{\partial(\partial\phi/\partial x_\mu)}\delta\left(\frac{\partial\phi}{\partial x_\mu}\right)\right] \\ &\quad + \left[\frac{\partial\mathcal{L}}{\partial\phi^*}\delta\phi^* + \frac{\partial\mathcal{L}}{\partial(\partial\phi^*/\partial x_\mu)}\delta\left(\frac{\partial\phi^*}{\partial x_\mu}\right)\right] \\ &= \left[\frac{\partial\mathcal{L}}{\partial\phi} - \frac{\partial}{\partial x_\mu}\left(\frac{\partial\mathcal{L}}{\partial(\partial\phi/\partial x_\mu)}\right)\right]\delta\phi \\ &\quad + \left[\frac{\partial\mathcal{L}}{\partial\phi^*} - \frac{\partial}{\partial x_\mu}\left(\frac{\partial\mathcal{L}}{\partial(\partial\phi^*/\partial x_\mu)}\right)\right]\delta\phi^* \\ &\quad + \frac{\partial}{\partial x_\mu}\left[\frac{\partial\mathcal{L}}{\partial(\partial\phi/\partial x_\mu)}\delta\phi + \frac{\partial\mathcal{L}}{\partial(\partial\phi^*/\partial x_\mu)}\delta\phi^*\right] \\ &= -i\lambda\frac{\partial}{\partial x_\mu}\left(\frac{\partial\phi^*}{\partial x_\mu}\phi - \phi^*\frac{\partial\phi}{\partial x_\mu}\right). \end{aligned}$$

In a small neighborhood of the solutions ϕ and ϕ^* the Lagrangian density is invarinat so we must have

$$\delta\mathcal{L} = 0.$$

Thus we get

$$\frac{\partial s_\mu}{\partial x_\mu} = 0,$$

where

$$s_\mu = i\left(\frac{\partial\phi^*}{\partial x_\mu}\phi - \phi^*\frac{\partial\phi}{\partial x_\mu}\right).$$

We see that

- a complex field ϕ is associated with a conserved four-vector density s_μ,
- if we exchange $\phi \longleftrightarrow \phi^*$, then $s_\mu \longleftrightarrow -s_\mu$.

We interpret this so that

- s_μ is the charge current density,
- ϕ carries the charge e,
- ϕ^* carries the charge $-e$,
- the previous real field corresponds to neutral mesons.

Photons

We consider a radiation field whose vector potential $\boldsymbol{A}$ satisfies the transversality condition

$$\nabla \cdot \boldsymbol{A} = 0.$$

Because the electric and magnetic fields

$$\begin{aligned} \boldsymbol{E} &= -\frac{1}{c}\frac{\partial}{\partial t}\boldsymbol{A} \\ \boldsymbol{B} &= \nabla \times \boldsymbol{A} \end{aligned}$$

satisfy the free space Maxwell equations

$$\begin{aligned} \nabla \cdot \boldsymbol{E} &= 0 \\ \nabla \times \boldsymbol{E} &= -\frac{\partial \boldsymbol{B}}{\partial t} \\ \nabla \cdot \boldsymbol{B} &= 0 \\ \nabla \times \boldsymbol{B} &= \frac{1}{c}\frac{\partial \boldsymbol{E}}{\partial t}, \end{aligned}$$

the vector potential satisfies the wave equation

$$\nabla^2 \boldsymbol{A} - \frac{1}{c^2}\frac{\partial^2 \boldsymbol{A}}{\partial t^2} = 0.$$

We write the vector potential at the moment $t = 0$ as a superposition of the periodically normalized plane waves in an L-sided cube,

$$\boldsymbol{u}_{\boldsymbol{k},\alpha}(\boldsymbol{x}) = \hat{\boldsymbol{\epsilon}}^{(\alpha)} e^{i\boldsymbol{k}\cdot\boldsymbol{x}},$$

like:

$$\begin{aligned} \boldsymbol{A}(\boldsymbol{x},t)|_{t=0} &= \frac{1}{\sqrt{V}}\sum_{\boldsymbol{k}}\sum_{\alpha=1,2}(c_{\boldsymbol{k},\alpha}(0)\boldsymbol{u}_{\boldsymbol{k},\alpha}(\boldsymbol{x}) \\ &\quad + c^*_{\boldsymbol{k},\alpha}(0)\boldsymbol{u}^*_{\boldsymbol{k},\alpha}(\boldsymbol{x})). \end{aligned}$$

Here $V = L^3$ and $\hat{\boldsymbol{\epsilon}}^{(\alpha)}, \alpha = 1, 2$ are real polarization vectors.
Due to the transversality condition we have

$$\hat{\boldsymbol{\epsilon}}^{(\alpha)} \cdot \boldsymbol{k} = 0,$$

so the polarization can chosen so that the vectors $(\hat{\boldsymbol{\epsilon}}^{(1)}, \hat{\boldsymbol{\epsilon}}^{(2)}, \boldsymbol{k}/|\boldsymbol{k}|)$ form a righthanded rectangular coordinate system. The Fourier components $\boldsymbol{u}_{\boldsymbol{k},\alpha}$ satisfy the orthogonality conditions

$$\frac{1}{V}\int d^3x\, \boldsymbol{u}_{\boldsymbol{k},\alpha} \cdot \boldsymbol{u}^*_{\boldsymbol{k}',\alpha'} = \delta_{\boldsymbol{k}\boldsymbol{k}'}\delta_{\alpha\alpha'}.$$

Due to the periodicity conditions the wave vectors can take the values

$$k_x, k_y, k_z = 2n\pi/L, \quad n = \pm 1, \pm 2, \ldots.$$

At the moment $t \neq 0$ the vector potential is obtained simply by setting

$$\begin{aligned} c_{\boldsymbol{k},\alpha}(t) &= c_{\boldsymbol{k},\alpha}(0)e^{-i\omega t} \\ c^*_{\boldsymbol{k},\alpha}(t) &= c^*_{\boldsymbol{k},\alpha}(0)e^{i\omega t}, \end{aligned}$$

where

$$\omega = |\boldsymbol{k}|c.$$

Now

$$\begin{aligned} &\boldsymbol{A}(\boldsymbol{x},t) \\ &\quad = \frac{1}{\sqrt{V}}\sum_{\boldsymbol{k}}\sum_{\alpha}(c_{\boldsymbol{k},\alpha}(t)\hat{\boldsymbol{\epsilon}}^{(\alpha)}e^{i\boldsymbol{k}\cdot\boldsymbol{x}} + c^*_{\boldsymbol{k},\alpha}(t)\hat{\boldsymbol{\epsilon}}^{(\alpha)}e^{-i\boldsymbol{k}\cdot\boldsymbol{x}}) \\ &\quad = \frac{1}{\sqrt{V}}\sum_{\boldsymbol{k}}\sum_{\alpha}(c_{\boldsymbol{k},\alpha}(0)\hat{\boldsymbol{\epsilon}}^{(\alpha)}e^{ik\cdot x} + c^*_{\boldsymbol{k},\alpha}(0)\hat{\boldsymbol{\epsilon}}^{(\alpha)}e^{-ik\cdot x}), \end{aligned}$$

where we have employed the four-vector notation

$$k \cdot x = \boldsymbol{k}\cdot\boldsymbol{x} - \omega t = \boldsymbol{k}\cdot\boldsymbol{x} - |\boldsymbol{k}|ct.$$

The Hamiltonian function of the classical radiation field is

$$\begin{aligned} H &= \frac{1}{2}\int (|\boldsymbol{B}|^2 + |\boldsymbol{E}|^2)\, d^3x \\ &= \frac{1}{2}\int \left[|\nabla \times \boldsymbol{A}|^2 + |(1/c)(\partial \boldsymbol{A}/\partial t)|^2\right]\, d^3x. \end{aligned}$$

A straightforward calculation shows that

$$H = \sum_{\boldsymbol{k}}\sum_{\alpha} 2(\omega/c)^2 c^*_{\boldsymbol{k},\alpha}c_{\boldsymbol{k},\alpha}.$$

Because the coefficients

$$c_{\boldsymbol{k},\alpha}(t) = c_{\boldsymbol{k},\alpha}(0)e^{-i\omega t}$$

satisfy the equation of motion

$$\ddot{c}_{\boldsymbol{k},\alpha} = -\omega^2 c_{\boldsymbol{k},\alpha},$$

it would look like the classical radiation field were composed of independent harmonic oscillators.
We define the variables

$$\begin{aligned} Q_{\boldsymbol{k},\alpha} &= \frac{1}{c}(c_{\boldsymbol{k},\alpha} + c^*_{\boldsymbol{k},\alpha}) \\ P_{\boldsymbol{k},\alpha} &= -\frac{i\omega}{c}(c_{\boldsymbol{k},\alpha} - c^*_{\boldsymbol{k},\alpha}). \end{aligned}$$

With the help of these the Hamiltonian function can be written as

$$H = \sum_{\boldsymbol{k}}\sum_{\alpha}\frac{1}{2}(P^2_{\boldsymbol{k},\alpha} + \omega^2 Q^2_{\boldsymbol{k},\alpha}).$$

Since

$$\begin{aligned} \frac{\partial H}{\partial Q_{\boldsymbol{k},\alpha}} &= -\dot{P}_{\boldsymbol{k},\alpha} \\ \frac{\partial H}{\partial P_{\boldsymbol{k},\alpha}} &= +\dot{Q}_{\boldsymbol{k},\alpha}, \end{aligned}$$

the variables $P_{\boldsymbol{k},\alpha}$ and $Q_{\boldsymbol{k},\alpha}$ are canonically conjugated and the Hamiltonian function the sum of the total energies of the corresponding harmonic oscillators.
Thus the classical radiation field can be thought to be a collection of independent harmonic oscillators. There

- every oscillator is characterized by the wave vector $\boldsymbol{k}$ and the polarization $\hat{\boldsymbol{\epsilon}}^{(\alpha)}$,
- the dynamic variables of every oscillator are combinations of Fourier coefficients.

We quantize these oscillators by postulating that $P_{\boldsymbol{k},\alpha}$ and $Q_{\boldsymbol{k},\alpha}$ are not any more pure numbers but *operators* which satisfy the canonical commutation rules

$$\begin{aligned}[Q_{\boldsymbol{k},\alpha}, P_{\boldsymbol{k}',\alpha'}] &= i\hbar\delta_{\boldsymbol{k}\boldsymbol{k}'}\delta_{\alpha\alpha'}\\ [Q_{\boldsymbol{k},\alpha}, Q_{\boldsymbol{k}',\alpha'}] &= 0\\ [P_{\boldsymbol{k},\alpha}, P_{\boldsymbol{k}',\alpha'}] &= 0.\end{aligned}$$

We define dimensionless combinations $a_{\boldsymbol{k},\alpha}$ and $a^\dagger_{\boldsymbol{k},\alpha}$ of the operators $P_{\boldsymbol{k},\alpha}$ and $Q_{\boldsymbol{k},\alpha}$ as

$$\begin{aligned}a_{\boldsymbol{k},\alpha} &= \frac{1}{\sqrt{2\hbar\omega}}(\omega Q_{\boldsymbol{k},\alpha} + iP_{\boldsymbol{k},\alpha})\\ a^\dagger_{\boldsymbol{k},\alpha} &= \frac{1}{\sqrt{2\hbar\omega}}(\omega Q_{\boldsymbol{k},\alpha} - iP_{\boldsymbol{k},\alpha}).\end{aligned}$$

It is easy to see that they satisfy the commutation relations

$$\begin{aligned}[a_{\boldsymbol{k},\alpha}, a^\dagger_{\boldsymbol{k}',\alpha'}] &= \delta_{\boldsymbol{k}\boldsymbol{k}'}\delta_{\alpha\alpha'}\\ [a_{\boldsymbol{k},\alpha}, a_{\boldsymbol{k}',\alpha'}] &= [a^\dagger_{\boldsymbol{k},\alpha}, a^\dagger_{\boldsymbol{k}',\alpha'}] = 0.\end{aligned}$$

Note In these relations the operators must be evaluated at the same moment, i.e. $[a_{\boldsymbol{k},\alpha}, a^\dagger_{\boldsymbol{k}',\alpha'}]$ stands in fact for the commutator $[a_{\boldsymbol{k},\alpha}(t), a^\dagger_{\boldsymbol{k}',\alpha'}(t)]$.
We further define the Hermitean operator

$$N_{\boldsymbol{k},\alpha} = a^\dagger_{\boldsymbol{k},\alpha}a_{\boldsymbol{k},\alpha}.$$

It is easy to see that

$$\begin{aligned}[a_{\boldsymbol{k},\alpha}, N_{\boldsymbol{k}',\alpha'}] &= \delta_{\boldsymbol{k}\boldsymbol{k}'}\delta_{\alpha\alpha'}a_{\boldsymbol{k},\alpha}\\ [a^\dagger_{\boldsymbol{k},\alpha}, N_{\boldsymbol{k}',\alpha'}] &= -\delta_{\boldsymbol{k}\boldsymbol{k}'}\delta_{\alpha\alpha'}a^\dagger_{\boldsymbol{k},\alpha}.\end{aligned}$$

Due to the Hermiticity the eigenvalues $n_{\boldsymbol{k},\alpha}$ of the operator $N_{\boldsymbol{k},\alpha}$ are real and the eigenvectors

$$N_{\boldsymbol{k},\alpha}|n_{\boldsymbol{k},\alpha}\rangle = n_{\boldsymbol{k},\alpha}|n_{\boldsymbol{k},\alpha}\rangle$$

form an orthonormal complete basis.
With the help of the commutation rule

$$[a^\dagger_{\boldsymbol{k},\alpha}, N_{\boldsymbol{k}',\alpha'}] = -\delta_{\boldsymbol{k}\boldsymbol{k}'}\delta_{\alpha\alpha'}a^\dagger_{\boldsymbol{k},\alpha}$$

we see that

$$\begin{aligned}N_{\boldsymbol{k},\alpha}a^\dagger_{\boldsymbol{k},\alpha}|n_{\boldsymbol{k},\alpha}\rangle &= (a^\dagger_{\boldsymbol{k},\alpha}N_{\boldsymbol{k},\alpha} + a^\dagger_{\boldsymbol{k},\alpha})|n_{\boldsymbol{k},\alpha}\rangle\\ &= (n_{\boldsymbol{k},\alpha}+1)a^\dagger_{\boldsymbol{k},\alpha}|n_{\boldsymbol{k},\alpha}\rangle.\end{aligned}$$

Similarly we can show that

$$N_{\boldsymbol{k},\alpha}a_{\boldsymbol{k},\alpha}|n_{\boldsymbol{k},\alpha}\rangle = (n_{\boldsymbol{k},\alpha}-1)a_{\boldsymbol{k},\alpha}|n_{\boldsymbol{k},\alpha}\rangle.$$

Thus we can write

$$\begin{aligned}a^\dagger_{\boldsymbol{k},\alpha}|n_{\boldsymbol{k},\alpha}\rangle &= c_+|n_{\boldsymbol{k},\alpha}+1\rangle\\ a_{\boldsymbol{k},\alpha}|n_{\boldsymbol{k},\alpha}\rangle &= c_-|n_{\boldsymbol{k},\alpha}-1\rangle.\end{aligned}$$

Because the states $|n_{\boldsymbol{k},\alpha}\rangle$ are normalized we can calculate the coefficients as

$$\begin{aligned}|c_+|^2 &= |c_+|^2\langle n_{\boldsymbol{k},\alpha}+1|n_{\boldsymbol{k},\alpha}+1\rangle\\ &= \langle n_{\boldsymbol{k},\alpha}|a_{\boldsymbol{k},\alpha}a^\dagger_{\boldsymbol{k},\alpha}|n_{\boldsymbol{k},\alpha}\rangle\\ &= \langle n_{\boldsymbol{k},\alpha}|N_{\boldsymbol{k},\alpha} + [a_{\boldsymbol{k},\alpha}, a^\dagger_{\boldsymbol{k},\alpha}]|n_{\boldsymbol{k},\alpha}\rangle\\ &= n_{\boldsymbol{k},\alpha}+1,\\ |c_-|^2 &= \langle n_{\boldsymbol{k},\alpha}|a^\dagger_{\boldsymbol{k},\alpha}a_{\boldsymbol{k},\alpha}|n_{\boldsymbol{k},\alpha}\rangle = n_{\boldsymbol{k},\alpha}.\end{aligned}$$

We choose the phase of the coefficients so that at the moment $t=0$ we have

$$\begin{aligned}a^\dagger_{\boldsymbol{k},\alpha}|n_{\boldsymbol{k},\alpha}\rangle &= \sqrt{n_{\boldsymbol{k},\alpha}+1}|n_{\boldsymbol{k},\alpha}+1\rangle\\ a_{\boldsymbol{k},\alpha}|n_{\boldsymbol{k},\alpha}\rangle &= \sqrt{n_{\boldsymbol{k},\alpha}}|n_{\boldsymbol{k},\alpha}-1\rangle.\end{aligned}$$

Because

$$n_{\boldsymbol{k},\alpha} = \langle n_{\boldsymbol{k},\alpha}|N_{\boldsymbol{k},\alpha}|n_{\boldsymbol{k},\alpha}\rangle = \langle n_{\boldsymbol{k},\alpha}|a^\dagger_{\boldsymbol{k},\alpha}a_{\boldsymbol{k},\alpha}|n_{\boldsymbol{k},\alpha}\rangle$$

and because the norm of a vectors is always non-negative we must have

$$n_{\boldsymbol{k},\alpha} \geq 0.$$

From this we can deduce that the only possible eigenvalues are

$$n_{\boldsymbol{k},\alpha} = 0, 1, 2, \ldots.$$

We interprete

- the state $|n_{\boldsymbol{k},\alpha}\rangle$ to contain exactly $n_{\boldsymbol{k},\alpha}$ *photons*, each of which is characterized by a wave vector $\boldsymbol{k}$ and a polarization $\hat{\boldsymbol{\epsilon}}^{(\alpha)}$.
- the operator $a^\dagger_{\boldsymbol{k},\alpha}$ to create a photon with the wave vector $\boldsymbol{k}$ and the polarization $\hat{\boldsymbol{\epsilon}}^{(\alpha)}$.
- the operator $a_{\boldsymbol{k},\alpha}$ to destroy a photon with the wave vector $\boldsymbol{k}$ and the polarizartion $\hat{\boldsymbol{\epsilon}}^{(\alpha)}$.
- the operator $N_{\boldsymbol{k},\alpha}$ to count the number of photons with the wave vector $\boldsymbol{k}$ and the polarization $\hat{\boldsymbol{\epsilon}}^{(\alpha)}$ in the state

The state composed of various kind of photons is a direct product of individual vectors $|n_{\boldsymbol{k}_i,\alpha_i}\rangle$:

$$\begin{aligned}&|n_{\boldsymbol{k}_1,\alpha_1}, n_{\boldsymbol{k}_2,\alpha_2}, \ldots, n_{\boldsymbol{k}_i,\alpha_i}, \ldots\rangle\\ &\quad = |n_{\boldsymbol{k}_1,\alpha_1}\rangle \otimes |n_{\boldsymbol{k}_2,\alpha_2}\rangle \otimes \cdots \otimes |n_{\boldsymbol{k}_i,\alpha_i}\rangle \otimes \cdots.\end{aligned}$$

The vector $|0\rangle$ stands for the state that has no kind of photons, i.e.

$$|0\rangle = |0_{\boldsymbol{k}_1,\alpha_1}\rangle \otimes |0_{\boldsymbol{k}_2,\alpha_2}\rangle \otimes \cdots.$$

Application of any operator $a_{\boldsymbol{k},\alpha}$ onto this results always zero. We say that $|0\rangle$ represents the vacuum.
It is easy to see that a general normalized photon state can be constructed applying operations $a^\dagger_{\boldsymbol{k},\alpha}$ consecutively:

$$|n_{\boldsymbol{k}_1,\alpha_1}, n_{\boldsymbol{k}_2,\alpha_2}, \ldots\rangle = \prod_{\boldsymbol{k}_i,\alpha_i} \frac{(a^\dagger_{\boldsymbol{k}_i,\alpha_i})^{n_{\boldsymbol{k}_i,\alpha_i}}}{\sqrt{n_{\boldsymbol{k}_i,\alpha_i}!}}|0\rangle.$$

Note Since the operators $a^\dagger_{\boldsymbol{k},\alpha}$ and $a^\dagger_{\boldsymbol{k}',\alpha'}$ commute the order of operators does not matter. The many photon states are symmetric with respect to the exchange of photons. We say that the photons obey the *Bose-Einstein statistics* or that they are *bosons*.
Since the numbers $n_{\boldsymbol{k},\alpha}$ tell us the number of photons of type $(\boldsymbol{k},\alpha)$ in the volume under consideration we call them the *occupation numbers* of the state.
Correspondingly the space spanned by the state vectors is called the *occupation number space*.
In the quantum theory the Fourier coefficients of a classical radiation field must be replaced by the corresponding non-commuting creation and annihilation operators. Substituting

$$\begin{aligned} c_{\boldsymbol{k},\alpha} &\mapsto c\sqrt{\hbar/2\omega}\, a_{\boldsymbol{k},\alpha}(t) \\ c^*_{\boldsymbol{k},\alpha} &\mapsto c\sqrt{\hbar/2\omega}\, a^\dagger_{\boldsymbol{k},\alpha}(t) \end{aligned}$$

we get

$$\boldsymbol{A}(\boldsymbol{x},t) = \frac{1}{\sqrt{V}}\sum_{\boldsymbol{k},\alpha} c\sqrt{\frac{\hbar}{2\omega}}\left[a_{\boldsymbol{k},\alpha}(t)\hat{\boldsymbol{\epsilon}}^{(\alpha)}e^{i\boldsymbol{k}\cdot\boldsymbol{x}} + a^\dagger_{\boldsymbol{k},\alpha}(t)\hat{\boldsymbol{\epsilon}}^{(\alpha)}e^{-i\boldsymbol{k}\cdot\boldsymbol{x}}\right].$$

Note Here $\boldsymbol{A}$ is an *operator* defined at every point of the space whereas $\boldsymbol{A}$ of the classical theory is a three component field defined at every point. The variables $\boldsymbol{x}$ and t are both in classical and quantum mechanical cases variables parametrizing the fields. Fields like the operator $\boldsymbol{A}$ are called *field operators* or *quantized fields*.
Also in the quantum theory the Hamiltonian is of the form

$$H = \frac{1}{2}\int (\boldsymbol{B}\cdot\boldsymbol{B} + \boldsymbol{E}\cdot\boldsymbol{E})\, d^3x.$$

Substituting the field operator $\boldsymbol{A}$ into the equations

$$\begin{aligned} \boldsymbol{E} &= -\frac{1}{c}\frac{\partial}{\partial t}\boldsymbol{A} \\ \boldsymbol{B} &= \nabla\times\boldsymbol{A} \end{aligned}$$

and noting that this time the Fourier coefficients do not commute we get

$$\begin{aligned} H &= \frac{1}{2}\sum_{\boldsymbol{k}}\sum_{\alpha}\hbar\omega(a^\dagger_{\boldsymbol{k},\alpha}a_{\boldsymbol{k},\alpha} + a_{\boldsymbol{k},\alpha}a^\dagger_{\boldsymbol{k},\alpha}) \\ &= \sum_{\boldsymbol{k}}\sum_{\alpha}(N_{\boldsymbol{k},\alpha} + \frac{1}{2})\hbar\omega, \end{aligned}$$

where

$$\omega = |\boldsymbol{k}|c.$$

When we choose the energy scale so that

$$H|0\rangle = 0,$$

the Hamiltonian takes the form

$$H = \sum_{\boldsymbol{k}}\sum_{\alpha}\hbar\omega N_{\boldsymbol{k},\alpha}.$$

When it acts on a many photon state the result is

$$\begin{aligned} &H|n_{\boldsymbol{k}_1,\alpha_1}, n_{\boldsymbol{k}_2,\alpha_2}, \ldots\rangle \\ &\quad = \sum_i n_{\boldsymbol{k}_i,\alpha_i}\hbar\omega_i|n_{\boldsymbol{k}_1,\alpha_1}, n_{\boldsymbol{k}_2,\alpha_2}, \ldots\rangle. \end{aligned}$$

The quantum mechanical momentum operator is exactly of the same form as the classical function (the Poynting vector):

$$\begin{aligned} \boldsymbol{P} &= \frac{1}{c}\int(\boldsymbol{E}\times\boldsymbol{B})\, d^3x \\ &= \sum_{\boldsymbol{k}}\sum_{\alpha}\frac{1}{2}\hbar\boldsymbol{k}(a^\dagger_{\boldsymbol{k},\alpha}a_{\boldsymbol{k},\alpha} + a_{\boldsymbol{k},\alpha}a^\dagger_{\boldsymbol{k},\alpha}) \\ &= \sum_{\boldsymbol{k}}\sum_{\alpha}\hbar\boldsymbol{k}(N_{\boldsymbol{k},\alpha} + \frac{1}{2}). \end{aligned}$$

Since here the summation goes over all wave vectors the term associated with the factor 1/2 will not appear in the final result the terms $\hbar\boldsymbol{k}$ and $-\hbar\boldsymbol{k}$ cancelling each other. For the momentum operator we get thus

$$\boldsymbol{P} = \sum_{\boldsymbol{k}}\sum_{\alpha}\hbar\boldsymbol{k}N_{\boldsymbol{k},\alpha}.$$

For one photon states we have

$$\begin{aligned} Ha^\dagger_{\boldsymbol{k},\alpha}|0\rangle &= \hbar\omega a^\dagger_{\boldsymbol{k},\alpha}|0\rangle \\ \boldsymbol{P}a^\dagger_{\boldsymbol{k},\alpha}|0\rangle &= \hbar\boldsymbol{k}a^\dagger_{\boldsymbol{k},\alpha}|0\rangle, \end{aligned}$$

so

$$\begin{aligned} \hbar\omega = \hbar|\boldsymbol{k}|c &= \text{photon energy} \\ \hbar\boldsymbol{k} &= \text{photon momentum.} \end{aligned}$$

The photon mass will be

$$\begin{aligned} (\text{mass})^2 &= \frac{1}{c^4}(E^2 - |\boldsymbol{p}|^2c^2) \\ &= \frac{1}{c^4}[(\hbar\omega)^2 - (\hbar|\boldsymbol{k}|c)^2] \\ &= 0. \end{aligned}$$

The photon state is also characterized by its polarization $\hat{\boldsymbol{\epsilon}}^{(\alpha)}$. Since $\hat{\boldsymbol{\epsilon}}^{(\alpha)}$ transforms under rotations like a vector the photon is associated with one unit of angular momentum, i.e. the spin angular momentum of the

photon is one. We define the *circularly polarized* combinations

$$\hat{\boldsymbol{\epsilon}}^{(\pm)} = \mp\frac{1}{\sqrt{2}}(\hat{\boldsymbol{\epsilon}}^{(1)} \pm i\hat{\boldsymbol{\epsilon}}^{(2)}).$$

We rotate these vectors by an infinitesimal angle $\delta\phi$ around the progation direction $\boldsymbol{k}$. Their changes are

$$\begin{aligned}\delta\hat{\boldsymbol{\epsilon}}^{(\pm)} &= \mp\frac{\delta\phi}{\sqrt{2}}(\hat{\boldsymbol{\epsilon}}^{(2)} \mp i\hat{\boldsymbol{\epsilon}}^{(1)}) \\ &= \mp i\delta\phi\,\hat{\boldsymbol{\epsilon}}^{(\pm)}.\end{aligned}$$

We select the propagation direction $\boldsymbol{k}$ as the quantization axis and compare this expression with the transformation properties of angular momentum eigenstates

$$|jm\rangle_R = \left(1 - \frac{i}{\hbar}J_z\delta\phi\right)|jm\rangle = (1 - im\,\delta\phi)|jm\rangle.$$

We see that

- the spin components of the polarizations $\hat{\boldsymbol{\epsilon}}^{(\pm)}$ are $m = \pm 1$.
- the state $m = 0$ is missing due to the transversality condition.
- our original linear polarization states are 50/50 mixtures of $m = 1$ and $m = -1$ states.

Hence the photon spin is always either parallel or antiparallel to the direction of the propagation.
The operators $a_{\boldsymbol{k},\alpha}$ and $a^\dagger_{\boldsymbol{k},\alpha}$ are time dependent and so they satisfy the Heisenberg equations of motion

$$\begin{aligned}\dot{a}_{\boldsymbol{k},\alpha} &= \frac{i}{\hbar}[H, a_{\boldsymbol{k},\alpha}] \\ &= \frac{i}{\hbar}\sum_{\boldsymbol{k}'}\sum_{\alpha'}[\hbar\omega' N_{\boldsymbol{k}',\alpha'}, a_{\boldsymbol{k},\alpha}] \\ &= -i\omega a_{\boldsymbol{k},\alpha}\end{aligned}$$

like also

$$\dot{a}^\dagger_{\boldsymbol{k},\alpha} = i\omega a^\dagger_{\boldsymbol{k},\alpha}.$$

These equations have solutions

$$\begin{aligned}a_{\boldsymbol{k},\alpha} &= a_{\boldsymbol{k},\alpha}(0)e^{-i\omega t} \\ a^\dagger_{\boldsymbol{k},\alpha} &= a^\dagger_{\boldsymbol{k},\alpha}(0)e^{i\omega t}.\end{aligned}$$

The final form of the field operator is then

$$\begin{aligned}\boldsymbol{A}(\boldsymbol{x},t) &= \frac{1}{\sqrt{V}}\sum_{\boldsymbol{k},\alpha} c\sqrt{\frac{\hbar}{2\omega}}\left[a_{\boldsymbol{k},\alpha}(0)\hat{\boldsymbol{\epsilon}}^{(\alpha)}e^{i\boldsymbol{k}\cdot\boldsymbol{x}-i\omega t}\right. \\ &\quad \left. + a^\dagger_{\boldsymbol{k},\alpha}(0)\hat{\boldsymbol{\epsilon}}^{(\alpha)}e^{-i\boldsymbol{k}\cdot\boldsymbol{x}+i\omega t}\right].\end{aligned}$$

We should note that

- the operator $\boldsymbol{A}$ is Hermitean.
- $\boldsymbol{x}$ and t in the expression for the field operator $\boldsymbol{A}$ are not quantum mechanical variables but simply parameters which the operator $\boldsymbol{A}$ depends on. For example, it is not allowed to interprete the variables $\boldsymbol{x}$ and t as the space-time coordinates of a photon.
- the quantized field $\boldsymbol{A}$ operates at every point $(\boldsymbol{x}, t)$ of the space where it with a certain probability creates and annihilates excitation states called photons. Thus photons can be interpreted as the quantum mechanical excitations of the radiation field.

We consider photon emission and and absorption of non relativistic atomic electrons. The relevant interaction Hamiltonian is of the form

$$\begin{aligned}H_{\rm int} = \sum_i \Bigg[&-\frac{e}{m_e c}\boldsymbol{A}(\boldsymbol{x}_i,t)\cdot\boldsymbol{p}_i \\ &+\frac{e^2}{2m_e^2c^2}\boldsymbol{A}(\boldsymbol{x}_i,t)\cdot\boldsymbol{A}(\boldsymbol{x}_i,t)\Bigg],\end{aligned}$$

where the transversality condition is taken into account by replacing the operator $\boldsymbol{p}_i \cdot \boldsymbol{A}$ with the operator $\boldsymbol{A}\cdot\boldsymbol{p}_i$. The summation goes over all electrons participating in the process. The symbols $\boldsymbol{x}_i$ stand for their position coordinates.
Note If we had to consider the interaction of spin and radiation we should also include the term

$$H^{(\rm spin)}_{\rm int} = -\sum_i \frac{e\hbar}{2m_e c}\boldsymbol{\sigma}_i \cdot [\nabla \times \boldsymbol{A}(\boldsymbol{x},t)]|_{\boldsymbol{x}=\boldsymbol{x}_i}.$$

This time the Hamiltonian operator $H_{\rm int}$ operates not only on the atomic states but also on the photon states. In the quantum theory of radiation

- the vector describing the initial state $|i\rangle$ is the direct product of an atomic state A and a (many) photon state characterized by the occupation numbers $n_{\boldsymbol{k},\alpha}$:

$$|i\rangle = |A\rangle \otimes |n_{\boldsymbol{k},\alpha}\rangle = |A; n_{\boldsymbol{k},\alpha}\rangle.$$

- the vector describing the final state $|f\rangle$ is the direct product of an atomic state B and a (many) photon state characterized by the occupation numbers $n_{\boldsymbol{k}',\alpha'}$:

$$|f\rangle = |A\rangle \otimes |n_{\boldsymbol{k}',\alpha'}\rangle = |A; n_{\boldsymbol{k}',\alpha'}\rangle.$$

Absorption
Now

$$\begin{aligned}|i\rangle &= |A; n_{\boldsymbol{k},\alpha}\rangle \\ |f\rangle &= |B; n_{\boldsymbol{k},\alpha} - 1\rangle.\end{aligned}$$

In the first order perturbation theory the amplitude of the process

$$|i\rangle \longrightarrow |f\rangle$$

is the matrix element of the interaction operator H_I between the states $|i\rangle$ and $|f\rangle$. Up to this order

- only $a_{\boldsymbol{k},\alpha}$ leads to a nonzero matrix element, eventhough the field operator $\boldsymbol{A}$ is a linear superposition of creation and annihilation operators $a^\dagger_{\boldsymbol{k},\alpha}$ and $a_{\boldsymbol{k},\alpha}$, respectively.
- the term $\boldsymbol{A}\cdot\boldsymbol{A}$ is out of the question in this process because it either changes the number of photons by two or does not change it at all.

The first order transition matrix element is now

$$\begin{aligned}
&\langle B; n_{\boldsymbol{k},\alpha}-1|H_{\rm int}|A; n_{\boldsymbol{k},\alpha}\rangle \\
&\quad = -\frac{e}{m_e c}\langle B; n_{\boldsymbol{k},\alpha}-1| \\
&\qquad \sum_i c\sqrt{\frac{\hbar}{2\omega V}}a_{\boldsymbol{k},\alpha}(0)e^{i\boldsymbol{k}\cdot\boldsymbol{x}_i-i\omega t}\boldsymbol{p}_i\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)}|A; n_{\boldsymbol{k},\alpha}\rangle \\
&\quad = -\frac{e}{m_e}\sqrt{\frac{n_{\boldsymbol{k},\alpha}\hbar}{2\omega V}}\sum_i\langle B|e^{i\boldsymbol{k}\cdot\boldsymbol{x}_i}\boldsymbol{p}_i\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)}|A\rangle e^{-i\omega t}.
\end{aligned}$$

Comparing this with the matrix element of the semiclassical perturbation potential

$$\mathcal{V}^\dagger_{ni} = -\frac{eA_0}{m_e c}\left(e^{i(\omega/c)\hat{\boldsymbol{n}}\cdot\boldsymbol{x}}\hat{\boldsymbol{\epsilon}}\cdot\boldsymbol{p}\right)_{ni}$$

we see that they both give exactly the same result provided we use in the semiclassical theory the equivalent radiation field

$$\boldsymbol{A}^{(\rm abs)} = \boldsymbol{A}^{(\rm abs)}_0 e^{i\boldsymbol{k}\cdot\boldsymbol{x}-i\omega t},$$

where the amplitude is

$$\boldsymbol{A}^{(\rm abs)}_0 = c\sqrt{\frac{n_{\boldsymbol{k},\alpha}\hbar}{2\omega V}}\hat{\boldsymbol{\epsilon}}^{(\alpha)}.$$

Because the transition probability is

- according to the semiclassical theory directly proportional to the intensity of the radiation,

$$|\boldsymbol{A}_0|^2 \propto n_{\boldsymbol{k},\alpha},$$

- according to the quantum theory directly proportional to the occupation number $n_{\boldsymbol{k},\alpha}$,

both the semiclassical and quantum mechanical results give equivalent results also at low intensities, i.e. when $n_{\boldsymbol{k},\alpha}$ is small.

Emission
Now

$$\begin{aligned}
|i\rangle &= |A; n_{\boldsymbol{k},\alpha}\rangle \\
|f\rangle &= |B; n_{\boldsymbol{k},\alpha}+1\rangle
\end{aligned}$$

and in the first order the only potential term of the field

$$\begin{aligned}
\boldsymbol{A}(\boldsymbol{x},t) &= \frac{1}{\sqrt{V}}\sum_{\boldsymbol{k},\alpha}c\sqrt{\frac{\hbar}{2\omega}}\Big[a_{\boldsymbol{k},\alpha}(0)\hat{\boldsymbol{\epsilon}}^{(\alpha)}e^{i\boldsymbol{k}\cdot\boldsymbol{x}-i\omega t} \\
&\quad + a^\dagger_{\boldsymbol{k},\alpha}(0)\hat{\boldsymbol{\epsilon}}^{(\alpha)}e^{-i\boldsymbol{k}\cdot\boldsymbol{x}+i\omega t}\Big]
\end{aligned}$$

is $a^\dagger_{\boldsymbol{k},\alpha}$ which adds one photon to the final state. The relevant matrix element is now

$$\begin{aligned}
&\langle B; n_{\boldsymbol{k},\alpha}+1|H_{\rm int}|A; n_{\boldsymbol{k},\alpha}\rangle \\
&\quad = -\frac{e}{m_e}\sqrt{\frac{(n_{\boldsymbol{k},\alpha}+1)\hbar}{2\omega V}}\sum_i\langle B|e^{-i\boldsymbol{k}\cdot\boldsymbol{x}_i}\boldsymbol{p}_i\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)}|A\rangle e^{i\omega t}.
\end{aligned}$$

If $n_{\boldsymbol{k},\alpha}$ is very large then

$$\sqrt{n_{\boldsymbol{k},\alpha}+1} \approx \sqrt{n_{\boldsymbol{k},\alpha}},$$

and the semiclassical and quantum mechanical treatment coincide.
If $n_{\boldsymbol{k},\alpha}$ is small the semiclassical method fails completely. In particular, the semicalssical treatment of the spontaneous emission, $n_{\boldsymbol{k},\alpha}=0$, is impossible. The semiclassical method can be applied if we insert the atom into the fictitious radiation field

$$\boldsymbol{A}^{(\rm emis)} = \boldsymbol{A}^{(\rm emis)}_0 e^{-i\boldsymbol{k}\cdot\boldsymbol{x}+i\omega t},$$

where

$$\boldsymbol{A}^{(\rm emis)}_0 = c\sqrt{\frac{(n_{\boldsymbol{k},\alpha}+1)\hbar}{2\omega V}}\hat{\boldsymbol{\epsilon}}^{(\alpha)}.$$

The field $\boldsymbol{A}^{(\rm emis)}$ is not

- directly proportional to the number of photons $n_{\boldsymbol{k},\alpha}$,
- the complex conjugate of the field $\boldsymbol{A}^{(\rm abs)}$.

Example Spontaneous emission from the state A to the state B.
In the first order the transition rate is

$$\begin{aligned}
&w_{A\to B} \\
&\quad = \frac{2\pi}{\hbar}|\langle B; 1_{\boldsymbol{k},\alpha}|H_{\rm int}|A; 0\rangle|^2\delta(E_B-E_A+\hbar\omega) \\
&\quad = \frac{2\pi}{\hbar}\frac{e^2\hbar}{2m_e^2\omega V}\left|\sum_i\langle B|e^{-i\boldsymbol{k}\cdot\boldsymbol{x}_i}\hat{\boldsymbol{\epsilon}}^{(\alpha)}\cdot\boldsymbol{p}_i|A\rangle\right|^2 \\
&\qquad \times\delta(E_B-E_A+\hbar\omega).
\end{aligned}$$

Like in the photoelectric efect we can deduce that the number of the allowed photon states $\rho(E,d\Omega)$ in the energy interval $(\hbar\omega, \hbar\omega+d(\hbar\omega))$ and in the solid angle $d\Omega$ is

$$\rho(E,d\Omega) = n^2\,dn\,d\Omega = \frac{V}{(2\pi)^3}\frac{\omega^2}{\hbar c^3}\,d(\hbar\omega)\,d\Omega.$$

The transition rate of photons emitting into a certain solid angle is thus

$$w_{d\Omega} = \frac{2\pi}{\hbar}\frac{e^2\hbar}{2m_e^2\omega V}\left|\sum_i\langle B|e^{-i\boldsymbol{k}\cdot\boldsymbol{x}_i}\hat{\boldsymbol{\epsilon}}^{(\alpha)}\cdot\boldsymbol{p}_i|A\rangle\right|^2\frac{V\omega^2\,d\Omega}{(2\pi)^3\hbar c^3},$$

where $\hbar\omega = E_A - E_B$.
We consider only hydrogen like atoms so that only one electron participates in the process and we restrict to the dipole approximation. Then

$$w_{d\Omega} = \frac{e^2\omega}{8\pi^2 m_e^2\hbar c^3}|\langle B|\boldsymbol{p}|A\rangle\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)}|^2 d\Omega.$$

Earlier we saw that

$$\begin{aligned}\langle B|\boldsymbol{p}|A\rangle &= \frac{im_e(E_B-E_A)}{\hbar}\langle B|\boldsymbol{x}|A\rangle \\ &= -im_e\omega\boldsymbol{x}_{BA}.\end{aligned}$$

We let the symbol $\Theta^{(\alpha)}$ stand for the angle between the vector $\boldsymbol{x}_{BA}$ and the polarization direction $\hat{\boldsymbol{\epsilon}}^{(\alpha)}$, i.e.

$$\begin{aligned}\cos\Theta^{(1)} &= \sin\theta\cos\phi \\ \cos\Theta^{(2)} &= \sin\theta\sin\phi,\end{aligned}$$

when θ and ϕ are the direction angles of the vector $\boldsymbol{x}$. Then

$$w_{d\Omega} = \frac{e^2\omega^3}{8\pi^2\hbar c^3}|\boldsymbol{x}_{BA}|^2\cos^2\Theta^{(\alpha)}d\Omega.$$

The total transition rate is obtained by integrating over all propagation directions $\boldsymbol{k}/|\boldsymbol{k}|$ and summing over both polarizations:

$$w = \frac{e^2\omega^3}{3\pi\hbar c^3}|\boldsymbol{x}_{BA}|^2.$$

The life time of a state was obtained from the formula

$$\frac{1}{\tau_A} = \sum_i w_{A\to B_i},$$

where we have to sum also over the magnetic quantum numbers m. For example the life time of the hydrogen $2p$ state is

$$\tau(2p\longrightarrow 1s) = 1.6\times 10^{-9}\text{s}.$$

Electron photon scattering
We consider the process

$$|1_{\boldsymbol{k},\alpha}\rangle \longrightarrow |1_{\boldsymbol{k}',\alpha'}\rangle,$$

i.e.

- before the scattering the atom is in the state A, and $\boldsymbol{k}$ and $\hat{\boldsymbol{\epsilon}}^{(\alpha)}$ are the wave vector and polarization of the incoming photon.
- after the scattering the atom is in the state B, $\boldsymbol{k}'$ is the wave vector and $\hat{\boldsymbol{\epsilon}}^{(\alpha')}$ the polarization vector of the outgoing photon.

The Hamiltonian of the interaction is

$$H_{\text{int}} = -\frac{e}{m_ec}\boldsymbol{A}(\boldsymbol{x},t)\cdot\boldsymbol{p} + \frac{e^2}{2m_e^2c^2}\boldsymbol{A}(\boldsymbol{x},t)\cdot\boldsymbol{A}(\boldsymbol{x},t).$$

Because

- the number of photons does not change in the scattering,
- in order to be non zero the matrix element of the interaction must contain products of photon creation and annihilation operators,
- in the term $\boldsymbol{A}\cdot\boldsymbol{p}$ creation and annihilation operators appear as linear,
- in the term $\boldsymbol{A}\cdot\boldsymbol{A}$ creation and annihilation operators appear as quadratic,

only the quadratic term $\boldsymbol{A}\cdot\boldsymbol{A}$ contributes in the first order perturbation theory.
Only two of the terms of the form

$$aa^\dagger, a^\dagger a, aa, a^\dagger a^\dagger$$

in the operator $\boldsymbol{A}\cdot\boldsymbol{A}$ have non zero matrix elements provided that

- $a^\dagger$ creates a photon of the type $(\boldsymbol{k}', \hat{\boldsymbol{\epsilon}}^{(\alpha')})$,
- a annihilates a photon of the type $(\boldsymbol{k}, \hat{\boldsymbol{\epsilon}}^{(\alpha)})$,

and then

$$\langle 1_{\boldsymbol{k}',\alpha'}|a_{\boldsymbol{k},\alpha}a^\dagger_{\boldsymbol{k}',\alpha'}|1_{\boldsymbol{k},\alpha}\rangle = 1.$$

Now

$$\begin{aligned}&\langle B;1_{\boldsymbol{k}',\alpha'}|H_{\text{int}}|A;1_{\boldsymbol{k},\alpha}\rangle \\ &\quad= \langle B;1_{\boldsymbol{k}',\alpha'}\left|\frac{e^2}{2m_ec^2}\boldsymbol{A}(\boldsymbol{x},t)\cdot\boldsymbol{A}(\boldsymbol{x},t)\right|A;1_{\boldsymbol{k},\alpha}\rangle \\ &\quad= \langle B;1_{\boldsymbol{k}',\alpha'}\left|\frac{e^2}{2m_ec^2}(a_{\boldsymbol{k},\alpha}a^\dagger_{\boldsymbol{k}',\alpha'} + a^\dagger_{\boldsymbol{k}',\alpha'}a_{\boldsymbol{k},\alpha})\right. \\ &\qquad\left.\times\frac{c^2\hbar}{2V\sqrt{\omega\omega'}}\hat{\boldsymbol{\epsilon}}^{(\alpha)}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')}e^{i(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{x}-i(\omega-\omega')t}\right|A;1_{\boldsymbol{k},\alpha}\rangle \\ &\quad= \frac{e^2}{2m_ec^2}\frac{c^2\hbar}{2V\sqrt{\omega\omega'}}2\hat{\boldsymbol{\epsilon}}^{(\alpha)}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')}e^{-i(\omega-\omega')t}\langle B|A\rangle,\end{aligned}$$

where again the exponential functions $e^{\pm\boldsymbol{k}\cdot\boldsymbol{x}}$ are replaced by the constant 1 (the long wave length approximation). In the first order we have thus

$$\begin{aligned}c^{(1)}(t) &= -\frac{i}{\hbar}\int_{t_0}^t e^{i\omega_{fi}t'}V_{fi}(t')\,dt' \\ &= \frac{1}{i\hbar}\frac{e^2}{2m_ec^2}\frac{c^2\hbar}{2V\sqrt{\omega\omega'}}2\delta_{AB}\hat{\boldsymbol{\epsilon}}^{(\alpha)}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')} \\ &\quad\times\int_0^t e^{i(\hbar\omega'+E_B-\hbar\omega-E_A)t'/\hbar}\,dt',\end{aligned}$$

where $\omega = |\boldsymbol{k}|c$ and $\omega' = |\boldsymbol{k}'|c$. Now

- in the transition amplitude $c^{(1)}(t)$ the interaction is in fact of second order: $\boldsymbol{A}\cdot\boldsymbol{A}$.
- in the second order correction $c^{(2)}(t)$ the term $\boldsymbol{A}\cdot\boldsymbol{p}$ is also of second order.

To collect all contributions up to the second order in the interaction we have to consider also the correction $c^{(2)}(t)$, into which we take all double actions of the operator $\boldsymbol{A}\cdot\boldsymbol{p}$. Now

$$\begin{aligned}c^{(2)}(t) &= \left(-\frac{i}{\hbar}\right)^2\sum_m\int_{t_0}^t dt'\int_{t_0}^{t'}dt''\,e^{i\omega_{fm}t'}V_{fm}(t') \\ &\quad\times e^{i\omega_{mi}t''}V_{mi}(t'').\end{aligned}$$

Thus there are two possibilities: the interaction $\boldsymbol{A}\cdot\boldsymbol{p}$ can

- at the moment t_1 annihilate the incoming photon $(\boldsymbol{k}, \hat{\boldsymbol{\epsilon}}^{(\alpha)})$ and at some later time t_2 create the outgoing photon $(\boldsymbol{k}', \hat{\boldsymbol{\epsilon}}^{(\alpha')})$ or
- at the moment t_1 create the outgoing photon $(\boldsymbol{k}', \hat{\boldsymbol{\epsilon}}^{(\alpha')})$ and at some later time t_2 annihilate the incoming photon $(\boldsymbol{k}, \hat{\boldsymbol{\epsilon}}^{(\alpha)})$.

Between the moments t_1 and t_2 the atom is in the state I, which normally is neither of the states A and B.
In the intermediate state I there are thus two possibilities: either there are no photons present or both incoming and outgoing photons are present. We get thus (in the dipole approximation)

$$\begin{aligned} c^{(2)}(t) &= \frac{1}{(i\hbar)^2}\frac{c^2\hbar}{2V\sqrt{\omega\omega'}}\left(-\frac{e}{m_e c}\right)^2\int_0^t dt_2\int_0^{t_2} dt_1 \\ &\quad\times\Bigg[\sum_I \langle B|\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')}|I\rangle e^{i(E_B-E_I+\hbar\omega')t_2/\hbar} \\ &\qquad\times\langle I|\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)}|A\rangle e^{i(E_I-E_A-\hbar\omega)t_1/\hbar} \\ &\quad+\sum_I \langle B|\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)}|I\rangle e^{i(E_B-E_I+\hbar\omega)t_2/\hbar} \\ &\qquad\times\langle I|\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')}|A\rangle e^{i(E_I-E_A-\hbar\omega')t_1/\hbar}\Bigg] \\ &= -\frac{c^2\hbar}{i\hbar 2V\sqrt{\omega\omega'}}\left(\frac{e}{m_e c}\right)^2 \\ &\quad\times\sum_i\left(\frac{(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{BI}(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{IA}}{E_I-E_A-\hbar\omega}\right. \\ &\qquad\left.+\frac{(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{BI}(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{IA}}{E_I-E_A+\hbar\omega'}\right) \\ &\quad\times\int_0^t dt_2\, e^{i(E_B-E_A+\hbar\omega'-\hbar\omega)t_2/\hbar}. \end{aligned}$$

For the transition rate we get combining the terms $c^{(1)}(t)$ and $c^{(2)}(t)$ and taking into account the relation

$$\lim_{t\to\infty}\left|\int_0^t e^{ixt'}\,dt'\right|^2 = 2\pi t\delta(x)$$

the expression

$$\begin{aligned} w_{d\Omega} &= \int(|c^{(1)}+c^{(2)}|^2/t)\rho(E,d\Omega)\,dE \\ &= \frac{2\pi}{\hbar}\left(\frac{c^2\hbar}{2V\sqrt{\omega\omega'}}\right)^2\left(\frac{e^2}{m_e c^2}\right)^2\frac{V}{(2\pi)^3}\frac{\omega'^2}{\hbar c^3}\,d\Omega \\ &\quad\times\left|\delta_{AB}\hat{\boldsymbol{\epsilon}}^{(\alpha)}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')}\right. \\ &\quad-\frac{1}{m_e}\sum_I\left(\frac{(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{BI}(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{IA}}{E_I-E_A-\hbar\omega}\right. \\ &\qquad\left.\left.+\frac{(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{BI}(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{IA}}{E_I-E_A+\hbar\omega'}\right)\right|^2. \end{aligned}$$

Because in the initial state there was exactly one photon in the volume V and the flux density of the incoming photons c/V, so the differential cross section is

$$\begin{aligned} \frac{d\sigma}{d\Omega} &= r_0^2\left(\frac{\omega'}{\omega}\right)\left|\delta_{AB}\hat{\boldsymbol{\epsilon}}^{(\alpha)}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')}\right. \\ &\quad-\frac{1}{m_e}\sum_I\left(\frac{(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{BI}(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{IA}}{E_I-E_A-\hbar\omega}\right. \\ &\qquad\left.\left.+\frac{(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{BI}(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{IA}}{E_I-E_A+\hbar\omega'}\right)\right|^2, \end{aligned}$$

where $r_0 \approx 2.82\times10^{-13}$cm is the classical radius of electron. This expression is known as the *Kramers-Heisenberg formula*.

Example Elastic scattering.
Now $A = B$ ja $\hbar\omega = \hbar\omega'$. Using the commutation relations of the operators $\boldsymbol{x}$ and $\boldsymbol{p}$, the completeness of the intermediate states and the relation

$$\boldsymbol{p}_{AB} = im_e\omega_{AB}\boldsymbol{x}_{AB}$$

we can write

$$\begin{aligned} \hat{\boldsymbol{\epsilon}}^{(\alpha)}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')} &= \frac{1}{i\hbar}\sum_I\Big[(\boldsymbol{x}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{AI}(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{IA} \\ &\qquad-(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{AI}(\boldsymbol{x}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{IA}\Big] \\ &= \frac{1}{m_e\hbar}\sum_I\frac{2}{\omega_{IA}}(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{AI}(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{IA}, \end{aligned}$$

where $\omega_{IA} = (E_I - E_A)/\hbar$.
We see that

$$\begin{aligned} &\delta_{AA}\hat{\boldsymbol{\epsilon}}^{(\alpha)}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')} \\ &\quad-\frac{1}{m_e\hbar}\sum_I\left[\frac{(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{AI}(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{IA}}{\omega_{IA}-\omega}\right. \\ &\qquad\left.+\frac{(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{AI}(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{IA}}{\omega_{IA}+\omega}\right] \\ &\quad=-\frac{1}{m_e\hbar}\sum_I\left[\frac{\omega(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{AI}(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{IA}}{\omega_{IA}(\omega_{IA}-\omega)}\right. \\ &\qquad\left.-\frac{\omega(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{AI}(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{IA}}{\omega_{IA}(\omega_{IA}+\omega)}\right]. \end{aligned}$$

If ω is small then

$$\frac{1}{\omega_{IA}\mp\omega} \approx \frac{1\pm(\omega/\omega_{IA})}{\omega_{IA}}.$$

Then

$$\begin{aligned} &\sum_I\frac{1}{\omega_{IA}^2}\Big[(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{AI}(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{IA} \\ &\qquad-(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{AI}(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{IA}\Big] \\ &= m_e^2\sum_I\Big[(\boldsymbol{x}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{AI}(\boldsymbol{x}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{IA} \\ &\qquad-(\boldsymbol{x}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{AI}(\boldsymbol{x}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{IA}\Big] \\ &= m_e^2([\boldsymbol{x}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')},\boldsymbol{x}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)}])_{AA} \\ &= 0. \end{aligned}$$

The differential cross section is now

$$\begin{aligned}\frac{d\sigma}{d\Omega} &= \left(\frac{r_0}{m_e\hbar}\right)^2\omega^4\left|\sum_I\left(\frac{1}{\omega_{IA}}\right)^3\right.\\ &\quad\times[(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{AI}(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{IA}\\ &\quad\left.+(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{AI}(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{IA}]\right|^2\\ &= \left(\frac{r_0m_e}{\hbar}\right)^2\omega^4\left|\sum_I\frac{1}{\omega_{IA}}\right.\\ &\quad\times[(\boldsymbol{x}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{AI}(\boldsymbol{x}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{IA}\\ &\quad\left.+(\boldsymbol{x}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{AI}(\boldsymbol{x}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{IA}]\right|^2.\end{aligned}$$

At long wave lengths the differential cross section obeys the *Rayleigh law* or

$$\frac{d\sigma}{d\Omega}\propto\frac{1}{\lambda^4}.$$

Now

- for ordinary colourless gases ω_{IA} corresponds to wave lengths in the ultraviolet,
- for the visible light we have then $\omega\ll\omega_{IA}$,

so our approximations are valid in the atmossphere. The theory explains why the sky is blue and the sunset red.

Dirac's equation

We construct relativistically covariant equation that takes into account also the spin.
The kinetic energy operator is

$$H^{(\mathrm{KE})} = \frac{\boldsymbol{p}^2}{2m}.$$

Previously we derived for Pauli spin matrices the relation

$$(\boldsymbol{\sigma}\cdot\boldsymbol{a})^2 = |\boldsymbol{a}|^2,$$

so we can also write

$$H^{(\mathrm{KE})} = \frac{(\boldsymbol{\sigma}\cdot\boldsymbol{p})(\boldsymbol{\sigma}\cdot\boldsymbol{p})}{2m}.$$

However, when the particle moves under the influence of a vector potential these expressions differ. Substituting

$$\boldsymbol{p} \mapsto \boldsymbol{p} - e\boldsymbol{A}/c$$

the latter takes the form

$$\begin{aligned}
&\frac{1}{2m}\boldsymbol{\sigma}\cdot\left(\boldsymbol{p}-\frac{e\boldsymbol{A}}{c}\right)\boldsymbol{\sigma}\cdot\left(\boldsymbol{p}-\frac{e\boldsymbol{A}}{c}\right)\\
&\quad= \frac{1}{2m}\left(\boldsymbol{p}-\frac{e\boldsymbol{A}}{c}\right)^2\\
&\qquad+\frac{i}{2m}\boldsymbol{\sigma}\cdot\left[\left(\boldsymbol{p}-\frac{e\boldsymbol{A}}{c}\right)\times\left(\boldsymbol{p}-\frac{e\boldsymbol{A}}{c}\right)\right]\\
&\quad= \frac{1}{2m}\left(\boldsymbol{p}-\frac{e\boldsymbol{A}}{c}\right)^2 - \frac{e\hbar}{2mc}\boldsymbol{\sigma}\cdot\boldsymbol{B},
\end{aligned}$$

where we have used the identities

$$(\boldsymbol{\sigma}\cdot\boldsymbol{a})(\boldsymbol{\sigma}\cdot\boldsymbol{b}) = \boldsymbol{a}\cdot\boldsymbol{b} + i\boldsymbol{\sigma}\cdot(\boldsymbol{a}\times\boldsymbol{b})$$

and

$$\boldsymbol{p}\times\boldsymbol{A} = -i\hbar(\nabla\times\boldsymbol{A}) - \boldsymbol{A}\times\boldsymbol{p}.$$

Let us suppose that for the relativistically invariant expression

$$(E^2/c^2) - \boldsymbol{p}^2 = (mc)^2$$

the operator analogy

$$\frac{1}{c^2}{E^{(\mathrm{op})}}^2 - \boldsymbol{p}^2 = (mc)^2$$

holds. Here

$$E^{(\mathrm{op})} = i\hbar\frac{\partial}{\partial t} = i\hbar c\frac{\partial}{\partial x_0}$$

and

$$\boldsymbol{p} = -i\hbar\nabla.$$

We write the operator equation into the form

$$\left(\frac{E^{(\mathrm{op})}}{c} - \boldsymbol{\sigma}\cdot\boldsymbol{p}\right)\left(\frac{E^{(\mathrm{op})}}{c} + \boldsymbol{\sigma}\cdot\boldsymbol{p}\right) = (mc)^2$$

or

$$\left(i\hbar\frac{\partial}{\partial x_0} + \boldsymbol{\sigma}\cdot i\hbar\nabla\right)\left(i\hbar\frac{\partial}{\partial x_0} - \boldsymbol{\sigma}\cdot i\hbar\nabla\right)\phi = (mc)^2\phi.$$

Here ϕ is a two component wave function (spinor).
We define new two component wave functions

$$\begin{aligned}
\phi^{(R)} &= \frac{1}{mc}\left(i\hbar\frac{\partial}{\partial x_0} - i\hbar\boldsymbol{\sigma}\cdot\nabla\right)\phi\\
\phi^{(L)} &= \phi.
\end{aligned}$$

It is easy to see that these satisfy the set of simultaneous equations

$$\begin{aligned}
\left[i\hbar\boldsymbol{\sigma}\cdot\nabla - i\hbar\frac{\partial}{\partial x_0}\right]\phi^{(L)} &= -mc\phi^{(R)}\\
\left[-i\hbar\boldsymbol{\sigma}\cdot\nabla - i\hbar\frac{\partial}{\partial x_0}\right]\phi^{(R)} &= -mc\phi^{(L)}.
\end{aligned}$$

We define yet new two component wave functions

$$\begin{aligned}
\psi_A &= \phi^{(R)} + \phi^{(L)}\\
\psi_B &= \phi^{(R)} - \phi^{(L)}.
\end{aligned}$$

These in turn satisfy the matrix equation

$$\begin{pmatrix} -i\hbar\frac{\partial}{\partial x_0} & -i\hbar\boldsymbol{\sigma}\cdot\nabla \\ i\hbar\boldsymbol{\sigma}\cdot\nabla & i\hbar\frac{\partial}{\partial x_0}\end{pmatrix}\begin{pmatrix}\psi_A\\ \psi_B\end{pmatrix} = -mc\begin{pmatrix}\psi_A\\ \psi_B\end{pmatrix}.$$

We now define the four component wave function

$$\psi = \begin{pmatrix}\psi_A\\ \psi_B\end{pmatrix} = \begin{pmatrix}\phi^{(R)} + \phi^{(L)}\\ \phi^{(R)} - \phi^{(L)}\end{pmatrix}$$

and the 4×4-matrices

$$\begin{aligned}
\gamma_k &= \begin{pmatrix} 0 & -i\sigma_k\\ i\sigma_k & 0\end{pmatrix}\\
\gamma_4 &= \begin{pmatrix} 1 & 0\\ 0 & -1\end{pmatrix}.
\end{aligned}$$

We end up with the *Dirac's equation*

$$\left(\boldsymbol{\gamma}\cdot\nabla + \gamma_4\frac{\partial}{\partial(ix_0)}\right)\psi + \frac{mc}{\hbar}\psi = 0$$

for free spin-$\frac{1}{2}$ particles. Employing the four vector notation the equation takes the form

$$\left(\gamma_\mu\frac{\partial}{\partial x_\mu} + \frac{mc}{\hbar}\right)\psi = 0.$$

Note The Dirac equation is in fact a set of *four* coupled linear differential equations. The wave function ψ is the four component vector

$$\psi = \begin{pmatrix}\psi_1\\ \psi_2\\ \psi_3\\ \psi_4\end{pmatrix}.$$

This kind of a four component object is called *bispinor* or Dirac's spinor. Explicitely written down the Dirac equation is

$$\sum_{\mu=1}^{4}\sum_{\beta=1}^{4}\left[(\gamma_\mu)_{\alpha\beta}\frac{\partial}{\partial x_\mu} + \left(\frac{mc}{\hbar}\right)\delta_{\alpha\beta}\right]\psi_\beta = 0.$$

Note The fact that the Dirac spinor happens to have four components has nothing to do with our four dimensional space-time; ψ_β does not transform like a four vector under Lorentz transformations.
It is easy to verify that the *gamma-matrices* (*Dirac matrices*) γ_μ satisfy the anticommutation rule

$$\{\gamma_\mu, \gamma_\nu\} = \gamma_\mu\gamma_\nu + \gamma_\nu\gamma_\mu = 2\delta_{\mu\nu}.$$

Furthermore, every γ_μ is Hermitian,

$$\gamma_\mu^\dagger = \gamma_\mu,$$

and traceless, i.e.

$$\mathrm{Tr}\,\gamma_\mu = 0.$$

Let's multiply the equation

$$\left(\boldsymbol{\gamma}\cdot\nabla + \gamma_4\frac{\partial}{\partial(ix_0)}\right)\psi + \frac{mc}{\hbar}\psi = 0$$

on both sides by the matrix γ_4 and we get

$$\left(c\hbar\gamma_4\boldsymbol{\gamma}\cdot\nabla - i\hbar\frac{\partial}{\partial t}\right)\psi + \gamma_4 mc^2\psi = 0.$$

Denote

$$\begin{aligned}\beta &= \gamma_4 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \\ \alpha_k &= i\gamma_4\gamma_k = \begin{pmatrix} 0 & \sigma_k \\ \sigma_k & 0 \end{pmatrix},\end{aligned}$$

which satisfy the relations

$$\begin{aligned}\{\alpha_k, \beta\} &= 0 \\ \beta^2 &= 1 \\ \{\alpha_k, \alpha_l\} &= 2\delta_{kl}.\end{aligned}$$

When we now write

$$H = -ic\hbar\boldsymbol{\alpha}\cdot\nabla + \beta mc^2,$$

the Dirac equation takes the familiar form

$$H\psi = i\hbar\frac{\partial\psi}{\partial t}.$$

We define the *adjungated* spinor $\bar\psi$ like:

$$\bar\psi = \psi^\dagger\gamma_4.$$

Explicitely, if ψ is a column vector

$$\psi = \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix},$$

then $\psi^\dagger$ and $\bar\psi$ are row vectors

$$\begin{aligned}\psi^\dagger &= (\psi_1^*, \psi_2^*, \psi_3^*, \psi_4^*) \\ \bar\psi &= (\psi_1^*, \psi_2^*, -\psi_3^*, -\psi_4^*).\end{aligned}$$

Forming the Hermitean conjugate of the Dirac equation

$$\left(\gamma_\mu\frac{\partial}{\partial x_\mu} + \frac{mc}{\hbar}\right)\psi = 0$$

we get

$$\frac{\partial}{\partial x_k}\psi^\dagger\gamma_k + \frac{\partial}{\partial x_4^*}\psi^\dagger\gamma_4 + \frac{mc}{\hbar}\psi^\dagger = 0.$$

We multiply this from right by the matrix γ_4 and end up with the *adjungated equation*

$$-\frac{\partial}{\partial x_\mu}\bar\psi\gamma_\mu + \frac{mc}{\hbar}\bar\psi = 0.$$

Here we have used the relations

$$\begin{aligned}\frac{\partial}{\partial x_4^*} &= \frac{\partial}{\partial(ict)^*} = -\frac{\partial}{\partial x_4} \\ \gamma_k\gamma_4 &= -\gamma_4\gamma_k.\end{aligned}$$

Let's multiply the original Dirac equation

$$\left(\gamma_\mu\frac{\partial}{\partial x_\mu} + \frac{mc}{\hbar}\right)\psi = 0$$

from left with the adjungated spinor $\bar\psi$ and the adjungated equation

$$-\frac{\partial}{\partial x_\mu}\bar\psi\gamma_\mu + \frac{mc}{\hbar}\bar\psi = 0$$

from right with the spinor ψ and subtract the resulting equations. We then get

$$\frac{\partial}{\partial x_\mu}(\bar\psi\gamma_\mu\psi) = 0.$$

The quantity

$$s_\mu = ic\bar\psi\gamma_\mu\psi = (c\psi^\dagger\boldsymbol{\alpha}\psi, ic\psi^\dagger\psi)$$

thus satisfies a continuity equation. According to Green's theorem we have

$$\int\bar\psi\gamma_4\psi\,d^3x = \int\psi^\dagger\psi\,d^3x = \text{constant},$$

where the constant can be taken to be 1 with a suitable normalization of ψ. Because $\bar\psi\gamma_4\psi = \psi^\dagger\psi$ is positively definite it can be interpreted as a probability density. Then

$$s_k = ic\bar\psi\gamma_k\psi = c\psi^\dagger\alpha_k\psi$$

can be identified as the density of the probability current.
Note It can be shown that s_μ transforms like a four vector, so the continuity equation is relativistically covariant.
It can be proved that any sets of four matrices γ_μ and γ'_μ satisfying the anticommutation relations

$$\begin{aligned}\{\gamma_\mu, \gamma_\nu\} &= 2\delta_{\mu\nu} \\ \{\gamma'_\mu, \gamma'_\nu\} &= 2\delta_{\mu\nu},\end{aligned}$$

are related to eachother through a similarity transformation with a non-singular 4×4-matrix S:

$$S\gamma_\mu S^{-1} = \gamma'_\mu.$$

With the help of the matrices γ'_μ the original Dirac equation can be written as

$$\left(S^{-1}\gamma'_\mu S\frac{\partial}{\partial x_\mu} + \frac{mc}{\hbar}\right) S^{-1}S\psi = 0.$$

Multiplying this from left with the matrix S we get

$$\left(\gamma'_\mu\frac{\partial}{\partial x_\mu} + \frac{mc}{\hbar}\right)\psi' = 0,$$

where

$$\psi' = S\psi.$$

Thus Dirac's equation is independent on the explicit form of the matrices γ_μ; only the anticommutation of the matrices is relevant. If the matrices γ'_μ are Hermitean the transformation matrix S can be taken to be unitary. It is easy to show that then the probability density and current, for example, are independent on the representation:

$$\bar\psi'\gamma'_\mu\psi' = \bar\psi\gamma_\mu\psi.$$

Vector potential

When the system is subjected to a vector potential

$$A_\mu = (\boldsymbol{A}, iA_0),$$

we make the ordinary substitutions

$$-i\hbar(\partial/\partial x_\mu) \mapsto -i\hbar(\partial/\partial x_\mu) - eA_\mu/c.$$

The Dirac equation takes now the form

$$\left(\frac{\partial}{\partial x_\mu} - \frac{ie}{\hbar c}A_\mu\right)\gamma_\mu\psi + \frac{mc}{\hbar}\psi = 0.$$

Assuming that A_μ does not depend on time the time dependence of the spinor ψ can be written as

$$\psi = \psi(\boldsymbol{x}, t)|_{t=0}\, e^{-iEt/\hbar}.$$

Let us write now the Dirac equation for the components ψ_A and ψ_B:

$$\begin{aligned}\left[\boldsymbol{\sigma}\cdot\left(\boldsymbol{p} - \frac{e\boldsymbol{A}}{c}\right)\right]\psi_B &= \frac{1}{c}(E - eA_0 - mc^2)\psi_A \\ -\left[\boldsymbol{\sigma}\cdot\left(\boldsymbol{p} - \frac{e\boldsymbol{A}}{c}\right)\right]\psi_A &= -\frac{1}{c}(E - eA_0 + mc^2)\psi_B.\end{aligned}$$

With the help of the latter equation we eliminate ψ_B from the upper equation and get

$$\left[\boldsymbol{\sigma}\cdot\left(\boldsymbol{p} - \frac{e\boldsymbol{A}}{c}\right)\right]\left[\frac{c^2}{E - eA_0 + mc^2}\right]\left[\boldsymbol{\sigma}\cdot\left(\boldsymbol{p} - \frac{e\boldsymbol{A}}{c}\right)\right]\psi_A = (E - eA_0 - mc^2)\psi_A.$$

Suppose now that

$$E \approx mc^2, \quad |eA_0| \ll mc^2$$

and measure the energy starting from the rest energy:

$$E^{(\mathrm{NR})} = E - mc^2.$$

We expand

$$\begin{aligned}\frac{c^2}{E - eA_0 + mc^2} &= \frac{1}{2m}\left[\frac{2mc^2}{2mc^2 + E^{(\mathrm{NR})} - eA_0}\right] \\ &= \frac{1}{2m}\left[1 - \frac{E^{(\mathrm{NR})} - eA_0}{2mc^2} + \cdots\right].\end{aligned}$$

This can be taken to be the power series in $(v/c)^2$ since

$$E^{(\mathrm{NR})} - eA_0 \approx [\boldsymbol{p} - (e\boldsymbol{A}/c)]^2/2m \approx mv^2/2.$$

Taking into account only the leading term we get

$$\frac{1}{2m}\boldsymbol{\sigma}\cdot\left(\boldsymbol{p} - \frac{e\boldsymbol{A}}{c}\right)\boldsymbol{\sigma}\cdot\left(\boldsymbol{p} - \frac{e\boldsymbol{A}}{c}\right)\psi_A = (E^{(\mathrm{NR})} - eA_0)\psi_A.$$

This can be written as

$$\left[\frac{1}{2m}\left(\boldsymbol{p} - \frac{e\boldsymbol{A}}{c}\right)^2 - \frac{e\hbar}{2mc}\boldsymbol{\sigma}\cdot\boldsymbol{B} + eA_0\right]\psi_A = E^{(\mathrm{NR})}\psi_A.$$

Up to the zeroth order of $(v/c)^2$ the component ψ_A is thus the two component Schrödinger-Pauli wave function (multiplied with the factor e^{-imc^2t}) familiar from the non-relativistic quantum mechanics. The equation

$$-\left[\boldsymbol{\sigma}\cdot\left(\boldsymbol{p} - \frac{e\boldsymbol{A}}{c}\right)\right]\psi_A = -\frac{1}{c}(E - eA_0 + mc^2)\psi_B$$

tells us that the component ψ_B is roughly by the factor

$$|\boldsymbol{p} - (e\boldsymbol{A}/c)|/2mc \approx v/2c$$

"less" than ψ_A. Due to this, provided that $E \approx mc^2$, ψ_A is known as the *big* and ψ_B as the *small* component of the Dirac wave function ψ.

We obtain relativistic corrections only when we consider the second or higher order terms of the expansion

$$\begin{aligned}\frac{c^2}{E - eA_0 + mc^2} &= \frac{1}{2m}\left[\frac{2mc^2}{2mc^2 + E^{(\mathrm{NR})} - eA_0}\right] \\ &= \frac{1}{2m}\left[1 - \frac{E^{(\mathrm{NR})} - eA_0}{2mc^2} + \cdots\right].\end{aligned}$$

Let us suppose now that

$$\boldsymbol{A} = 0.$$

The wave equation is then

$$H_A\psi_A = E^{(\mathrm{NR})}\psi_A,$$

where

$$H_A = (\boldsymbol{\sigma}\cdot\boldsymbol{p})\frac{1}{2m}\left(1 - \frac{E^{(\mathrm{NR})} - eA_0}{2mc^2}\right)(\boldsymbol{\sigma}\cdot\boldsymbol{p}) + eA_0.$$

This wave equation looks like a time independent Schrödinger equation for the wave function ψ_A. However,

- evaluating corrections up to the order $(v/c)^2$ the wave function ψ_A is not normalized because the probability interpretation of Dirac's theory requires that
$$\int (\psi_A^\dagger \psi_A + \psi_B^\dagger \psi_B)\, d^3x = 1,$$
where ψ_B already of the order v/c.
- explicitely writing down the expression for the operator H_A we see that it contains the non-Hermitian term $i\hbar \boldsymbol{E}\cdot\boldsymbol{p}$.
- the equation is not an eigenvalue equation since H_A itself contains the term $E^{(\mathrm{NR})}$.

Up to the order $(v/c)^2$ the normalization condition can now be written as
$$\int \psi_A^\dagger \left(1 + \frac{\boldsymbol{p}^2}{4m^2c^2}\right)\psi_A\, d^3x \approx 1,$$
because according to the equation
$$-\left[\boldsymbol{\sigma}\cdot\left(\boldsymbol{p} - \frac{e\boldsymbol{A}}{c}\right)\right]\psi_A = -\frac{1}{c}(E - eA_0 + mc^2)\psi_B$$
we have
$$\psi_B \approx \frac{\boldsymbol{\sigma}\cdot\boldsymbol{p}}{2mc}\psi_A.$$
It is worthwhile to define the new two component wave function Ψ:
$$\Psi = \Omega\psi_A,$$
where
$$\Omega = 1 + \frac{\boldsymbol{p}^2}{8m^2c^2}.$$
Now Ψ is up to the order $(v/c)^2$ normalized correctly because
$$\int \Psi^\dagger\Psi\, d^3x \approx \int \psi_A^\dagger \left(1 + \frac{\boldsymbol{p}^2}{4m^2c^2}\right)\psi_A\, d^3x.$$
We multiply the equation
$$H_A\psi_A = E^{(\mathrm{NR})}\psi_A,$$
on both sides with the operator
$$\Omega^{-1} = 1 - (\boldsymbol{p}^2/8m^2c^2),$$
and get
$$\Omega^{-1}H_A\Omega^{-1}\Psi = E^{(\mathrm{NR})}\Omega^{-2}\Psi.$$
Explicitely, up to the order $(v/c)^2$ this can be written as
$$\left[\frac{\boldsymbol{p}^2}{2m} + eA_0 - \left\{\frac{\boldsymbol{p}^2}{8m^2c^2}, \left(\frac{\boldsymbol{p}^2}{2m} + eA_0\right)\right\} - \frac{(\boldsymbol{\sigma}\cdot\boldsymbol{p})}{2m}\left(\frac{E^{(\mathrm{NR})} - eA_0}{2mc^2}\right)(\boldsymbol{\sigma}\cdot\boldsymbol{p})\right]\Psi = E^{(\mathrm{NR})}\left(1 - \frac{\boldsymbol{p}^2}{4m^2c^2}\right)\Psi.$$
Writing $E^{(\mathrm{NR})}\boldsymbol{p}^2$ in the form $\frac{1}{2}\{E^{(\mathrm{NR})}, \boldsymbol{p}^2\}$ we get
$$\left[\frac{\boldsymbol{p}^2}{2m} + eA_0 - \frac{\boldsymbol{p}^4}{8m^3c^2} + \frac{1}{8m^2c^2}\Big(\{\boldsymbol{p}^2, (E^{(\mathrm{NR})} - eA_0)\} - 2(\boldsymbol{\sigma}\cdot\boldsymbol{p})(E^{(\mathrm{NR})} - eA_0)(\boldsymbol{\sigma}\cdot\boldsymbol{p})\Big)\right]\Psi = E^{(\mathrm{NR})}\Psi.$$
Because for arbitrary operators A and B
$$\{A^2, B\} - 2ABA = [A, [A, B]]$$
holds we can, by setting
$$\begin{aligned}\boldsymbol{\sigma}\cdot\boldsymbol{p} &= A\\ E^{(\mathrm{NR})} - eA_0 &= B,\end{aligned}$$
reduce the equation into the form
$$\left[\frac{\boldsymbol{p}^2}{2m} + eA_0 - \frac{\boldsymbol{p}^4}{8m^3c^2} - \frac{e\hbar\boldsymbol{\sigma}\cdot(\boldsymbol{E}\times\boldsymbol{p})}{4m^2c^2} - \frac{e\hbar^2}{8m^2c^2}\nabla\cdot\boldsymbol{E}\right]\Psi = E^{(\mathrm{NR})}\Psi.$$
In the derivation of the equation we have employed the relations
$$\begin{aligned}[\boldsymbol{\sigma}\cdot\boldsymbol{p}, (E^{(\mathrm{NR})} - eA_0)] &= -ie\hbar\boldsymbol{\sigma}\cdot\boldsymbol{E}\\ [\boldsymbol{\sigma}\cdot\boldsymbol{p}, -ie\hbar\boldsymbol{\sigma}\cdot\boldsymbol{E}] &= -e\hbar^2\nabla\cdot\boldsymbol{E}\\ &\quad -2e\hbar\boldsymbol{\sigma}\cdot(\boldsymbol{E}\times\boldsymbol{p}),\end{aligned}$$
the validity of which can be verified by noting that
$$\begin{aligned}\nabla A_0 &= -\boldsymbol{E}\\ \nabla\times\boldsymbol{E} &= 0.\end{aligned}$$
The resulting equation is a proper Schrödinger equation for a two component wave function.
Physical interpretation
We look at the meaning of the terms in the equation
$$\left[\frac{\boldsymbol{p}^2}{2m} + eA_0 - \frac{\boldsymbol{p}^4}{8m^3c^2} - \frac{e\hbar\boldsymbol{\sigma}\cdot(\boldsymbol{E}\times\boldsymbol{p})}{4m^2c^2} - \frac{e\hbar^2}{8m^2c^2}\nabla\cdot\boldsymbol{E}\right]\Psi = E^{(\mathrm{NR})}\Psi.$$
1. The term $\frac{\boldsymbol{p}^2}{2m} + eA_0$ gives the non-realtivistic Schrödinger equation.
2. The term $-\frac{\boldsymbol{p}^4}{8m^3c^2}$ is a relativistic correction to the kinetic energy as can be seen from the expansion
$$\sqrt{(mc^2)^2 + |\boldsymbol{p}|^2c^2} - mc^2 = \frac{|\boldsymbol{p}|^2}{2m} - \frac{|\boldsymbol{p}|^4}{8m^3c^2} + \cdots.$$

3. The term $-\dfrac{e\hbar\boldsymbol{\sigma}\cdot(\boldsymbol{E}\times\boldsymbol{p})}{4m^2c^2}$ describes the interaction between the spin of a moving electron and electric field. Intuitively this, so called *Thomas term*, is due to the fact that the moving electron experiences an apparent magnetic field $\boldsymbol{E}\times(\boldsymbol{v}/c)$. If the electric field is a central field,

$$eA_0 = V(r),$$

it can be written in the form

$$\begin{aligned} -\frac{e\hbar}{4m^2c^2}\boldsymbol{\sigma}\cdot(\boldsymbol{E}\times\boldsymbol{p}) &= -\frac{\hbar}{4m^2c^2}\left(-\frac{1}{r}\frac{dV}{dr}\right)\boldsymbol{\sigma}\cdot(\boldsymbol{x}\times\boldsymbol{p}) \\ &= \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\boldsymbol{S}\cdot\boldsymbol{L}, \end{aligned}$$

where we have substituted

$$\boldsymbol{S} = \hbar\boldsymbol{\sigma}/2.$$

So we actually have a spin orbit interaction.

4. The term $-\dfrac{e\hbar^2}{8m^2c^2}\nabla\cdot\boldsymbol{E}$ is known as the *Darwin term*. Its meaning can be deduced when we note that $\nabla\cdot\boldsymbol{E}$ is the charge density. For example, in the hydrogen atom where $\nabla\cdot\boldsymbol{E} = -e\delta(\boldsymbol{x})$ it causes the energy shift

$$\int \frac{e^2\hbar^2}{8m^2c^2}\delta(\boldsymbol{x})|\psi^{(\text{Schrö})}|^2\,d^3x = \left.\frac{e^2\hbar^2}{8m^2c^2}|\psi^{(\text{Schrö})}|^2\right|_{\boldsymbol{x}=0},$$

which differs from zero only in the s-state.