Lecture 4. Application of Group Theory to Quantum Mechanics. Part I

1 Elements of quantum mechanics

In quantum mechanics the behaviour of a system with n degrees of freedom described by $\vec{r} = \{\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_n,\}$ is fully determined by its wave function $\psi(\vec{r}, t)$. The quantity $|\psi(\vec{r}, t)|^2 dV$ is interpreted as a probability that at the time t the coordinates of the system have the values inside the element of the volume dV near the point $\vec{r}$. Thus the wave function should be normalized as

$$\int |\psi(\vec{r}, t)|^2 dV = 1\,, \tag{1}$$

when the integral is taken over all coordinates.

The wave functions are solutions of the Schrödinger equation

$$\hat{H}(\vec{r}, t)\psi(\vec{r}, t) = \mathrm{i}\hbar \frac{\partial}{\partial t}\psi(\vec{r}, t)\,, \tag{2}$$

where $\hat{H}(\vec{r}, t)$ is the Hamiltonian corresponding to the classical Hamilton function $H = T + V$, where T is a kinetic energy and V is a potential energy. To get the quantum mechanical operator $\hat{H}(\vec{r}, t)$, we substitute the classical coordinates and conjugate momenta by operators (e.g., $x \to \hat{x}$, $p_x \to -\mathrm{i}\hbar\frac{\partial}{\partial x}$). The boundary conditions for the equation (2) guarantee that the wave function $\psi(\vec{r}, t)$ is uniquely determined at any time t.

If the Hamiltonian does not depend on time, then the solutions of the equation (2) have the form

$$\psi_E(\vec{r}, t) = \psi_E(\vec{r}) \exp\left(-\mathrm{i}Et/\hbar\right), \tag{3}$$

where $\psi_E(\vec{r})$ is a solution of the time-independent secular equation

$$\hat{H}(\vec{r})\psi_E(\vec{r}) = E\psi_E(\vec{r})\,, \tag{4}$$

and E is a corresponding eigenvalue. The set of functions $\psi_E(\vec{r})$ is a complete set, i.e. any solution of the equation (2) can be expressed as

$$\psi(\vec{r}, t) = \sum_E a_E \psi_E(\vec{r}) \exp\left(-\mathrm{i}Et/\hbar\right), \tag{5}$$

where a_E are parameters. Solution of the type (3) are called the *stationary* solutions, because the probability density $|\psi(\vec{r}, t)|^2 dV$ does not depend on time. The eigenvalues E are interpreted as the energy of the system.

The set of the continuous functions satisfying the boundary conditions for the equation (2) form a functional space called a *Hilbert space*. The scalar product is convenient to define as

$$(\psi', \psi) = \int \psi'^* \psi dV \tag{6}$$

where integration goes over all possible values of the coordinates. If we require that the energy E be real, then the Hamiltonian should be a Hermitian operator. In this case, the eigenfunctions $\psi_E(\vec{r})$ are orthogonal (and normalized due to (1)).

Similarly, we can put into correspondence to any classical variable T a Hermitian operator $\hat{T}$ defined in a Hilbert space of wave functions. Each such operator has its own set of eigenvalues and eigenfunctions

$$\hat{T}\phi_\lambda(\vec{r}) = \lambda\phi_\lambda(\vec{r})\,, \tag{7}$$

and the eigenfunctions $\phi_\lambda(\vec{r})$ being the complete orthogonal set of functions. The eigenvalues λ can be related to the measurements of the physical observable T. The given value λ will be obtained only if the wave function of the system at this moment of time coincides with the eigenfunction $\phi_\lambda(\vec{r})$ of the operator $\hat{T}$. In general the wave function does not coincide with one of the eigenfunctions of the operator $\hat{T}$, but due to the completeness of the set of functions $\phi_\lambda(\vec{r})$ we can always write

$$\psi(\vec{r},t) = \sum_\lambda c_\lambda(t)\phi_\lambda(\vec{r})\,. \tag{8}$$

The result of the measurement of the observable T in this state is not uniquely determined, but $|c_\lambda(t)|^2$ is a probability that the observable has a value λ. The mean value of the operator $\hat{T}$ in a state $\psi(\vec{r},t)$ is

$$(\psi,\hat{T}\psi) \equiv \langle\psi|\hat{T}|\psi\rangle = \sum_\lambda |c_\lambda(t)|^2\lambda\,. \tag{9}$$

If the spectrum of the operator λ is discrete we have a quantization: the measured values of the observable T are discrete. If the spectrum of the operator $\hat{T}$ is continuous then expression (8) has the form

$$\psi(\vec{r},t) = \int c(\lambda,t)\phi_\lambda(\vec{r})d\lambda\,. \tag{10}$$

If we want to study a quantum system experimentally, we can measure its energy and the mean values of the operators and then compare them with the results calculated using a model Hamiltonian. Another important measurement is a rate of the transition, or a probability that the system being in the initial state ψ_i transforms to a final state ψ_f. This probability is given by

$$W_{if} \sim |\langle\psi_i|\hat{T}|\psi_f\rangle|^2, \tag{11}$$

where $\hat{T}$ is the operator characterizing a given process.

2 Symmetry of quantum system

2.1 Classification of energy levels

Let us consider a system characterized by a time-independent Hamiltonian $\hat{H}(\vec{r})$ with a wave function $\psi(\vec{r})$. Any arbitrary transformation of the coordinates (e.g., rotation or reflection),

$$\vec{r} \xrightarrow{G} \vec{r}\,' = G\vec{r}, \tag{12}$$

will induce the corresponding transformation in the space of wave functions, which we denote by the operator $\hat{D}(G)$:

$$\psi(\vec{r}) \overset{G}{\to} \psi'(\vec{r}) = \hat{D}(G)\psi(\vec{r}) = \psi(G^{-1}\vec{r})\,. \tag{13}$$

Let us suppose that $\hat{T}$ is an operator in the space of functions. Under transformation of the coordinates G, this operator will also be transformed as

$$\hat{T} \overset{G}{\to} \hat{T}' = \hat{D}(G)\hat{T}\hat{D}^{-1}(G)\ . \tag{14}$$

Consider the group **G** of all such the transformations G. According to (14), this group also determines the transformation of the Hamiltonian of the system:

$$\hat{H}(\vec{r}) \overset{G}{\to} \hat{H}'(\vec{r}) = \hat{D}(G)\hat{H}(\vec{r})\hat{D}^{-1}(G)\,. \tag{15}$$

If the Hamiltonian is invariant under these transformations, i.e.

$$\hat{D}(G)\hat{H}(\vec{r})\hat{D}^{-1}(G) = \hat{H}(\vec{r})\,, \tag{16}$$

for all elements G, then the group **G** is a *symmetry group* of the Hamiltonian.

An equivalent form of the condition (16) is

$$\hat{D}(G)\hat{H}(\vec{r}) = \hat{H}(\vec{r})\hat{D}(G)\,, \quad \text{or} \quad [\hat{D}(G), \hat{H}(\vec{r})] = 0 \tag{17}$$

i.e. the Hamiltonian commutes with the induced transformations of the group.

Remark

The kinetic energy operator is invariant under many transformations, such as rotations, reflections and translations, so usually the condition of the invariance of the Hamiltonian reduces to the condition on the potential energy operator.

What are the consequences of the symmetry?

Suppose that **G** is a symmetry group of the Hamiltonian of a quantum mechanical system. Let the operators $\hat{D}(G)$ describe the transformations of the wave functions of the system and of the operators of physical observables. The symmetry requires that the Hamiltonian commute with the operators $\hat{D}(G)$, see (17).

Let $\psi(\vec{r})$ be an eigenfunction of the Hamiltonian $\hat{H}$ corresponding to the eigenvalue E:

$$\hat{H}\psi(\vec{r}) = E\psi(\vec{r})\,. \tag{18}$$

Let us multiply the equation (18) by the operators $\hat{D}(G)$ from the left:

$$\hat{D}(G)\hat{H}\psi(\vec{r}) = \hat{H}\hat{D}(G)\psi(\vec{r}) = E\hat{D}(G)\psi(\vec{r})\,, \tag{19}$$

that means that the transformed function $\hat{D}(G)\psi(\vec{r})$ is also the eigenfunction of the Hamiltonian $\hat{H}$ and corresponds to the same eigenvalue E.

Suppose now that the eigenvalue E is l-fold degenerate and the corresponding eigenfunctions are $\psi_i(\vec{r})$ $(i = 1, \ldots, l)$. Obviously, each of the transformed functions $\hat{D}(G)\psi_i(\vec{r})$ is also an eigenfunction, belonging to the same eigenvalue E, and it can be nothing else but the superposition of these functions

$$\hat{D}(G)\psi_i(\vec{r}) = \sum_j D_{ji}(G)\psi_j(\vec{r}) \tag{20}$$

for any element G of the group $\mathbf{G}$. This means that the operators $\hat{D}(G)$ form a *representation* of the group $\mathbf{G}$ and the functions $\psi_i(\vec{r})$ is the *basis* of this representation.

If the Hamiltonian of a system is invariant with respect to a group $\mathbf{G}$ *then each of its eigenvalues* E *can be associated with a certain representation of the group* $\mathbf{G}$*, while the corresponding eigenfunctions* $\psi_i(\vec{r})$ $(i = 1, \ldots, l)$ *form a basis of this representation. The degeneracy of the level* E *is equal to the dimension* l *of this representation.*

Normally, if $\mathbf{G}$ is a full symmetry group of the Hamiltonian, the representations corresponding to its eigenvalues are *irreducible representations.* This is called a *normal* degeneracy of the level.

However, it can happen that for some Hamiltonian parameters two or more irreducible representations correspond to one energy level. This is called an *accidental degeneracy.* For example, sometimes if we put a system in the electric or magnetic field and change the field strength the levels normally corresponding to two different irreducible representations can intersect.

If for a certain Hamiltonian with a symmetry group $\mathbf{G}$ such accidental degeneracy happens systematically, then it can be usually explained by a presence of a larger symmetry group G_0: $G \supset G_0$.

Example 1

Let us consider the rotational Hamiltonian of a rigid triaxial rotor:

$$\hat{H}_{rot} = \sum_{k=1}^{3} \frac{\hbar^2}{2\mathcal{I}_k} \hat{J}_k^2 \, , \tag{21}$$

where $\mathcal{I}_k$ are the principle moments of inertia and $\hat{J}_k$ are operators of the projections of the angular momentum on the intrinsic axes (such a form has the most general rotational Hamiltonian of an even-A nucleus). The Hamiltonian is invariant under rotations around each of the three principle axes of the rotor through the angle π:

$$R_k(\pi) = \exp\left(-\mathrm{i}\pi \hat{J}_k\right) . \tag{22}$$

Three elements $R_1(\pi)$, $R_2(\pi)$ and $R_3(\pi)$, together with the identity element E form a point symmetry group $\mathbf{D}_2$ and this is a symmetry group of the Hamiltonian (21). $\mathbf{D}_2$ has four 1-dimensional irreducible representations, therefore the energy levels of the triaxial rotor will be non-degenerate and of four different types.

Example 2

Let us consider a system whose Hamiltonian is invariant with respect to the group $\mathbf{C}_{3v}$. Group $\mathbf{C}_{3v}$ has three irreducible representations: two 1-dimensional (A_1, A_2) and one 2-dimensional (E). This means that the spectrum of eigenvalues of the Hamiltonian consists of the non-degenerate and 2-fold degenerate levels belonging to the representations A_1, A_2 or E.

Example 3

If the potential energy of a system is invariant with respect to rotation in a plane

$$V(\vec{r}) \equiv V(r,\theta,\phi) = V(r,\theta)\,, \tag{23}$$

then the symmetry group of the Hamiltonian is the rotational group in 2-dimensions $\mathbf{SO(2)}$.

The group $\mathbf{SO(2)}$ is a one-parameter group. The rotation in the plane (x, y) through an angle a ($0 \leq a < 2\pi$ is sufficient)

$$\phi \overset{a}{\to} \phi' = \phi + a \tag{24}$$

(here ϕ is a polar angle) induces a transformation of any function of ϕ as (see (13))

$$\psi(\phi) \overset{a}{\to} \psi'(\phi) = \psi(\phi - a)\,. \tag{25}$$

If we decompose this into Taylor series, we get

$$\psi(\phi - a) = \psi(\phi) - a\frac{\partial}{\partial\phi}\psi(\phi) + \frac{1}{2!}a^2\frac{\partial^2}{\partial\phi^2}\psi(\phi) + \ldots = \exp\left(-a\frac{\partial}{\partial\phi}\right)\psi(\phi)\,. \tag{26}$$

Thus the rotation operator is

$$\hat{D}(a) = \exp\left(-a\frac{\partial}{\partial\phi}\right)\,. \tag{27}$$

Since $-\mathrm{i}\frac{\partial}{\partial\phi} = \hat{J}_z$, it can be re-written as

$$\hat{D}(a) = \exp\left(-\mathrm{i}a\hat{J}_z\right)\,. \tag{28}$$

Any function of the type

$$\psi^{(m)}(\phi) = A_m \exp\left(\mathrm{i}m\phi\right) \tag{29}$$

where m is a number, can serve as a basis of the 1-dimensional irreducible representations which will be of the form

$$D^{(m)}(a) = \exp\left(-\mathrm{i}ma\right)\,. \tag{30}$$

The group $\mathbf{SO(2)}$ has an infinite number of the 1-dimensional irreducible representations (30). If m is real and integer, then these representations are unitary and continuous for $0 \leq a < 2\pi$. Thus, the Hamiltonian with $\mathbf{SO(2)}$ symmetry has non-degenerate eigenvalues which can be labelled by an integer m.

Example 4

If the potential energy of a system is invariant with respect to rotations in 3-dimensional space, i.e.

$$V(\vec{r}) = V(r)\,, \tag{31}$$

then the symmetry group of the Hamiltonian is the rotational group in 3-dimensions **SO(3)**.

The group **SO(3)** is a three-parameter group (three parameters are necessary in order to characterize a rotation, e.g. three Euler angles). Each rotation in a 3-dimensional space through an arbitrary angle around an arbitrary oriented axis can be represented by an operator

$$\hat{D}(\alpha,\beta,\gamma) = \exp\left(-\mathrm{i}\alpha\hat{J}_z\right)\exp\left(-\mathrm{i}\beta\hat{J}_y\right)\exp\left(-\mathrm{i}\gamma\hat{J}_z\right)\,, \tag{32}$$

where $0 \leq \alpha \leq 2\pi$, $0 \leq \beta < \pi$, $0 \leq \gamma < 2\pi$. A very well-known matrix representation of such operators can be obtained in the basis spanned by the eigenfunctions of the angular momentum operator $\hat{J}^2$ and its projection $\hat{J}_z$,

$$\begin{aligned} \hat{J}^2|jm\rangle &= j(j+1)|jm\rangle \\ \hat{J}_z|jm\rangle &= m|jm\rangle\,, \end{aligned} \tag{33}$$

and this is the so-called Wigner D-functions

$$D^{(j)}_{mm'}(\alpha,\beta,\gamma) \equiv \langle jm|\hat{D}(\alpha,\beta,\gamma)|jm'\rangle = \langle jm|\exp\left(-\mathrm{i}\alpha\hat{J}_z\right)\exp\left(-\mathrm{i}\beta\hat{J}_y\right)\exp\left(-\mathrm{i}\gamma\hat{J}_z\right)|jm'\rangle\,. \tag{34}$$

For a given j, the dimension of the representation $D^{(j)}$ is equal to $(2j+1)$ since $m, m' = -j, -j+1, \ldots, j-1, j$.

Example 5

An example of the accidental degeneracy is given by the LMR-technique. Suppose that a nucleus is placed in an external electric field with a non-zero gradient and a static magnetic field, such that the direction of the electric field gradient coincides with the magnetic field axis. The Hamiltonian of such a system has an **SO(2)** symmetry and as we have seen in the Example 3, its levels will be non-degenerate and can be labelled by m, a projection of the angular momentum on the axis of the field. However, a change of the value of the magnetic field will lead to sudden crossings of the levels belonging to two different irreducible representations $D^{(m)}$ of the group **SO(2)**, e.g., $m = 0$ and $m = -1$, i.e. at certain values of the magnetic field strength doubly degenerate levels appear. This phenomenon is *an accidental degeneracy.*

Example 6

Let us consider now two particular cases of the potential energy of a system, namely, the harmonic oscillator potential

$$V_{ho}(\vec{r}) = \frac{m\omega^2 r^2}{2}\,, \tag{35}$$

and the Coulomb potential

$$V_C(\vec{r}) = -\frac{Ze^2}{r}\,. \tag{36}$$

For example, the Hamiltonian

$$H(\vec{r}) = -\frac{\hbar^2}{2m}\Delta + \frac{m\omega^2 r^2}{2}\,, \tag{37}$$

describes the motion of a nucleon in a nuclear mean-field, while

$$H(\vec{r}) = -\frac{\hbar^2}{2m}\Delta - \frac{Ze^2}{r}\,, \tag{38}$$

is the Hamiltonian of the hydrogen-like atom.

Obviously, since the potential energy does not depend on the angles, both Hamiltonians are invariant with respect to the rotational group $\mathbf{SO(3)}$ and, in both cases, the energy levels will correspond to certain irreducible representations of the $\mathbf{SO(3)}$ group $D^{(l)}$. This means that the levels can be characterized by a quantum number l, the eigenvalue of the orbital angular momentum operator $\hat{l}$, and they will be $(2l+1)$-fold degenerate (let us at this moment not take into account the possible spin of the particles, like of a nucleon or of an electron).

However, we know that in the spectra of both Hamiltonians a higher degeneracy is present. The energy levels of the harmonic oscillator $E_N = (N + \frac{3}{2})\hbar\omega$ depend on the principle quantum number $N = 2n + l$, where n is a radial quantum number and l is the orbital angular momentum. For each N, l takes the values $l = N, N-2, N-4, \ldots, 1$ or 0 (then $n = (N-l)/2$). The total degeneracy of each oscillator level labelled by N is $\frac{1}{2}(N+1)(N+2)$ (for spin-less particles). Thus each level contains a number of irreducible representations of $\mathbf{SO(3)}$ $D^{(l)}$, i.e. it corresponds to a reducible representation of this group.

Similarly, the energy levels of the hydrogen atom are given by

$$E_n = -\frac{mZ^2e^4}{2\hbar^2 n^2}\,, \tag{39}$$

and for each n, the orbital angular momentum takes the values $l = 0, 1, 2, \ldots, n-1$, that results in a total degeneracy n^2. Thus each level contains a number of irreducible representations $D^{(l)}$ of $\mathbf{SO(3)}$.

This systematic occurrence of the accidental degeneracy suggests that in each case there exists a higher symmetry group such that the energy levels of a system correspond to irreducible representations of this group. It can be shown that the symmetry group of the harmonic oscillator potential is a unitary group $\mathbf{U(3)}$, while the symmetry group of the Coulomb potential is the orthogonal group in 4 dimensions $\mathbf{SO(4)}$. Both groups contain the group $\mathbf{SO(3)}$ as a subgroup:

$$\mathbf{SO(3)} \subset \mathbf{U(3)} \text{ and } \mathbf{SO(3)} \subset \mathbf{SO(4)}$$

2.2 Perturbation theory

Let us consider the Hamiltonian H_0 which is invariant under its symmetry group $\mathbf{G}$. Suppose that now the system is subjected to a perturbation V which is invariant under group $\mathbf{G}'$. If V has symmetry at least as great as H_0, then the total Hamiltonian $H = H_0 + V$ will be of the symmetry $\mathbf{G}$ and the types of the levels will be unchanged by the perturbation.

However, if V has a lower symmetry than H_0, e.g. the group $\mathbf{G}'$ is a subgroup of $\mathbf{G}$, then the symmetry group of the total Hamiltonian $H = H_0 + V$ will be $\mathbf{G}'$, and the types of the levels will be changed by the perturbation. The levels of the unperturbed Hamiltonian H_0 correspond to the irreducible representations $D(G)$ of the group $\mathbf{G}$. These representations may be reducible with respect to the group $\mathbf{G}'$ (let us call them $D'(G)$):

$$D(G) = \sum_{\gamma} m_{\gamma} D'^{(\gamma)}(G) \tag{40}$$

(here sum denotes the direct sum of the representations). This means that from the wave functions ψ_i, $i = 1, \ldots, l$ which span the basis of the irreducible representation $D(G)$, we can construct the linear combinations ψ_i' such that they can be divided into smaller subsets ψ_i', $i = 1, \ldots, k$, ψ_j', $j = k+1, \ldots, k+m$, etc., which transform among themselves according to the irreducible representations of the group $\mathbf{G}'$. As a result, the energy levels of the Hamiltonian H_0 will be splitted and the final spectrum of H will consist of the levels corresponding to the irreducible representations of the group $\mathbf{G}'$.

In order to estimate the magnitude of the splitting, we have to follow the receipt of the standard perturbation theory:

$$\Delta E_i = \langle \psi_i' | V | \psi_i' \rangle \,. \tag{41}$$

Example

Consider a system having the symmetry $\mathbf{O}$*. Suppose a perturbation is applied which reduces the symmetry to* $\mathbf{C}_{3v}$*. How will the 3-fold degenerate levels be splitted?*

From the table of characters for the group $\mathbf{O}$ it is seen that this group has two different 3-dimensional irreducible representations, labelled by F_1 and F_2. The characters are given in the table below for all 5 classes of elements:

	E	C_3 (8)	C_4^2 (3)	C_2 (6)	C_4 (6)
F_1	3	0	-1	-1	1
F_2	3	0	-1	1	-1

$\mathbf{D}_3$ group has six following elements: E; C_3, C_3^2; three rotations C_2. Let us re-write the character table for this group and below add two lines with the characters of the representations F_1 and F_2 of the group $\mathbf{O}$ for the elements which are common with the group $\mathbf{D}_3$:

	E	C_3 (2)	C_2 (3)
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
F_1	3	0	-1
F_2	3	0	1

In order to find how many times each of the representations A_1, A_2, E of the group $\mathbf{D}_3$ enters in the representations F_1 and F_2 of the group $\mathbf{O}$, we should use the formula (49) of the previous lecture:

$$m_\alpha = \frac{1}{n}\sum_G \chi^{(\alpha)*}(G)\chi(G) \ , \tag{42}$$

which can be re-written using the classes as

$$m_\alpha = \frac{1}{n}\sum_C n_C\chi^{(\alpha)*}(C)\chi(C) \ . \tag{43}$$

Substituting the characters from the table, we have for F_1:

$$\begin{aligned} m_{A_1} &= \frac{1}{6}(1\cdot 1\cdot 3 + 2\cdot 1\cdot 0 + 3\cdot 1\cdot (-1)) = 0 \ , \\ m_{A_2} &= \frac{1}{6}(1\cdot 1\cdot 3 + 2\cdot 1\cdot 0 + 3\cdot (-1)\cdot (-1)) = 1 \ , \\ m_E &= \frac{1}{6}(1\cdot 2\cdot 3 + 2\cdot (-1)\cdot 0 + 3\cdot 0\cdot (-1)) = 1 \ , \end{aligned} \tag{44}$$

from where we get the final result:

$$F_1 = A_2 \oplus E \ . \tag{45}$$

This means that the 3-fold degenerate level of the Hamiltonian H_0 corresponding to the irreducible representation F_1 of the group $\mathbf{O}$ will be splitted by the perturbation V into two levels, 1-fold and 2-fold degenerate, corresponding to the irreducible representations A_2 and E of the group $\mathbf{D}_3$. Similarly, we will get for F_2:

$$F_2 = A_1 \oplus E \ . \tag{46}$$

2.3 Coupled systems

Let us consider two systems, with coordinates $\vec{r}_1$ and $\vec{r}_2$, respectively. The Hamiltonians for the two systems, H_1 and H_2, have the same form, and are invariant under the same group $\mathbf{G}$. If we consider the system 1 alone, we can classify its states according to the irreducible representations of the symmetry group $\mathbf{G}$ and we will denote its wave functions by $\psi_i^{(\alpha)}(\vec{r}_1)$. Similarly, for the system 2, $\psi_j^{(\beta)}(\vec{r}_2)$. Here α and β refer to different irreducible representations of the group $\mathbf{G}$.

2.3.1 No interaction

Let us suppose that the two systems are completely independent from each other. Then the total Hamiltonian of the system is $H = H_1 + H_2$ and it is invariant with respect to the group **G**. Its eigenvalue, $E = E_1 + E_2$, will belong to the representation $D^{(\alpha\times\beta)}(G)$, if the levels E_1 and E_2 correspond to the representations $D^{(\alpha)}(G)$ and $D^{(\beta)}(G)$, respectively. The eigenfunctions of H are the products $\psi_i^{(\alpha)}(\vec{r}_1)\psi_j^{(\beta)}(\vec{r}_2)$ and they form a basis of the representation $D^{(\alpha\times\beta)}(G)$.

2.3.2 With interaction

Suppose that two systems interact with each other, i.e. the total Hamiltonian is $H = H_1 + H_2 + V_{12}$, and that the interaction term has the symmetry at least as great as of H_1, H_2. The interaction provides that the levels corresponding to the reducible in general representation $D^{(\alpha\times\beta)}(G)$ of the group **G**, i.e. $l_\alpha l_\beta$-fold degenerate, be splitted. The resulting degeneracy of the levels can be obtained from the decomposition of the representation $D^{(\alpha\times\beta)}(G)$ into irreducible components $D^{(\gamma)}(G)$:

$$D^{(\alpha\times\beta)}(G) = \sum_\gamma m_\gamma D^{(\gamma)}(G) \tag{47}$$

This expansion is called a *Clebsch-Gordan series.* The values m_γ can be found from

$$m_\gamma = \frac{1}{n}\sum_C n_C \chi^{(\gamma)\,*}(C)\chi^{(\alpha\times\beta)}(C)\ , \tag{48}$$

where $\chi^{(\gamma)}(C)$ are the character in the representation $D^{(\gamma)}(G)$ and $\chi^{(\alpha\times\beta)}(C)$ are the characters in the representation $D^{(\alpha\times\beta)}(G)$.

This means that we have just reorganized the space of the wave functions $\psi_i^{(\alpha)}(\vec{r}_1)\psi_j^{(\beta)}(\vec{r}_2)$, i.e. we have found their certain linear combinations which transform according to different irreducible representations $D^{(\gamma)}(G)$:

$$\Psi_k^{(\gamma)t}(\vec{r}_1,\vec{r}_2) = \sum_{i,j}(\alpha i\beta j|\gamma k t)\psi_i^{(\alpha)}(\vec{r}_1)\psi_j^{(\beta)}(\vec{r}_2)\ . \tag{49}$$

The wave functions $\psi_i^{(\alpha)}(\vec{r}_1)\psi_j^{(\beta)}(\vec{r}_2)$ provide a basis of the representation $D^{(\alpha\times\beta)}(G)$ of the group **G**, while the wave functions $\Psi_k^{(\gamma)t}(\vec{r}_1,\vec{r}_2)$ provide a basis of the representation $D^{(\gamma)}(G)$ (the index t is required in order to distinguish between the functions with equal γ and k in case the representation $D^{(\gamma)}(G)$ enters the decomposition (47) two or more times. The coefficients of this transformation $(\alpha i\beta j|\gamma k t)$ are called *Clebsch-Gordan coefficients* for the group **G**.

From the mathematical point of view, the Clebsch-Gordan coefficients perform the decomposition of the direct product of two irreducible representations of a group into irreducible components. The physical meaning of the Clebsch-Gordan coefficients is that $|(\alpha i\beta j|\gamma k t)|^2$ *represents the probability of finding each of the subsystems in the states characterized by the wave functions* $\psi_i^{(\alpha)}(\vec{r}_1)$ *and* $\psi_j^{(\beta)}(\vec{r}_2)$*, respectively, while the total* *system is in a state characterized by the wave function the wave functions* $\Psi_k^{(\gamma)t}(\vec{r}_1,\vec{r}_2)$. Hence, the Clebsch-Gordan coefficients are normalized:

$$\sum_{i,j} |(\alpha i \beta j|\gamma k t)|^2 = 1\,. \tag{50}$$

Since the wave functions $\psi_i^{(\alpha)}(\vec{r}_1)\psi_j^{(\beta)}(\vec{r}_2)$ form an orthogonal set of functions, the functions $\Psi_k^{(\gamma)t}(\vec{r}_1,\vec{r}_2)$ can also be orthogonalized. This means that the transformation (51) is unitary and there exists an inverse transformation

$$\psi_i^{(\alpha)}(\vec{r}_1)\psi_j^{(\beta)}(\vec{r}_2) = \sum_{\gamma,k,t}(\alpha i\beta j|\gamma k t)^*\Psi_k^{(\gamma)t}(\vec{r}_1,\vec{r}_2) \tag{51}$$

and

$$\begin{aligned} &\sum_{i,j}(\alpha i\beta j|\gamma k t)^*(\alpha i\beta j|\gamma' k' t') = \delta_{\gamma\gamma'}\delta_{kk'}\delta_{tt'}\ , \\ &\sum_{\gamma,k,t}(\alpha i\beta j|\gamma k t)^*(\alpha i'\beta j'|\gamma k t) = \delta_{ii'}\delta_{jj'}\ . \end{aligned} \tag{52}$$

Example 1

Consider an atom of ^4He *placed in a crystal of* $\mathbf{C}_{3v}$ *symmetry. Classify two-electron wave functions.*

The symmetry group of a free atom is the rotational group **SO(3)**, so the individual electrons can be assigned to angular momenta l_1, l_2, according to the irreducible representations of this group. Let us put the atom in a crystal. If we first neglect the Coulomb interaction between the electrons and assume that the field produced by the ions in the lattice is large, the states of the individual electrons will be classified according to the representations of the symmetry group of the crystalline field, i.e. a_1, a_2 and e in our case of the group $\mathbf{C}_{3v}$ (we denote the representations for the individual electrons by the small letters and reserve the capital letters for the total system).

If the first electron is in a state belonging to the representation a_1 and the second is in a state belonging to the representation e, then the states of the total system will belong to the representation $a_1 \times e = E$. If both the electrons are in states belonging to the representation e then the total system will be in a state belonging to the representation $e \times e = A_1 \oplus A_2 \oplus E$ (such decompositions are obtained from (48)). Continuing in this way, we get the table:

$a_1 \times a_1$	A_1
$a_1 \times a_2$	A_2
$a_2 \times a_2$	A_1
$a_1 \times e$	E
$a_2 \times e$	E
$e \times e$	$A_1 \oplus A_2 \oplus E$

which shows the symmetry of all levels of the system.

If we do not take into account the Coulomb interaction between the electrons, then it does not make any difference which type of notations to use in order to classify the two-electron states: left or right column of this table. The degeneracy of the levels will be the same.

However, if we now take into account the interaction between the electrons, which has at least **SO(3)** symmetry, then we get the splitting of the levels according to decomposition of the direct product of this representations (left column) to the irreducible components (right column). In fact, only the last 4-fold degenerate level will be splitted into two non-degenerate and one 2-fold degenerate levels, as seen from the last row of this table.

What are now the basis functions of the total system? For non-interacting systems, the product of two wave functions were valid. With interaction, we should find the proper linear combinations of these wave functions. E.g., since $a_1 \times a_1 = A_1$, it means that

$$\Psi_1^{(A_1)}(\vec{r}_1, \vec{r}_2) = \psi_1^{(a_1)}(\vec{r}_1)\psi_1^{(a_1)}(\vec{r}_2)\,, \tag{53}$$

so the transformed wave function still coincides with the direct product. In the notations of the formula (51), it means that the only Clebsch-Gordan coefficient $(a_1, 1, a_1, 1|A_1, 1) = 1$.

Similarly, we find for the 2-dimensional representation $a_1 \times e = E$, the two components of the basis functions are just the products

$$\Psi_1^{(E)}(\vec{r}_1, \vec{r}_2) = \psi_1^{(a_1)}(\vec{r}_1)\psi_1^{(e)}(\vec{r}_2)\,, \qquad \Psi_2^{(E)}(\vec{r}_1, \vec{r}_2) = \psi_1^{(a_1)}(\vec{r}_1)\psi_2^{(e)}(\vec{r}_2)\,. \tag{54}$$

The Clebsch-Gordan coefficients are $(a_1, 1, e, 1|E, 1) = 1$ and $(a_1, 1, e, 2|E, 2) = 1$, and so on.

For the decomposition $e \times e = A_1 \oplus A_2 \oplus E$ we have:

$$\begin{aligned}
\Psi_1^{(A_1)}(\vec{r}_1, \vec{r}_2) &= \tfrac{1}{\sqrt{2}}\left(\psi_1^{(e)}(\vec{r}_1)\psi_2^{(e)}(\vec{r}_2) + \psi_2^{(e)}(\vec{r}_1)\psi_1^{(e)}(\vec{r}_2)\right)\,,\\
\Psi_1^{(A_2)}(\vec{r}_1, \vec{r}_2) &= \tfrac{1}{\sqrt{2}}\left(\psi_1^{(e)}(\vec{r}_1)\psi_2^{(e)}(\vec{r}_2) - \psi_2^{(e)}(\vec{r}_1)\psi_1^{(e)}(\vec{r}_2)\right)\,,\\
\Psi_1^{(E)}(\vec{r}_1, \vec{r}_2) &= \psi_1^{(e_1)}(\vec{r}_1)\psi_1^{(e)}(\vec{r}_2)\,,\\
\Psi_2^{(E)}(\vec{r}_1, \vec{r}_2) &= \psi_2^{(e_1)}(\vec{r}_1)\psi_2^{(e)}(\vec{r}_2)\,.
\end{aligned} \tag{55}$$

The coefficients in these equations are the Clebsch-Gordan coefficients for the group $\mathbf{C}_{3v}$. For example, $(e, 1, e, 2|A_1, 1) = \frac{1}{\sqrt{2}}$ and $(e, 2, e, 1|A_2, 1) = -\frac{1}{\sqrt{2}}$.

Example 2

Consider a nucleon in a Woods-Saxon potential taking into account a spin-orbit coupling. Classify the single-particle states.

The Hamiltonian for a nucleon in a Woods-Saxon potential

$$H(\vec{r}) = -\frac{\hbar^2}{2m}\Delta + \frac{V_0}{1 + \exp\left(\frac{r - R_0}{a}\right)}\,, \tag{56}$$

is invariant with respect to **SO(3)** group in a coordinate space and thus its levels can be labelled by l, the eigenvalue of the orbital angular momentum. A nucleon also possesses a spin $s = 1/2$. The Hamiltonian is invariant with respect to the rotations in a spin space, i.e. the operator $\hat{s}$ commutes with the Hamiltonian. This means that its levels can be also labelled by s, the eigenvalue of the spin operator.

In total, we find that the symmetry group of the Hamiltonian (56) is a direct product of two rotational groups $\mathbf{SO}_l\mathbf{(3)}\otimes\mathbf{SO}_s\mathbf{(3)}$, and its energy levels correspond to the representation of this group $D^{(l)}\otimes D^{(s)}$. The basis of this representation is the direct product of the eigenstates of the orbital angular momentum operator $|lm_l\rangle$ and of the spin operator $|sm_s\rangle$:

$$|lm_l sm_s\rangle \equiv |lm_l\rangle|sm_s\rangle \tag{57}$$

and for fixed l and s there are $(2l+1)(2s+1)$ such states. So, we have $0s$, $0p$, $0d$, $1s$, etc sequence of levels (in these notations, numbers are the radial quantum number and the letter correspond to the value of the orbital angular momentum).

The Clebsch-Gordan series (47) for the group $\mathbf{SO(3)}$ looks like

$$D^{(l)}(G)\otimes D^{(s)}(G) = \sum_{j=|l-s|}^{l+s} D^{(j)}(G)\ . \tag{58}$$

For a given j, the irreducible representation $D^{(j)}(G)$ is $(2j+1)$-fold degenerate. The basis of the representation can be constructed from the states (57):

$$|lsjm\rangle = \sum_{m_l,m_s} (lm_l sm_s|jm)\, |lm_l\rangle|sm_s\rangle\ , \tag{59}$$

where the coefficients $(lm_l sm_s|jm)$ in this expression are the Clebsch-Gordan coefficients of the group $\mathbf{SO(3)}$. This coefficients do not require the introduction of the index t, since for the group $\mathbf{SO(3)}$, in the decomposition (58) each of the irreducible representations $D^{(j)}(G)$ with a fixed j enters only once.

Note that while there is no spin-orbit interaction in the Hamiltonian (57), both description of the levels in terms of the representations $D^{(l)}\otimes D^{(s)}(G)$ and $D^{(j)}(G)$ are equivalent, as well as the description of the eigenstates as $|lm_l\rangle|sm_s\rangle$ or $|lsjm\rangle$ (the degeneracy of the levels will be $(2l+1)(2s+1)$).

Let us now introduce the spin-orbit interaction in the Hamiltonian:

$$H(\vec{r}) = -\frac{\hbar^2}{2m}\Delta + \frac{V_0}{1+\exp\left(-\frac{r-R_0}{a}\right)} + f(r)(\vec{l}\cdot\vec{s})\ . \tag{60}$$

This Hamiltonian is invariant with respect to the group $\mathbf{SO}_j\mathbf{(3)}$. The spin-orbit interaction splits the $(2l+1)(2s+1)$-fold degenerate levels into $(2j+1)$-fold degenerate levels according to the irreducible representations $D^{(j)}(G)$. This splitting is called a spin-orbit splitting. The resulting levels can be denoted as $0s_{1/2}$, $0p_{1/2}$, $0p_{3/2}$, $0d_{3/2}$, $0d_{5/2}$, $1s_{1/2}$, etc (here the half-integer values refer to the total angular momentum j).

In order to estimate the value of this splitting we have to follow the receipt (41) and calculate the matrix elements

$$\Delta E_{nlsjm} = \langle nlsjm|f(r)(\vec{l}\cdot\vec{s})|nlsjm\rangle = \begin{cases} +\frac{1}{2}l\langle f(r)\rangle_{nl} \text{ for } j = l+\frac{1}{2} \\ -\frac{1}{2}(l+1)\langle f(r)\rangle_{nl} \text{ for } j = l-\frac{1}{2} \end{cases} \tag{61}$$

In the last formula the values of the radial quantum number n is also given, since the total wave functions will depend on it.

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