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GROUP THEORY—THE ROTATION GROUP

FEW subjects in modern physics have been more extensively studied and have a wider field of applications than the theory of representations of the group of spatial rotations, and the reader is likely to be already familiar with the subject. Two truly great books, *Group theory* (Wigner 1959) and *Irreducible tensorial sets* (Fano and Racah 1958), contain all the information on this subject that we might require. Excellent books such as *Quantum mechanics* (Messiah 1961) and more specifically *Group theory* (Tinkham 1964) and *Angular momentum in quantum mechanics* (Edmonds 1957), to name but three, also give a clear and comprehensive review of the subject. The importance of the group of spatial rotations for the study of paramagnetic resonance stems from the fact that although a paramagnetic ion embedded in bulk matter does not enjoy full rotational symmetry, the starting point for its study is the free ion. The wave-functions of the free ion do transform according to representations of the rotation group and the calculation of matrix elements between two such functions is greatly simplified by this fact. The sole aim of the developments to be given below is to remind the reader of those properties that are of direct interest for the calculation of wave-functions of low-lying energy levels of paramagnetic ions in the surroundings in which they are usually found in nature. Far more sophisticated developments based chiefly on the work of Racah and his school are utilized in atomic spectroscopy (see, for example, Judd (1963b)) but are not of immediate concern to us.

13.1. Angular momentum

Consider an electronic system with a Hamiltonian $\mathscr{H} = \mathscr{H}(\mathbf{p}_i, \mathbf{r}_i, \mathbf{s}_i)$ which may contain forces dependent on the spins $\mathbf{s}_i$ of the individual electrons. It is well known that the total angular momentum of the system, $\mathbf{J}$, is a Hermitian vector operator defined by

$$\begin{cases} \hbar\mathbf{J} = \hbar\mathbf{L}+\hbar\mathbf{S} = \sum_i (\hbar\mathbf{l}_i+\hbar\mathbf{s}_i), \\ \quad = \sum_i \mathbf{r}_i \wedge \mathbf{p}_i + \hbar \sum_i \mathbf{s}_i. \end{cases} \tag{13.1}$$

If the system is in a state described by a wave-function $\Psi(\mathbf{r}_i, \sigma_i)$ where the σ_i are the spin variables, the definition (13.1) enables one to calculate the wave-function resulting from the operation on Ψ of any

of the components J_x, J_y, J_z of $\mathbf{J}$. It is also well known that the components of $\mathbf{J}$ obey the commutation rules $[J_x, J_y] = \mathrm{i}J_z$, etc.

From these commutation rules it can be deduced that the operator $\mathbf{J}^2 = J_x^2 + J_y^2 + J_z^2$ commutes with the three components of $\mathbf{J}$ and that it has eigenvalues of the form $j(j+1)$ where j is an integer or half integer. For brevity we shall call (somewhat incorrectly) j an eigenvalue of the operator $\mathbf{J}$. For each value of j there are $(2j+1)$ states such that $\mathbf{J}^2 = j(j+1)$.

Since J_z commutes with $\mathbf{J}^2$, these states can be specified by the eigenvalues of $J_z = m$ and it can be shown that m can take the values $m = j, j-1, \ldots, -j$. If we take as basis functions $\Psi_{j,m} = |j, m\rangle$, which are eigenfunctions of $\mathbf{J}^2$ and J_z, it is possible to choose their phases in such a way that

$$\langle j, m|\, J_\pm\, |j, m\mp 1\rangle = \{j(j+1) - m(m\mp 1)\}^{\frac{1}{2}}, \tag{13.2a}$$

where $J_\pm = J_x \pm \mathrm{i}J_y$, and also

$$\langle j, m|\, J_z\, |j, m\rangle = m. \tag{13.2b}$$

The commutation relations are a consequence of the fact that under infinitesimal rotation by an angle ε around an axis, say Oz, the wavefunction Ψ is changed into a function

$$\Phi = (1 - \mathrm{i}\epsilon J_z)\Psi. \tag{13.3}$$

Indeed, although the definition (13.1) for $\mathbf{J}$ is the more usual one, it would be more logical to derive it as a consequence of (13.3). It follows from (13.3) that a finite rotation by an angle φ around an axis of unit vector $\mathbf{n}$, transforms Ψ into a function

$$\Phi = \mathrm{e}^{-\mathrm{i}\varphi(\mathbf{n}.\mathbf{J})}\Psi. \tag{13.4}$$

Since $\mathbf{J}^2$ commutes with the three components of $\mathbf{J}$ it also commutes with all rotational operators $R = \exp\{-\mathrm{i}\varphi(\mathbf{n} \cdot \mathbf{J})\}$. It follows that if a function $\Psi_{j,m}$ is an eigenstate of $\mathbf{J}^2$ so is $R\Psi_{j,m}$ and, since there are $(2j+1)$ linearly independent functions $\Psi_{j,m}$,

$$R\Psi_{j,m} = \sum_{m'=-j}^{j} D^j_{m'm}(R)\Psi_{j,m'}. \tag{13.5}$$

The $2j+1$ functions $\Psi_{j,m}$, where m takes the values $j, j-1, \ldots, -j$, provide a representation of the rotation group of order $2j+1$ which is denoted as $\mathscr{D}^j$. It can be shown that these representations are irreducible and that the rotation group has no other representations. It is often

convenient to specify a rotation by the well-known Euler angles, already mentioned in § 12.3.

It can be shown by a straightforward geometrical reasoning (see for instance Edmonds (1957)) that to a rotation specified by these three angles there corresponds an operator

$$R(\alpha, \beta, \gamma) = \mathrm{e}^{-\mathrm{i}\alpha J_z}\mathrm{e}^{-\mathrm{i}\beta J_y}\mathrm{e}^{-\mathrm{i}\gamma J_z}. \tag{13.6}$$

13.2. The irreducible representations

Consider more particularly the case $j = \frac{1}{2}$ when (13.6) can be written

$$R(\alpha, \beta, \gamma) = \mathrm{e}^{-\mathrm{i}(\alpha/2)\sigma_z}\mathrm{e}^{-\mathrm{i}(\beta/2)\sigma_y}\mathrm{e}^{-\mathrm{i}(\gamma/2)\sigma_z}, \tag{13.7}$$

where σ_x, σ_y, σ_z are the well-known Pauli matrices. Inside the manifold $\Psi_{j,m}$ where $j = \frac{1}{2}$, $m = \pm\frac{1}{2}$ it is easy to show that the matrix representing (13.7) is

$$D^{\frac{1}{2}}(\alpha, \beta, \gamma) = \begin{pmatrix} \mathrm{e}^{-\mathrm{i}(\alpha+\gamma)/2} \cos\dfrac{\beta}{2} & -\mathrm{e}^{-\mathrm{i}(\alpha-\gamma)/2} \sin\dfrac{\beta}{2} \\ \mathrm{e}^{-\mathrm{i}(\alpha-\gamma)/2} \sin\dfrac{\beta}{2} & \mathrm{e}^{-\mathrm{i}(\alpha+\gamma)/2} \cos\dfrac{\beta}{2} \end{pmatrix}. \tag{13.8}$$

This follows immediately from (13.7) through the relation

$$\mathrm{e}^{-\mathrm{i}(\beta/2)\sigma_y} = \cos\frac{\beta}{2} - \mathrm{i}\sigma_y \sin\frac{\beta}{2}. \tag{13.9}$$

An inspection of the matrix (13.8) shows that it is unitary (as indeed it must be since it represents a unitary operator) and that its determinant is equal to unity. Conversely it can be shown that any unitary matrix u with determinant equal to unity can be cast in the form (13.8). It is also often written in the form

$$\begin{pmatrix} a & b \\ -b^* & a^* \end{pmatrix} \text{ with } aa^* + bb^* = 1, \tag{13.10}$$

which exhibits its properties; (13.10) can be rewritten as

$$\begin{pmatrix} \alpha' + \mathrm{i}\beta' & \gamma' + \mathrm{i}\delta' \\ -\gamma' + \mathrm{i}\delta' & \alpha' - \mathrm{i}\beta' \end{pmatrix} \tag{13.11}$$

with $\alpha'^2 + \beta'^2 + \gamma'^2 + \delta'^2 = 1$, or in the operator form

$$\alpha' + \mathrm{i}\beta'\sigma_z + \mathrm{i}\delta'\sigma_x + \mathrm{i}\gamma'\sigma_y. \tag{13.12}$$

Unitary matrices u with a determinant equal to unity clearly form a

group U that is called the unitary unimodular group. We can thus say that U and $\mathscr{D}^{\frac{1}{2}}$ are the same group. The correspondence between this group and the group of spatial rotations is established as follows: every two-dimensional Hermitian matrix h with zero trace can be written

$$\begin{aligned} h &= \mathbf{r} \cdot \boldsymbol{\sigma} = x\sigma_x + y\sigma_y + z\sigma_z \\ &= \begin{pmatrix} z & x - \mathrm{i}y \\ x + \mathrm{i}y & -z \end{pmatrix}, \end{aligned} \tag{13.13}$$

where the coefficients x, y, z are real and its determinant is $-(x^2+y^2+z^2)$. Consider the matrix

$$h' = uhu^+ \tag{13.14}$$

where u is unitary and unimodular. h' is clearly Hermitian and also has trace zero. It can therefore be written as

$$h' = x'\sigma_x + y'\sigma_y + z'\sigma_z = \mathbf{r}' \cdot \boldsymbol{\sigma},$$

where x', y', z' are real; as is apparent from (13.14) they are linear functions of x, y, z with coefficients that are necessarily real and depend on the elements of the matrix u in a manner we need not specify. The determinant of h', $-(x'^2+y'^2+z'^2)$ is equal to that $-(x^2+y^2+z^2)$ of h. It is therefore clear that the relation resulting from (13.14), between x', y', z' and x, y, z or $\mathbf{r}' = R_u\mathbf{r}$, is a real orthogonal matrix. It will be a spatial rotation if its determinant is $+1$, which is easy to check by a direct calculation.

From the relations

$$h = \mathbf{r} \cdot \boldsymbol{\sigma}, \qquad h' = uhu^+ = \mathbf{r}' \cdot \boldsymbol{\sigma}, \qquad r' = R_u\mathbf{r},$$

we have

$$h'' = vh'v^+ = (vuhu^+v^+) = \mathbf{r}''.\boldsymbol{\sigma},$$

or

$$\mathbf{r}'' = R_v\mathbf{r}' = R_vR_u\mathbf{r},$$

and it follows that if to the matrix u there corresponds the rotation R_u and to the matrix v the rotation R_v, to the product uv there corresponds the rotation R_uR_v. On the other hand, the correspondence between the matrix u and the rotation R_u is not one-to-one for it appears from the relation (13.14), which actually specifies R_u, that a change of u into $-u$ does not change h' and therefore leaves R_u unchanged. Hence to each rotation R_u there correspond two matrices u and $-u$. In particular, to the element unity of the rotation group there correspond the two

matrices $\begin{pmatrix} 1 & \\ & 1 \end{pmatrix}$ and $\begin{pmatrix} -1 & \\ & -1 \end{pmatrix}$. It follows that $\mathscr{D}^{\frac{1}{2}}$ is not strictly speaking a representation of the group of spatial rotations: it is what is called a two-valued representation. This appears very clearly in formula (13.8) since an increase of, say, α by an angle 2π, which brings the system (or the coordinate axes) back into the original position, changes $D^{\frac{1}{2}}$ into $-D^{\frac{1}{2}}$. The fact that a rotation by an angle 2π leads to a change in the sign of the wave-function is not a paradox. The value Ψ of the wave-function is not a physically observable quantity as contrasted for instance with $|\Psi|^2$, which is observable and indeed remains unchanged under a rotation through 2π. The same two-valuedness applies to all representations D^j when j is half an odd integer (we shall say for brevity half-integer). This is seen most easily by considering rotations around the z-axis when the rotation operator can be written $e^{-i\varphi J_z}$. This operator acting upon a wave-function $|j, m\rangle$ multiplies it by $e^{-i\varphi m}$, which is -1 for $\varphi = 2\pi$ if j is half integer.

It is thus more correct to say that the representations D^j are representations of the group U, which is the group of the matrices $u = D^{\frac{1}{2}}$. To each matrix u there corresponds a single spatial rotation R_u and a single matrix $D^j(R_u)$ for each j. On the other hand, corresponding to two opposite matrices u and $-u$ we have the same rotation R_u, the single matrix $D^j(R_u)$ for j integer, and two opposite matrices $\pm D^j(R_u)$ if j is half-integer.

It is useful to know the matrix elements $D^j_{mm'}(R)$ which, according to (13.5), determine the transformation of the wave-functions $\Psi_{j,m} = (j, m)$, which for a free ion are eigenstates of the energy and thus form a convenient basis for the study of the bound ion. For $j = \frac{1}{2}$ they are given by (13.8). For higher values of j they have no simple analytical form and the usual advice of looking them up in tables still holds. At a pinch they can be calculated using the following remarks. The relation

$$\begin{aligned} D^j_{m'm}(\alpha, \beta, \gamma) &= \langle jm' |\, e^{-i\alpha J_z} e^{-i\beta J_y} e^{-i\gamma J_z} \,| jm \rangle \\ &= e^{-i(\alpha m' + \gamma m)} \langle jm' |\, e^{-i\beta J_y} \,| jm \rangle \\ &= e^{-i(\alpha m' + \gamma m)} D^j_{mm'}(0, \beta, 0), \end{aligned} \tag{13.15}$$

shows that only the simpler quantity $d^j_{mm'}(\beta) = D^j_{mm'}(0, \beta, 0)$ need be computed. Its evaluation is greatly facilitated by the following property that we quote without proof. Let ξ and η be the two components of a two-dimensional vector that transform through the $D^{\frac{1}{2}}$ matrices. It can

be shown that the $2j+1$ quantities

$$\frac{\xi^{j+m}\eta^{j-m}}{\sqrt{\{(j+m)!\,(j-m)!\}}}$$

with $m = j, j-1, \ldots, -j$ transform according to the matrices $D^j_{mm'}$. This provides a method of calculating the latter, knowing $D^{\frac{1}{2}}$.

The characters of the representation D^j are easiest to calculate by considering the rotations through an angle φ around the z-axis. Rotations through the same angle φ around another axis belong to the same class and have the same characters. The operator R takes the form $e^{-i\varphi J_z}$ and

$$D^j_{m'm}(R) = \delta_{mm'}e^{-im\varphi},$$

whence

$$\chi^j(\varphi) = \sum_{m=-j}^{j} e^{-im\varphi} = \frac{\sin(j+\frac{1}{2})\varphi}{\sin(\frac{1}{2}\varphi)}. \tag{13.16}$$

13.3. The coupling of angular momenta

Clebsch–Gordan and Wigner coefficients

The coupling of angular momenta is one of the best known laws of physics. Given two angular momenta $\mathbf{j}_1$ and $\mathbf{j}_2$ with eigenvalues j_1, j_2 the vector $\mathbf{j} = \mathbf{j}_1+\mathbf{j}_2$ has eigenvalues $j = j_1+j_2, j_1+j_2-1, \ldots, |j_1-j_2|$. In particular, the value $j = 0$ appears only if $j_1 = j_2$.

From the viewpoint of group representation it has the following meaning. Consider two sets of wave-functions $\Psi_{j_1m_1} = |j_1m_1\rangle$ and $\Psi_{j_2m_2} = |j_2m_2\rangle$, which are respectively bases for the representations $\mathscr{D}^{j_1}$ and $\mathscr{D}^{j_2}$. The set of all the products $\Psi_{j_1m_1}\Psi_{j_2m_2}$ is a basis for the representation $\mathscr{D}^{j_1}\times\mathscr{D}^{j_2}$. This representation is reducible and contains the following irreducible representations:

$$\mathscr{D}^{j_1}\times\mathscr{D}^{j_2} = \mathscr{D}^{j_1+j_2}+\mathscr{D}^{j_1+j_2-1}+\ldots+\mathscr{D}^{|j_1-j_2|}. \tag{13.17}$$

An important point is that every representation $\mathscr{D}^j$ with

$$|j_1-j_2| \leqslant j < j_1+j_2$$

is contained only once in the decomposition (13.17).

The equation (13.17) has a symbolical character. Its matrix transcription is

$$S(D^{j_1}\times D^{j_2})S^{-1} = D^{j_1+j_2}+\ldots+D^{|j_1-j_2|}, \tag{13.18}$$

where S is a unitary matrix that relates the basic states $|j_1m_1\rangle|j_2m_2\rangle$ of $D^{j_1}\times D^{j_2}$ to the basic states $|j_1j_2jm\rangle$ with respect to which the matrices

of the representation $\mathscr{D}^{j_1} \times \mathscr{D}^{j_2}$ take the reduced quasi-diagonal form

$$\begin{pmatrix} D^{j_1+j_2} & & & \\ & \cdot & & \\ & & \cdot & \\ & & & D^{|j_1-j_2|} \end{pmatrix} \tag{13.19}$$

The elements of the matrix S are represented by the self-evident symbols $\langle j_1 m_1, j_2 m_2 \,|\, j_1 j_2, jm \rangle$, which are known in the literature as Clebsch–Gordan coefficients. Their properties have been studied extensively and tables of their numerical values have been prepared; we shall therefore be very brief on this subject. According to the vector coupling law they vanish unless $|j_1 - j_2| \leqslant j \leqslant j_1 + j_2$ and also if $m \neq m_1 + m_2$. The latter follows from the fact that a rotation by an angle φ around the z-axis multiplies $|j_1 m_1\rangle |j_2 m_2\rangle$ by $\mathrm{e}^{-i(m_1+m_2)\varphi}$ and $|j, m\rangle$ by $\mathrm{e}^{-im\varphi}$.

The phases of the various basis vectors can be chosen so that the Clebsch–Gordan coefficients are real, a point that is by no means trivial. From the unitary character of the S matrix, obvious orthogonality relations for the Clebsch–Gordan coefficients can be deduced such as, for instance,

$$\sum_{m_1 m_2} \langle j_1 j_2 m_1 m_2 \,|\, j_1 j_2 jm \rangle \langle j_1 j_2 m_1 m_2 \,|\, j_1 j_2 j'm \rangle = \delta_{jj'}. \tag{13.20}$$

Clebsch–Gordan coefficients possess somewhat complicated symmetry properties that are best exhibited by introducing related coefficients called Wigner coefficients or $3j$-symbols denoted by

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$$

with $m_1 + m_2 + m_3 = 0$ and defined by the relation

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \frac{(-1)^{j_1 - j_2 - m_3}}{\sqrt{(2j_3+1)}} \langle j_1 m_1 j_2 m_2 \,|\, j_1 j_2; j_3, -m_3 \rangle. \tag{13.21}$$

Wigner coefficients have very simple symmetry properties that are easy to memorize. An interchange of two columns multiplies a Wigner coefficient by $(-1)^{j_1+j_2+j_3}$ and so does the change of m_1, m_2, m_3 into $-m_1$, $-m_2$, $-m_3$. The more complicated symmetry properties of

Clebsch–Gordan coefficients can be obtained from these, using (13.21). It is worth noting that

$$\langle j_1 m_1 j_2 m_2 \,|\, j_1 j_2 j m\rangle \neq \langle j_2 m_2 j_1 m_1 \,|\, j_2 j_1 j m\rangle. \tag{13.22}$$

The following relations can be established between $|j_1 m_1\rangle|j_2 m_2\rangle$ and $|j_1 j_2 j m\rangle$.

$$|j_1 j_2 j m\rangle = (-1)^{j_2 - j_1 - m} \sum_{m_1 m_2} \sqrt{(2j+1)} \begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & -m \end{pmatrix} |j_1 m_1\rangle |j_2 m_2\rangle, \tag{13.23}$$

$$|j_1 m_1\rangle|j_2 m_2\rangle = \sum_{jm} (-1)^{j_2 - j_1 - m} \sqrt{(2j+1)} \begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & -m \end{pmatrix} |j_1 j_2 j m\rangle. \tag{13.24}$$

13.4. Multiple vector coupling and Racah symbols

Given three vectors $\mathbf{j}_1$, $\mathbf{j}_2$, $\mathbf{j}_3$ there is more than one way of coupling them to a value $\mathbf{j}$. Consider first the case when $\mathbf{j} = 0$. According to the laws of vector coupling this can only be achieved by coupling $\mathbf{j}_1$ and $\mathbf{j}_2$ to a value $\mathbf{j}_{12}$ equal to $\mathbf{j}_3$, or $\mathbf{j}_1$ and $\mathbf{j}_3$ to $\mathbf{j}_2$, or $\mathbf{j}_2$ and $\mathbf{j}_3$ to $\mathbf{j}_1$. The important point is that all these coupling schemes, within a phase factor ± 1, lead to the same non-degenerate state, invariant under spatial rotation.

The symbol $|j_1 j_2 j_3, 00\rangle$ represents the state of zero angular momentum where $\mathbf{j}_1$ and $\mathbf{j}_2$ are coupled to a value $\mathbf{j}_{12} = \mathbf{j}_3$ and $\mathbf{j}_{12}$ is then coupled to $\mathbf{j}_3$ to give $\mathbf{j} = 0$. It can be shown that the following relation holds:

$$|j_1 j_2 j_3, 00\rangle = \sum_{m_1 m_2} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} |j_1 m_1\rangle |j_2 m_2\rangle |j_3 m_3\rangle. \tag{13.25}$$

The symmetry of $|j_1 j_2 j_3, 00\rangle$ with respect to an interchange of two indices follows immediately from that of the Wigner coefficients: an interchange of two indices multiplies the result by $(-1)^{j_1+j_2+j_3}$.

We consider now the general case when the sum $\mathbf{J}$ of the three vectors $\mathbf{j}_1$, $\mathbf{j}_2$, $\mathbf{j}_3$ is different from zero. We wish to calculate the scalar product of the two states

$$\begin{cases} |a\rangle = |(j_1 j_2) j_{12}, j_3; JM\rangle, \\ \text{and} \\ |b\rangle = |j_1, (j_2 j_3) j_{23}; JM'\rangle, \end{cases} \tag{13.26}$$

where $|a\rangle$ is obtained by coupling $\mathbf{j}_1$ and $\mathbf{j}_2$ to a value $\mathbf{j}_{12}$ and the resulting vector $\mathbf{j}_{12}$ to $\mathbf{j}_3$ to give $\mathbf{J}$ and $|b\rangle$ by first coupling $\mathbf{j}_2$ and $\mathbf{j}_3$ to $\mathbf{j}_{23}$. Since $|a\rangle$ and $|b\rangle$ are two basis states that both belong to the same irreducible

representation D^J, their scalar product vanishes if $M \neq M'$ and is independent of M if $M = M'$. This is a special case of eqn (12.33) where V is taken equal to unity. We can then drop the index M and write the product $\langle a \mid b \rangle$ as

$$\langle a \mid b \rangle = \langle (j_1 j_2) j_{12}, j_3, J \mid j_1, (j_2 j_3) j_{23}, J \rangle. \tag{13.27}$$

Racah introduces a function of six variables

$$\begin{pmatrix} j_1 & j_2 & j_{12} \\ j_3 & J & j_{23} \end{pmatrix}$$

called the six-j symbol which is essentially just this scalar product apart from a numerical factor. By definition of the six-j symbol, we have

$$\langle (j_1 j_2) j_{12}, j_3, J \mid j_1, (j_2 j_3) j_{23}, J \rangle \equiv (-1)^{j_1+j_2+j_3+J} \sqrt{\{(2j_{12}+1)(2j_{23}+1)\}} \begin{pmatrix} j_1 & j_2 & j_{12} \\ j_3 & J & j_{23} \end{pmatrix}. \tag{13.28}$$

We shall not attempt to give an analytical expression for the six-j symbol, which is rather complicated. Numerical values have been tabulated by Rotenberg, Bivins, Metropolis, and Wooten (1959). The six-j symbol

$$\begin{pmatrix} a & b & c \\ d & e & f \end{pmatrix}$$

has some remarkable symmetry properties that are easily memorized by means of the so-called tetrahedron diagram. Construct a tetrahedron and call the three edges of any one plane a, b, c and the three opposite edges respectively d, e, f. The symbol

$$\begin{pmatrix} a & b & c \\ d & e & f \end{pmatrix}$$

has the symmetry of this figure. For instance, selecting another plane, say aef, we obtain the symbol

$$\begin{pmatrix} a & e & f \\ d & b & c \end{pmatrix},$$

which is equal to the former.

From the definition (13.28) of the six-j symbol it appears that they can be expressed in a straightforward manner as a sum of products of four Clebsch–Gordan coefficients. We shall not write down these expressions explicitly.

13.5. Irreducible tensor operators, the Wigner-Eckart theorem, and equivalent operators

Consider an operator T that acts on a wave-function Ψ, the result being another function Φ as symbolized by the equation

$$\Phi = T\Psi. \tag{13.29}$$

Let R be a transformation belonging to a group G that transforms Ψ into $\overline{\Psi}$ and Φ into $\overline{\Phi}$ according to $\overline{\Psi} = R\Psi$, $\overline{\Phi} = R\Phi$. From (13.29) we obtain for the relationship between $\overline{\Phi}$ and $\overline{\Psi}$,

$$\overline{\Phi} = RTR^{-1}\overline{\Psi} = \overline{T}\overline{\Psi}. \tag{13.30}$$

The operator $\overline{T} = RTR^{-1}$ is said to be the transform of T under the transformation R.

A very important class of operators are the irreducible tensors. By definition, a tensor operator T_k of order k is a set of $2k+1$ operators T_k^q, where $q = k, k-1, \ldots, -k$, which under the group of spatial rotations transform according to the representation $\mathscr{D}^k$; i.e.,

$$RT_k^qR^{-1} = \sum_{q'} D^k_{q'q}(R)T_k^{q'}. \tag{13.31}$$

The simplest tensor operator is a scalar, invariant under spatial rotations, with a single component. Next come vectors with three components, etc.

If we take for R the infinitesimal rotations $R = 1 - i\varepsilon J_z$ and $R = 1 - i\varepsilon J_\pm$, we obtain from (13.31),

$$(1 - i\varepsilon J_z)T_k^q(1 + i\varepsilon J_z) = \sum_{q'} (kq'|\ 1 - i\varepsilon J_z\ |kq)T_k^{q'}, \tag{13.32}$$

$$(1 - i\varepsilon J_\pm)T_k^q(1 + i\varepsilon J_\pm) = \sum_{q'} (kq'|\ 1 - i\varepsilon J_\pm\ |kq)T_k^{q'}. \tag{13.33}$$

Expansion of these relations, neglecting terms of order ε^2, gives, using equations (13.2),

$$\begin{cases} [J_z, T_k^q] = qT_k^q, \\ [J_\pm, T_k^q] = \{k(k+1) - q(q\pm 1)\}^{\frac{1}{2}} T_k^{q\pm 1}. \end{cases} \tag{13.34}$$

The importance of irreducible tensors stems from the following theorem known in the literature as the Wigner–Eckart theorem. Given a tensor operator T_k^q, consider the set of all the matrix elements $(\alpha jm|\ T_k^q\ |\alpha' j'm')$ where α and α' stand for any extra parameters that may be necessary to specify the states $|jm\rangle$ and $|j'm'\rangle$. For fixed values of α, j, k, α', j', k' there are altogether $(2j+1)(2k+1)(2j'+1)$ such matrix elements. The Wigner–Eckart theorem states that all these

matrix elements are uniquely determined within a single multiplying factor. The proof is as follows. Let us for brevity represent the matrix element $(\alpha jm|\ T_k^q\ |\alpha' j' m')$ as f_i, the index i standing for the indices m, q, m'. Under a rotation of the coordinate axes, f_i transforms according to the triple direct product $D^{j*} \times D^k \times D^{j'}$. We can reduce this product by a similarity transformation to a sum of irreducible representations D^J by introducing a set of symbols $g_M^{\beta J}$ which transform according to D^J and are linear combinations of the f_i,

$$\begin{cases} f_i = \sum\limits_{J,\beta} (i \mid \beta JM) g_M^{\beta J}, \\ g_M^{\beta J} = \sum\limits_i (\beta JM \mid i) f_i. \end{cases} \tag{13.35}$$

The index β takes into account the fact that in the reduction of the product $D^{j*} \times D^k \times D^{j'}$ to $\sum D^J$, a given value J may appear more than once. The value $J = 0$, however, can appear only once since there is only one way of coupling three angular momenta to zero and the first formula (13.35) can be rewritten:

$$f_i = \sum_{\beta, J \neq 0} (i \mid \beta JM) g_M^{\beta J} + (i \mid 00) g_0^0. \tag{13.36}$$

The coefficients $(i \mid \beta JM)$ depend solely on the properties of the rotation group and are independent of the tensor T_k^q and of the parameters α, α' needed to specify the states $|\alpha jm\rangle$ and $|\alpha' j' m'\rangle$. In particular, the coefficient $(i \mid 00)$ is, according to eqn (13.25) for the invariant triple product, proportional to the Wigner coefficient

$$\begin{pmatrix} j & k & j' \\ -m & q & m' \end{pmatrix}$$

times a phase factor $(-1)^{j-m}$. Here the change of m into $-m$ in the Wigner coefficient, and the phase factor, are due to the fact that in the matrix element $(jm|\ T_k^q\ |j' m')$ it is the complex conjugate function Ψ_j^{m*} that appears.

Using the symmetry properties of the Wigner coefficients and the definition (13.21), we find

$$\begin{aligned} (-1)^{j-m} \begin{pmatrix} j & k & j' \\ -m & q & m' \end{pmatrix} &= (-1)^{j-m} (-1)^{j+k+j'} \begin{pmatrix} j' & k & j \\ m' & q & -m \end{pmatrix} \\ &= (-1)^{j-m+j+k+j'+j'-k+m} \frac{\langle j' m' kq \mid j' qjm \rangle}{\sqrt{(2j+1)}} = \frac{\langle j' m' kq \mid j' qjm \rangle}{\sqrt{(2j+1)}}. \end{aligned} \tag{13.37}$$

On the other hand, a matrix element such as f_i does *not* depend on the orientation of the coordinate axes since it is an integral over space (and possibly spin) variables and a rotation of the axes is simply a change of integration variables. This is only possible if in (13.35) and (13.36) all the $g_M^{\beta J}$ with $J \neq 0$ vanish, whence $f_i = (i \mid 00) g_0^0$ which establishes the theorem, since a single constant g_0^0 distinguishes the set of matrix elements of T_k^q from those of another tensor operator of the same order k.

The gist of the proof is that in the reduction of the triple product $D^{j^*} \times D^k \times D^{j'}$ the unit representation D^0 appears only once. We shall see later that for groups of lower symmetry this is not always true and that matrix elements of the form $(\Psi_\alpha | V_\beta | \Psi_\gamma)$, where Ψ_α, V_β, Ψ_γ belong to three representations of, say, the cubic group, may require more than one constant.

The Wigner–Eckart theorem is usually expressed in the following form, consistent with (13.37),

$$(\alpha jm | T_k^q | \alpha' j' m') = \frac{1}{\sqrt{(2j+1)}} (\alpha j \| T_k \| \alpha' j') \langle j' m', kq \mid j' k; jm \rangle, \quad (13.38)$$

where $(\alpha j \| T_k \| \alpha' j')$ is independent of the magnetic quantum numbers m', q, m. The factor $1/\sqrt{(2j+1)}$ could equally well be included in its definition; we conform to the usual practice in leaving it out. Once a single matrix element $(\alpha j m_0 | T_k^{q_0} | \alpha' j' m_0')$ has been calculated for one set of magnetic quantum numbers m_0, q_0, m_0' (this is the hard part), all the other matrix elements can be computed from (13.38) if a numerical table of the relevant Clebsch–Gordan coefficients is available.

A slightly different way of applying the Wigner–Eckart theorem, sometimes more convenient than the direct use of formula (13.38), especially for the calculation of diagonal matrix elements $j = j'$, $\alpha = \alpha'$, is the so-called method of operator equivalents. Consider a component S_k^q of a tensor operator whose matrix elements are for some reason particularly easy to compute such as, for instance,

$$S_2^0 = 3J_z^2 - J(J+1)$$

for which

$$(\alpha jm | S_2^0 | \alpha jm') = \delta_{mm'} \{3m^2 - J(J+1)\}. \quad (13.39)$$

If we are interested in, say, the operator $T_2^0 = \sum_p (3z_p^2 - r_p^2)$ where the summation is over all the electrons of the ion, the Wigner–Eckart theorem enables us to write that inside the manifold $|\alpha, j)$.

$$T_2^0 = \beta S_2^0,$$

Here the constant β may be obtained by calculating the expectation value of T_2^0 over a selected substate $|\alpha, j, m_0)$ and writing

$$\beta\{3m_0^2-j(j+1)\} = (\alpha, j, m_0|\ T_2^0\ |\alpha, j, m_0)$$
$$= \int \Psi^*(\mathbf{r}) \left|\sum_p (3z_p^2-r_p^2)\right| \Psi(\mathbf{r})\, \mathrm{d}\tau. \quad (13.40)$$

The method of operator equivalents is also convenient when a non-standard set of components such as, for instance, Cartesian tensor components are used for the tensor operators. As an example, consider a vector with three Cartesian components V_x, V_y, V_z. The three linear combinations of these components which transform under rotation in a standard way by means of the matrices $D^1_{mm'}$ are

$$V_1^0 = V_z, \qquad V_1^1 = -\frac{V_x+\mathrm{i}V_y}{\sqrt{2}}, \qquad V_1^{-1} = \frac{V_x-\mathrm{i}V_y}{\sqrt{2}}. \quad (13.41)$$

Inside the manifold J we can write

$$V_1^0 = \beta J_z, \qquad V_1^1 = -\frac{\beta}{\sqrt{2}} J_+, \qquad V_1^{-1} = \frac{\beta}{\sqrt{2}} J_-, \quad (13.42)$$

which we can express in the condensed form $\mathbf{V} = \beta\mathbf{J}$ and use any set of components we please to express this relation in a coordinate form. (Anticipating the Wigner–Eckart theorem we already made use of this result in the calculation of the Landé factor in § 11.2.)

Similarly from the components of the vector $\mathbf{J}$ we can build up an irreducible tensor S_2 with components S_2^q given by

$$\begin{cases} S_2^0 = 3J_z^2-J(J+1), \\ S_2^{\pm 1} = \dfrac{\sqrt{6}}{2}(J_zJ_\pm+J_\pm J_z), \\ S_2^{\pm 2} = \dfrac{\sqrt{6}}{2} J_\pm^2, \end{cases} \quad (13.43)$$

and write that inside the manifold J all second-order irreducible tensors T_2^q have matrix elements proportional to those of S_2^q.

Here too it may be more convenient to introduce S_2 as a symmetrical traceless Cartesian tensor with components

$$S_{ik} = \tfrac{3}{2}(J_iJ_k+J_kJ_i)-J(J+1)\delta_{ik}, \quad (13.44)$$

and state that inside the manifold J any other symmetrical traceless tensor T_{ik} will be of the form $T_{ik} = \beta S_{ik}$. For instance the tensor T, for which

$$T_{ik} = \sum_p \{3x_i^p x_k^p-(r^p)^2\delta_{ik}\}, \quad (13.45)$$

where the x_i^p are the coordinates of the electrons of an atom, is called the electric quadrupole tensor of that atom and within a manifold J is proportional to the tensor (13.44).

The most cogent reason for preferring the equivalent operator formulation of the Wigner–Eckart theorem to the direct use of formula (13.38) is that most of the pioneer work in the field of magnetic resonance (including extensive and very useful numerical tables) is couched in that language. Despite some unfortunate inconsistencies of notation, such as the use of unnormalized spherical harmonics, we shall often use equivalent operators, pointing out occasionally the relationship with the more consistent notation of (13.38). A detailed study of the applications of this method to paramagnetic resonance is deferred until Chapter 16.

It may be useful to the reader to point out that Buckmaster (1962) has defined 'Racah operators' denoted by $\tilde{O}_k^q$ which correspond directly to the reduced spherical harmonics

$$C_k^q(\theta, \phi) = \{4\pi/(2k+1)\}^{\frac{1}{2}} Y_k^q(\theta, \phi)$$

and thus possess the consistency lacking in the operators defined by Stevens (1952a). Smith, and Thornley (1966) give a complete list of such operators up to $k = q = 6$, and their matrix elements are listed in Fortran notation by Birgeneau (1967b).