Lecture 5. Application of Group Theory to Quantum Mechanics. Part II

1 Matrix elements of operators

1.1 Irreducible operators

Let us consider a group **G** of transformations in the space, i.e. for each element G:

$$\vec{r} \stackrel{G}{\to} \vec{r}\,' = G\vec{r}\,. \tag{1}$$

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

$$\psi(\vec{r}) \stackrel{G}{\to} \psi'(\vec{r}) = \hat{D}(G)\psi(\vec{r}) = \psi(G^{-1}\vec{r})\,. \tag{2}$$

If $\hat{T}$ is an operator in the space of functions, then under transformation of the coordinates G, this operator will also be transformed as

$$\hat{T} \stackrel{G}{\to} \hat{T}\,' = \hat{D}(G)\hat{T}\hat{D}^{-1}(G)\,. \tag{3}$$

Let us suppose that there exists a set of operators $\hat{T}_i^{(\alpha)}$ such that each transformed operator will be a superposition of the operators of the set,

$$\hat{T}_i^{(\alpha)} \stackrel{G}{\to} \hat{T}\,_i'^{(\alpha)} = \hat{D}(G)\hat{T}_i^{(\alpha)}\hat{D}^{-1}(G) = \sum_j D_{ji}^{(\alpha)}(G)\hat{T}_j^{(\alpha)}\,, \tag{4}$$

where $D_{ji}^{(\alpha)}(G)$ are the matrix elements of the irreducible representation $D^{(\alpha)}(G)$. Then the set of operators $\hat{T}_i^{(\alpha)}$ is called an *irreducible set* of operators. The operators $\hat{T}_i^{(\alpha)}$ satisfying (4) are said to transform according to the irreducible representation $D^{(\alpha)}(G)$ of the group **G**. The number of the operators $\hat{T}_i^{(\alpha)}$ is equal to the dimension of the irreducible representation $D^{(\alpha)}(G)$.

In general, if an operator $\hat{T}$ is not irreducible, then it can be represented as a superposition of irreducible operators:

$$\hat{T} = \sum_\alpha \hat{T}^{(\alpha)}\,. \tag{5}$$

Example 1

Find the transformation properties of the electric dipole operator with respect to the group $\mathbf{C}_{3v}$.

1. The electric dipole operator

$$\vec{d} = e\vec{r} \tag{6}$$

is a vector and therefore is represented by three components, or by a set of three operators: (d_x, d_y, d_z). The operators $d_x = ex$, $d_y = ey$, $d_z = ez$ transform as operators x, y and z, respectively. It is known that x, y are the basis functions of the irreducible representation E, while z is the basis function of the irreducible representation A_1 of the group $\mathbf{C}_{3v}$ (see

Example 2 of Section 1.4 of lecture 3). This means that two operators (d_x, d_y) form an *irreducible set* and they transform according to the 2-dimensional irreducible representation E, while d_z is also an *irreducible operator* and it transforms according to the 1-dimensional irreducible representation A_1 of $\mathbf{C}_{3v}$:

$$\begin{aligned} &d_z \to \hat{T}^{(A_1)} \\ &d_x, d_y \to \hat{T}_1^{(E)}, \hat{T}_2^{(E)} \ . \end{aligned} \tag{7}$$

Example 2

Find the character of the electric dipole operator with respect to the group **SO(2)**.

Let us consider how the vectors $\vec{e}_x$, $\vec{e}_y$ and $\vec{e}_z$ transform under operations of the group **SO(2)**. If the axis of rotation coincides with axis z, then

$$\begin{aligned} &\hat{D}(a)\vec{e}_x = \cos a \vec{e}_x + \sin a \vec{e}_y \\ &\hat{D}(a)\vec{e}_y = -\sin a \vec{e}_x + \cos a \vec{e}_y \\ &\hat{D}(a)\vec{e}_z = \vec{e}_z \end{aligned} \tag{8}$$

or for the linear combinations of $\vec{e}_x$ and $\vec{e}_y$ we have

$$\begin{aligned} &\hat{D}(a)(\vec{e}_x + \mathrm{i}\vec{e}_y) = \exp{(-\mathrm{i}a)}(\vec{e}_x + \mathrm{i}\vec{e}_y) \\ &\hat{D}(a)(\vec{e}_x - \mathrm{i}\vec{e}_y) = \exp{(\mathrm{i}a)}(\vec{e}_x - \mathrm{i}\vec{e}_y) \\ &\hat{D}(a)\vec{e}_z = \vec{e}_z \end{aligned} \tag{9}$$

The operator $\hat{D}(a)$ is a rotation operator

$$\hat{D}(a) = \exp{(-a\frac{\partial}{\partial\phi})} \ . \tag{10}$$

The representations of the group **SO(2)** can be labelled by the integer m:

$$D^m(a) = \exp{(-\mathrm{i}ma)} \, . \tag{11}$$

Therefore, vector $\vec{e}_z$ is the basis vector of the irreducible representation D^0, while vectors $(\vec{e}_x \pm \mathrm{i}\vec{e}_y)$ are the basis vectors of the irreducible representations $D^{\pm 1}$.

This means that operators $d_x + \mathrm{i}d_y$, $d_x - \mathrm{i}d_y$ and d_z are *irreducible operators* and they transform according to the irreducible representations D^1, D^{-1} and D^0, respectively, of the group **SO(2)**:

$$\begin{aligned} &d_x + \mathrm{i}d_y \to \hat{T}^1 \\ &d_x - \mathrm{i}d_y \to \hat{T}^{-1} \\ &d_z \to \hat{T}^0 \ . \end{aligned} \tag{12}$$

Example 3

Find the character of the electric dipole operator with respect to the group **SO(3)**.

Let us define the operators

$$\mathcal{Y}_{lm}(\vec{r}) = r^l Y_{lm}(\theta, \phi) \ . \tag{13}$$

Under rotations, the spherical functions transform as

$$Y_{lm}(\vec{r}) \rightarrow \hat{D}(\alpha,\beta,\gamma)Y_{lm}(\theta,\phi) = \sum_{m'} D^{(l)}_{m'm}(\alpha,\beta,\gamma)Y_{lm'}(\theta,\phi) \ , \tag{14}$$

i.e. they form a basis of the irreducible representations of the group **SO(3)**. The transformation properties of the operators (13) are similar:

$$\mathcal{Y}_{lm}(\vec{r}) \rightarrow \hat{D}(\alpha,\beta,\gamma)\mathcal{Y}_{lm}(\vec{r})\hat{D}^{-1}(\alpha,\beta,\gamma) = \sum_{m'} D^{(l)}_{m'm}(\alpha,\beta,\gamma)\mathcal{Y}_{lm'}(\vec{r}) \ . \tag{15}$$

This means that operators $\mathcal{Y}_{lm}(\vec{r})$ for each l form an irreducible set of operators and they transform according to the irreducible representation $D^{(l)}$ of the group **SO(3)**, or in other words, they are tensors of rank l:

$$\mathcal{Y}_{lm}(\vec{r}) \rightarrow \hat{T}^{(l)} \ . \tag{16}$$

Since

$$\begin{aligned} \mathcal{Y}_{10}(\vec{r}) &= \sqrt{\tfrac{3}{4\pi}}z \\ \mathcal{Y}_{11}(\vec{r}) &= \sqrt{\tfrac{3}{8\pi}}(x+\mathrm{i}y) \\ \mathcal{Y}_{1-1}(\vec{r}) &= \sqrt{\tfrac{3}{8\pi}}(x-\mathrm{i}y) \end{aligned} \tag{17}$$

three spherical components of the radius-vector $x+\mathrm{i}y$, $x-\mathrm{i}y$ and z form an irreducible set with respect to the group **SO(3)** and they transform according to the irreducible representation $D^{(1)}$ of this group. Thus, the radius-vector $\vec{r}$ transforms according to the irreducible representation $D^{(1)}$ of **SO(3)**. Since $\vec{d} = e\vec{r}$, the electric dipole operator also transforms according to the irreducible representation $D^{(1)}$ of this group:

$$\vec{d} \rightarrow \hat{T}^{(1)} \ . \tag{18}$$

1.2 Calculation of matrix elements of operators

In order to calculate transition probabilities W_{IF}, we need to calculate the matrix elements of the operator, responsible for this transition between the states of interest, since

$$W_{IF} \sim |\langle\psi_F|\hat{T}|\psi_I\rangle|^2 \ . \tag{19}$$

ALGORITHM

1. Find the symmetry character of initial and final states, e.g. $\psi_I = \psi_i^{(\alpha)}$ and $\psi_F = \psi_k^{(\gamma)}$.

2. Find the tensor character of the transition operator, e.g. $\hat{T} = \hat{T}^{(\beta)}$ or decompose it into irreducible components according to (5) if necessary.

3. Calculate the matrix elements of the type

$$\langle\psi_k^{(\gamma)}|\hat{T}_j^{(\beta)}|\psi_i^{(\alpha)}\rangle \ . \tag{20}$$

For the matrix elements of the irreducible operators the *Wigner-Eckart theorem* holds:

$$\langle\psi_k^{(\gamma)}|\hat{T}_j^{(\beta)}|\psi_i^{(\alpha)}\rangle = \sum_t (\alpha i\beta j|\gamma kt)\langle\psi^{(\gamma)}||\hat{T}^{(\beta)}||\psi^{(\alpha)}\rangle_t \ , \tag{21}$$

where $(\alpha i\beta j|\gamma kt)$ are the Clebsch-Gordan coefficients of the group **G** and $\langle\psi^{(\gamma)}||\hat{T}^{(\beta)}||\psi^{(\alpha)}\rangle_t$ is called a *reduced matrix element.*

CONSEQUENCES OF THE WIGNER-ECKART THEOREM

1. The Wigner-Eckart theorem gives a simple receipt to calculate all matrix elements of the type (20). To do this, we should first calculate one matrix element (20) for particular values i, j and k. The Clebsch-Gordan coefficients for any groups are usually tabulated. So, we can find a value of the reduced matrix element $\langle \psi^{(\gamma)} || \hat{T}^{(\beta)} || \psi^{(\alpha)} \rangle_t$. Then using the tabulated Clebsch-Gordan coefficients, it is simple to compute all the rest matrix elements (20).

2. Often in the calculation of reaction cross-sections or transition probabilities, it is required to know not matrix elements themselves, but the sum of matrix elements on the i or j. Such problems appear in the calculation of reaction cross-sections if the beam and the target are not polarized and the detector is not sensible to the polarization of the incoming particles. The Wigner-Eckart theorem allows to perform the summations automatically.

   Example

   If the nuclear Hamiltonian is invariant with respect to **SO(3)** group, then the states can be characterized by a value of the total angular momentum J and they are $(2J+1)$-fold degenerate. If operator $\hat{T}(LM)$ describes a transition from an initial state $|\alpha_i; J_i M_i\rangle$ to a final state $|\alpha_f; J_f M_f\rangle$, then the reduced transition probability for a given (J_i, M_i) should be averaged over all projections M_i and summed over all values M_f of the final state and all values M of the transition operator:

   $$B(L; J_i \to J_f) = \frac{1}{2J_i + 1} \sum_{M_i, M, M_f} |\langle \alpha_f; J_f M_f | \hat{T}(LM) | \alpha_i; J_i M_i \rangle|^2 \,. \tag{22}$$

   The reduced matrix element of the **SO(3)** group is defined with an additional square root in front of it (by some historical reasons), i.e.

   $$\langle \alpha_f; J_f M_f | \hat{T}(LM) | \alpha_i; J_i M_i \rangle = \frac{(J_i M_i J M | J_f M_f)}{\sqrt{2J_f + 1}} \langle \alpha_f; J_f || \hat{T}(LM) || \alpha_i; J_i \rangle \,. \tag{23}$$

   Applying the Wigner-Eckart theorem and using the formulae (21) and (22) for the SO(3) Clebsch-Gordan coefficients from the first lecture, we get

   $$\begin{aligned} B(L; J_i \to J_f) = \frac{1}{2J_i + 1} \sum_{M, M_f} \frac{(J_i M_i J M | J_f M_f)^2}{2J_f + 1} |\langle \alpha_f; J_f || \hat{T}(L) || \alpha_i; J_i \rangle|^2 = \\ \frac{1}{2J_i + 1} |\langle \alpha_f; J_f || \hat{T}(L) || \alpha_i; J_i \rangle|^2 \,. \end{aligned} \tag{24}$$

3. **Selection rules**
   The matrix element (20) will be zero unless $D^{(\gamma)}(G)$ is contained in the decomposition of $D^{(\alpha \times \beta)}$:

   $$D^{(\alpha \times \beta)}(G) = \sum_{\gamma} m_{\gamma} D^{(\gamma)}(G) \tag{25}$$

   This means that if $\hat{T}^{(\beta)}$ is a transition operator, then from a state $\psi^{(\alpha)}$, transitions only to those states $\psi^{(\gamma)}$ are *allowed* for which (25) holds.

Example 1

Find the selection rules for electric dipole transitions for a system of $\mathbf{C}_{3v}$ *symmetry.*

The states of the system can be associated with the irreducible representations of the group $\mathbf{C}_{3v}$: A_1, A_2, E. From Example 1 of section 1.1 we know that the components of the electric dipole operator

$$\vec{d} = e\vec{r} \tag{26}$$

has the following transformation properties: operators d_x and d_y transform according to the irreducible representation E, while d_z transforms according to the irreducible representation A_1 of $\mathbf{C}_{3v}$.

From the table

$A_1 \times A_1$	A_1
$A_2 \times A_1$	A_2
$E \times A_1$	E
$A_1 \times E$	E
$A_2 \times E$	E
$E \times E$	$A_1 \oplus A_2 \oplus E$

we find the selection rules. The operator of the radiation linear polarized along z axis is d_z, transforming as A_1. It can connect only the states which have the same symmetry. So, allowed transitions are

$$d_z : \quad A_1 \leftrightarrow A_1 \ , \quad A_2 \leftrightarrow A_2 \ , \quad E \leftrightarrow E \ . \tag{27}$$

The operator of the radiation polarized in the xy-plane is characterized by d_x, d_y, transforming as E. The allowed transitions are

$$(d_x, d_y) : \quad A_1 \leftrightarrow E \ , \quad A_2 \leftrightarrow E \ , \quad E \leftrightarrow E \ . \tag{28}$$

Example 2

Find the selection rules for electric dipole transitions for an axially symmetric system.

The states of the system can be associated with the irreducible representations of the group $\mathbf{SO(2)}$ and thus can be labelled by an integer of half-integer m. From Example 2 of section 1.1 we know that the components of the electric dipole operator

$$\vec{d} = e\vec{r} \tag{29}$$

has the following transformation properties: operators $(d_x + \mathrm{i}d_y)$, $(d_x - \mathrm{i}d_y)$ and d_z transform according to the irreducible representation D^1, D^{-1} and D^0 of $\mathbf{SO(2)}$, respectively. For $\mathbf{SO(2)}$ the Clebsch-Gordan series (25) looks like follows

$$D^{m_1} \times D^{m_2} = D^{m_1+m_2} \ . \tag{30}$$

Thus the transitions of linear polarized radiation (d_z) are allowed between the states with $\Delta m = 0$, while the radiation polarized in the xy-plane ($d_x \pm \mathrm{i} d_y$) can be emitted or absorbed only between the states with $\Delta m = \pm 1$.

Example 3

Find the selection rules for the electric and magnetic multipole transitions in a spherically symmetric system.

The electric and magnetic transition operators have a form:

$$\begin{aligned} \hat{T}(\mathcal{E}; LM) &= \frac{1}{c}\sqrt{\frac{L}{L+1}}\frac{(2L+1)!!}{q^L}\int \vec{j}(\vec{r})\cdot \vec{A}^{\mathcal{E}}_{LM}(q\vec{r})d\vec{r} \\ \hat{T}(\mathcal{M}; LM) &= -\frac{\mathrm{i}}{c}\sqrt{\frac{L}{L+1}}\frac{(2L+1)!!}{q^L}\int \vec{j}(\vec{r})\cdot \vec{A}^{\mathcal{M}}_{LM}(q\vec{r})d\vec{r} \end{aligned} \tag{31}$$

where $q = \omega/c = 2\pi/\lambda$, and

$$\begin{aligned} \vec{A}^{\mathcal{E}}_{LM}(q\vec{r}) &= \frac{1}{q\sqrt{L(L+1)}}\vec{\nabla}\times\vec{L}j_L(qr)Y_{LM}(\vec{r}) \\ \vec{A}^{\mathcal{M}}_{LM}(q\vec{r}) &= \frac{\vec{L}}{\sqrt{L(L+1)}}j_L(qr)Y_{LM}(\vec{r})\ . \end{aligned} \tag{32}$$

From here it is seen that the operators $\hat{T}(\mathcal{E}; LM)$ and $\hat{T}(\mathcal{M}; LM)$ transform according to the irreducible representations $D^{(L)}$ of the group $\mathbf{SO(3)}$.

From the Clebsch-Gordan series for the $\mathbf{SO(3)}$ group

$$D^{(J_i\times L)}(G) = \sum_{J_f=|J_i-L|}^{J_i+L} D^{(J_f)}(G) \tag{33}$$

it follows that the transitions from the level J_i will go only to the levels with $J_f = |J_i - L|, \ldots, J_i + L$.

Suppose that the system is also invariant with respect to inversion $\mathbf{I}$ (the group of inversion consists of two elements: identity E and a space inversion I, which corresponds to the transformation $x \to -x, y \to -y, z \to -z$).

The group $\mathbf{I}$ has two 1-dimesional irreducible representations,

	E	I
$D^{(1)}$	1	1
$D^{(2)}$	1	-1

If the Hamiltonian of the system is invariant with respect to inversion, then its eigenstates will belong to either the irreducible representation $D^{(1)}$ or to the irreducible representation $D^{(2)}$. In other words, they will be characterized by a certain parity, +1 or -1 for

$$\hat{P}\psi(\vec{r}) = +\psi(\vec{r}) \quad \text{or} \quad \hat{P}\psi(\vec{r}) = -\psi(\vec{r})\ , \tag{34}$$

respectively, where $\hat{P}$ is a parity operator:

$$\hat{P}\psi(\vec{r}) = \psi(-\vec{r})\ . \tag{35}$$

From the table

$D^{(1)} \times D^{(1)}$	$D^{(1)}$
$D^{(2)} \times D^{(1)}$	$D^{(2)}$
$D^{(2)} \times D^{(2)}$	$D^{(1)}$

the selection rules for a matrix element follows:

$$\langle \psi_f | \hat{T} | \psi_i \rangle = 0 \quad \text{if} \quad P_i P_T P_f = -1 \ . \tag{36}$$

From equations (31)–(32) follows that $\hat{T}(\mathcal{E}; LM)$ possesses parity $(-1)^L$ and $\hat{T}(\mathcal{M}; LM)$ possesses parity $(-1)^{L+1}$. Thus, the selection rules with respect to the group **I** are

$$\begin{array}{ll} P_i P_f = (-1)^L & \text{for electric } 2^L \text{ pole transitions} \\ P_i P_f = (-1)^{L+1} & \text{for magnetic } 2^L \text{ pole transitions .} \end{array} \tag{37}$$

4. **Equivalent operator method**
If operators $\hat{T}^{(\beta)}$ and $\hat{S}^{(\beta)}$ has the same transformation properties with respect to the group **G**, then their matrix elements are proportional:

$$\frac{\langle \psi_k^{(\gamma)} | \hat{T}_j^{(\beta)} | \psi_i^{(\alpha)} \rangle}{\langle \psi_k^{(\gamma)} | \hat{S}_j^{(\beta)} | \psi_i^{(\alpha)} \rangle} = \frac{\langle \psi^{(\gamma)} || \hat{T}^{(\beta)} || \psi^{(\alpha)} \rangle}{\langle \psi^{(\gamma)} || \hat{S}^{(\beta)} || \psi^{(\alpha)} \rangle} \equiv A_{\alpha\beta\gamma} \ , \tag{38}$$

where $A_{\alpha\beta\gamma}$ is just a constant depending on α, β and γ.

The advantage of the formula (38) is the following. Sometimes it is difficult or even impossible to calculate the matrix elements of an operator $\hat{T}^{(\beta)}$, but it is simple to calculate the matrix elements of an equivalent operator $\hat{S}^{(\beta)}$. Then, the matrix elements of interest are

$$\langle \psi_k^{(\gamma)} | \hat{T}_j^{(\beta)} | \psi_i^{(\alpha)} \rangle = A_{\alpha\beta\gamma} \langle \psi_k^{(\gamma)} | \hat{S}_j^{(\beta)} | \psi_i^{(\alpha)} \rangle \ . \tag{39}$$

Example

Calculate the spin-orbit splitting in a many-electron atom.

The Hamiltonian of a many-electron atom can be presented as

$$H = \sum_i \left(-\frac{\hbar^2}{2m} \Delta_i \right) - \sum_i \frac{Ze^2}{r_i} + \sum_{i<j} \frac{e^2}{r_{ij}} + \sum_i f(r_i)(\vec{l}_i \cdot \vec{s}_i) \ , \tag{40}$$

where the first term is a kinetic energy of electrons, the second term is the Coulomb attraction between the nucleus and each electron, the third term is a Coulomb repulsion between the electrons and the last term is the spin-orbit interaction. The nucleus is assumed to be fixed. This Hamiltonian can be represented in a form

$$H = H_0 + H_1 + H_2 \ , \tag{41}$$

where

$$
\begin{aligned}
H_0 &= \sum_i \left(-\frac{\hbar^2}{2m}\Delta_i - \frac{Ze^2}{r_i} + U(r_i) \right) \\
H_1 &= \sum_{i<j} \frac{e^2}{r_{ij}} - \sum_i U(r_i) \\
H_2 &= \sum_i f(r_i)(\vec{l}_i \cdot \vec{s}_i) \, .
\end{aligned} \tag{42}
$$

Here we added $U(r_i)$ term to the Coulomb repulsion between the electrons, because the summed repulsion between the electrons is similar to the effective repulsion of an electron from a center. With such a definition, H_1 is rather small. Usually $H_0 \gg H_1 \gg H_2$.

The eigenfunctions of the Hamiltonian H_0 is just a linear combination of the direct products of single-electron eigenfunctions

$$
\prod \psi_i \, , \tag{43}
$$

where ψ_i is a product of radial, angular and spin wave functions:

$$
\psi_i = u_{nl}(r_i) Y_{lm_l}(\theta_i, \phi_i) \chi^{(1/2)}_{m_s} \, . \tag{44}
$$

Taking into account the Hamiltonian H_1 will bring to the LS-coupling between the orbital angular momenta and spins of individual electrons. The eigenfunctions of $H_0 + H_1$ can be characterized by the value of the total orbital angular momentum L, total spin S, and their projections:

$$
|\alpha L M_L S M_S\rangle \, , \tag{45}
$$

where $\vec{L} = \sum_i \vec{l}_i$, $\vec{S} = \sum_i \vec{s}_i$, while α denotes all other quantum numbers. The states (45) will be $(2L+1)(2S+1)$-fold degenerate.

Taking into account the Hamiltonian H_2 will bring to the spin-orbit splitting of the $(2L+1)(2S+1)$-fold degenerate multiplets of levels. The final wave function of a many-electron atom can be characterized by the value of the total orbital angular momentum L, total spin S, total angular momentum J and its projection M on the quantization axis:

$$
|\alpha LSJM\rangle = \sum_{M_L, M_S} (L M_L S M_S | JM) |\alpha L M_L S M_S\rangle \, . \tag{46}
$$

The value of the spin-orbit splitting is given by a matrix element

$$
\Delta_J = \langle \alpha LSJM | \sum_{i=1}^{Z} (\vec{l}_i \cdot \vec{s}_i) | \alpha LSJM \rangle \, . \tag{47}
$$

In order to calculate the matrix elements (47), we will make use of the Wigner-Eckart theorem. The operator $\sum_{i=1}^{Z}(\vec{l}_i \cdot \vec{s}_i)$ has the same transformation properties as the operator $(\vec{L}\cdot\vec{S})$ under groups $\mathbf{SO}_L(3)$ and $\mathbf{SO}_S(3)$, i.e. these operators are equivalent. This means that

$$
\begin{aligned}
\Delta_J &= \langle \alpha LSJM | \textstyle\sum_{i=1}^{Z} (\vec{l}_i \cdot \vec{s}_i) | \alpha LSJM \rangle = A_{\alpha LS} \langle \alpha LSJM | (\vec{L} \cdot \vec{S}) | \alpha LSJM \rangle \\
&= \tfrac{1}{2} A_{\alpha LS} \left[J(J+1) - L(L+1) - S(S+1) \right] \, ,
\end{aligned} \tag{48}
$$

where the coefficients $A_{\alpha LS}$ are just the ratios of the corresponding reduced matrix elements and they depend only on α, L and S. The difference

$$\Delta_J - \Delta_{J-1} = JA_{\alpha LS} \tag{49}$$

is known as Lande formula.

2 Some useful formulae for SO(3) tensorial operators

The irreducible operators with respect to **SO(3)** group are called *tensors of rank k* if they transform according to the irreducible representation $D^{(k)}$:

$$\hat{D}(\alpha,\beta,\gamma)\hat{T}_p^{(k)} = \sum_q D_{qp}^{(k)}(\alpha,\beta,\gamma)\hat{T}_q^{(k)}(\theta,\phi) \ . \tag{50}$$

Examples

The tensor of rank 0 contains one component $T_0^{(0)}$ which does not change under rotations. It is usually either a scalar, or a pseudoscalar depending on its transformation properties under inversion (the scalar does not change its sign under inversion, while the pseudoscalar changes its sign under inversion).

The tensor of rank 1 contains three components $T_0^{(1)}$, $T_1^{(1)}$ and $T_{-1}^{(1)}$. Three cartesian coordinates of any vector $\vec{a} = \{a_x, a_y, a_z\}$ can be re-written in suitable form as

$$\begin{aligned} T_1^{(1)} &= -\tfrac{1}{\sqrt{2}}(a_x + \mathrm{i}a_y) \\ T_{-1}^{(1)} &= \tfrac{1}{\sqrt{2}}(a_x - \mathrm{i}a_y) \\ T_0^{(1)} &= a_z \ . \end{aligned} \tag{51}$$

The tensor of rank 2 has five components $T_0^{(2)}$, $T_{\pm1}^{(2)}$, $T_{\pm2}^{(2)}$. They can be expressed in terms of the five components of the symmetric trace-less 2nd rank tensor defined in cartesian coordinates, e.g.

$$T_{ik} = x_{ik} - \frac{1}{3}r^2\delta_{ik} \ , \ i,k = x,y,z \ , \tag{52}$$

and $SpT_{ik} = 0$. The corresponding relations are:

$$\begin{aligned} T_0^{(2)} &= 3T_{33} \\ T_{\pm1}^{(2)} &= \mp\sqrt{6}(T_{13} \pm \mathrm{i}T_{23}) \\ T_{\pm2}^{(2)} &= \sqrt{6}(T_{11} + \tfrac{1}{2}T_{33} \pm \mathrm{i}T_{12}) \ . \end{aligned} \tag{53}$$

In particular, the tensors of the rank 2 are related to spherical harmonics:

$$T_q^{(2)} = \sqrt{\frac{16\pi}{5}}\mathcal{Y}_{2q}(\vec{r}) \ . \tag{54}$$

For example, the quadrupole moment of the atom with Z electrons is usually defined as a symmetric 2nd rank tensor

$$Q_{ik} = \sum_{\alpha=1}^{Z} e_\alpha \left(3x_{i\alpha}x_{k\alpha} - \delta_{ik}r_\alpha^2\right) \ . \tag{55}$$

In general, the operators (13) are examples of tensorial operators of rank l.

The *tensor product* of two irreducible operators $U^{(k_1)}$ and $V^{(k_2)}$ can be defined as

$$[U^{(k_1)} \times V^{(k_2)}]_q^{(k)} = \sum_{q_1,q_2} (k_1 q_1 k_2 q_2 | kq) U_{q_1}^{(k_1)} V_{q_2}^{(k_2)} \, . \tag{56}$$

The *scalar product* of two irreducible operators $U^{(k)}$ and $V^{(k)}$ can be defined as

$$(U^{(k)} \times V^{(k)}) \equiv (-1)^k \sqrt{2k+1} [U^{(k)} \times V^{(k)}]_0^{(0)} = \sum_q (-1)^q U_q^{(k)} V_{-q}^{(k)} \, . \tag{57}$$

The following formulae are useful for the calculations of matrix elements of different operators in quantum mechanics (of interaction or of transition operators).

1. If operators $U^{(k_1)}$ and $V^{(k_2)}$ act of the same coordinates of a system, then

$$\langle \alpha j ||[U^{(k_1)} \times V^{(k_2)}]^{(k)} || \alpha' j' \rangle = \sqrt{2k+1} (-1)^{j+j'+k} \times \sum_{\alpha'',j''} \langle \alpha j || U^{(k_1)} || \alpha'' j'' \rangle \langle \alpha'' j'' || V^{(k_2)} || \alpha' j' \rangle \left\{ \begin{array}{ccc} k_1 & k_2 & k \\ j' & j & j'' \end{array} \right\} . \tag{58}$$

   Here α refers to the other quantum numbers.

2. For a scalar product we have

$$\langle \alpha j || (U^{(k)} \cdot V^{(k)}) || \alpha' j' \rangle = \frac{\delta_{jj'}}{\sqrt{2j+1}} \sum_{\alpha'',j''} (-1)^{j+j''} \langle \alpha j || U^{(k)} || \alpha'' j'' \rangle \langle \alpha'' j'' || V^{(k)} || \alpha' j' \rangle \, . \tag{59}$$

3. If operators $U^{(k_1)}$ acts on the coordinates of the functions related to the angular momentum j_1 and $V^{(k_2)}$ acts on the coordinates of the functions related to the angular momentum j_2, then

$$\langle \alpha j_1 j_2; j ||[U^{(k_1)} \times V^{(k_2)}]^{(k)} || \alpha' j_1' j_2'; j' \rangle = \sum_{\alpha''} \left\{ \begin{array}{ccc} j_1 & j_2 & j \\ j_1' & j_2' & j' \\ k_1 & k_2 & k \end{array} \right\} \times \sqrt{(2j+1)(2j'+1)(2k+1)} \langle \alpha j_1 || U^{(k_1)} || \alpha'' j_1' \rangle \langle \alpha'' j_2 || V^{(k_2)} || \alpha' j_2' \rangle \tag{60}$$

   (the sum over α'' is included in case both operators acts on the same quantum number α).

4. For the scalar product of two operators $U^{(k)}$ and $V^{(k)}$ acting on the coordinates of the functions related to the angular momenta j_1 and j_2, respectively, we have

$$\langle \alpha j_1 j_2; jm | (U^{(k)} \cdot V^{(k)}) | \alpha' j_1' j_2'; j' m' \rangle = \delta_{jj'} \delta_{mm'} (-1)^{j_2 + j_1' + 2k + j} \left\{ \begin{array}{ccc} j_1 & j_2 & j \\ j_2' & j_1' & k \end{array} \right\} \times \sum_{\alpha''} \times \langle \alpha j_1 || U^{(k)} || \alpha'' j_1' \rangle \langle \alpha'' j_2 || V^{(k)} || \alpha' j_2' \rangle \, . \tag{61}$$

3 Conservation laws

The observable T is said to conserve if its mean value does not change in time in any state $\psi(\vec{r},t)$.

$$\begin{aligned} \frac{d}{dt}\langle\psi|\hat{T}|\psi\rangle &= \langle\frac{d}{dt}\psi|\hat{T}|\psi\rangle + \langle\psi|\hat{T}|\frac{d}{dt}\psi\rangle \\ &= \frac{1}{1\hbar}\{-\langle\hat{H}\psi|\hat{T}|\psi\rangle + \langle\psi|\hat{T}|\hat{H}\psi\rangle\} \\ &= \frac{1}{1\hbar}\langle\psi|[\hat{T},\hat{H}]|\psi\rangle = 0\ . \end{aligned} \tag{62}$$

This means that the observable T conserves if the operator $\hat{T}$ commutes with the Hamiltonian.

If the system possesses a certain symmetry, i.e. the Hamiltonian is invariant with respect to a group $\mathbf{G}$, then for all elements G, the transformation operators $D(G)$ commute with the Hamiltonian. At first glance, this suggests an existence of a huge number of conserved quantities. However, not all of them are independent. For example, the conservation of $D(G_3)$ relates to the conservation of $D(G_1)$ and $D(G_2)$ if $G_1 \cdot G_2 = G_3$. So, if the group $\mathbf{G}$ is of order n and $m \leq n$ elements of the group generate the rest of n elements, then the system will have only m conserved values, or integrals of motion.

Example

All elements of the group $\mathbf{C}_3$ can be generated from one element C_3, since $C_3 \cdot C_3 = C_3^2$, $C_3 \cdot C_3^2 = E$. Thus, the invariance of a system with respect to the group $\mathbf{C}_3$ will give rise to one conserving quantity.

References

[1] L.D.Landau, E.M.Lifshitz, *Quantum Mechanics. Non-Relaticistic Theory.* (Addison-Wesley Publishing Company, Inc., reading, MA., 1958).

[2] E.Wigner, *Group Theory and its Application to the Quantum Mechanics of Atomic Spectra* (Academic, New York, 1959).

[3] M.Hamermesh, *Group Theory and its Application to Physical Problems* (Addison-Wesley Reading, MA, 1962).

[4] J.P.Elliott, P.G.Dawber, *Symmetry in Physics* (The Macmillan Press, London, 1979).

[5] A.Frank, P. Van Isacker, *Algebraic Methods in Molecular and Nuclear Structure Physics* (John Wesley and Sons, Inc, 1994).