14

THE CUBIC GROUP AND SOME OTHER GROUPS

14.1. The cubic group

WE shall study this group in much greater detail than any other finite group, not only because cubic symmetry occurs quite often but even more so because it is the only type of symmetry for which the theory of group representations is really indispensable in paramagnetic resonance. This theory can often be dispensed with for environments of lower symmetry. Many of the results derived can be extended in a straightforward manner to other groups.

A level of a free ion with a given value J of its angular momentum and therefore a degeneracy of order $(2J+1)$ is spanned by a representation D^J of the rotation group with characters given by (13.16):

$$\chi^J(\varphi) = \sin\{(J+\tfrac{1}{2})\varphi\}/\sin(\tfrac{1}{2}\varphi).$$

In order to discover how this level is split in an environment of cubic symmetry we must obtain the irreducible representations of the cubic group O. We consider first the case when J is an integer. As we saw earlier, there is then a one-to-one correspondence between a rotation R and a matrix $D^J(R)$.

The cubic group O is the group of rotations that leaves invariant a cube or a regular octahedron. It contains the following classes:

E, the identity operation (1 element),

C_2, rotations through an angle π around the three axes perpendicular to the faces of the cube (3 elements),

C_4, rotations through the angles $\pm\pi/2$ around the same axes (6 elements),

C_2', rotations through π around the 6 axes passing through the centre points of opposite edges; these axes are parallel to the face-diagonals (6 elements),

C_3, rotations through angles $\pm(2\pi/3)$ around the 4 body-diagonals (8 elements).

We have altogether 24 elements and 5 classes. In contrast to the situation in the full rotation group, two rotations through the same angle but around two different axes X and Y do not belong to the same class if the rotation C that brings X to Y is not an element of the group. This is why the two rotations through an angle π, C_2, and C', belong to two different classes.

Since a regular octahedron is a figure obtained by joining the centres of the six faces of a cube it is clear that it is left invariant by the same group. Note also that each operation of O amounts to a permutation of the four body-diagonals. Hence the cubic group is isomorphic to the group of permutations S_4.

Since there are 5 classes and 24 elements, the cubic group has 5 irreducible representations with dimensions $l_1, \ldots, l_5$ which obey the relation

$$l_1^2+l_2^2+l_3^2+l_4^2+l_5^2 = 24. \tag{14.1}$$

It is easy to check that the only solution of (14.1) is the set of 5 integers 1, 1, 2, 3, 3. The corresponding representations are denoted in the literature by the symbols Γ_1, Γ_2, Γ_3, Γ_4, Γ_5 or A_1, A_2, E, T_1, T_2. The characters can be obtained by the method described in paragraph 12.4 and their values are listed in Table 1.

We shall see shortly that it is possible to choose the basis functions of the irreducible representations of O to be real. Then the unitary matrices of these representations become real orthogonal matrices (that the characters are all real in Table 1 is only a necessary condition). The calculation of matrix elements of the form $(\Psi_\alpha|\, V\, |\Psi_{\alpha'})$, where Ψ_α and $\Psi_{\alpha'}$ belong to representations Γ and Γ' of O, is facilitated by the knowledge of the reducibility of the direct products $\Gamma^*\times\Gamma'$ or, since all the Γ can be made real, of $\Gamma\times\Gamma'$. The results are given in Table 2. For diagonal direct products $\Gamma\times\Gamma$ we have indicated by a superscript S or A whether an irreducible representation Γ_i belongs to the symmetric or antisymmetric part of $\Gamma\times\Gamma$. This can be established by using the formulae (12.43) for the characters.

The formula (13.16) yields the following values for the characters of $D^J(R)$ where R is a rotation belonging to the cubic group,

$$\begin{aligned}
&\varphi = 0 && \chi(E) = 2J+1\\
&\varphi = \pi && \chi(C_2) = \chi(C_2') = (-1)^J\\
&\varphi = \pm\frac{\pi}{2} && \chi(C_4) = (-1)^{I(J/2)}\\
&\varphi = \pm\frac{2\pi}{3} && \chi(C_3) = \frac{\sin\left(\dfrac{2J+1}{3}\pi\right)}{\sin(\pi/3)}
\end{aligned} \tag{14.2}$$

where the symbol $I(J/2)$ means the integer part of $J/2$. With the help of

(14.2) and of the formulae (12.16), we obtain Table 3 for the reduction of D^J by the cubic group for integer values of J up to 10.

All free ions with an even number of electrons naturally have an integral value of J. However, even for an odd number of electrons, we saw earlier that in fields of intermediate strength such as occur in the iron group, the relevant quantum number of the free ion was not the total angular momentum J but the total orbital momentum L, which is always an integer. The wave-functions that span a representation D^J, where J is an integer, transform as the usual spherical harmonics. We observe in Table 3 that, up to and including $J = 4$, no representation appears more than once in D^J. The 'correct' zero-order wave-functions that span the various representations Γ_i are linear combinations of eigenfunctions of the free ion and can be obtained without explicit knowledge of the cubic Hamiltonian V for $J \leqslant 4$.

They are determined most conveniently by considering the functions

$$(p, q, r) = r^{2l+1}\frac{\partial^l(1/r)}{\partial x^p\, \partial y^q\, \partial z^r}, \tag{14.3}$$

with $p+q+r = l$. These functions are homogeneous polynomials of degree l which satisfy the Laplace equation. Equation (14.3) defines $(l+1)(l+2)/2$ such polynomials but the Laplace equation introduces $l(l-1)/2$ relations between them, leaving $(2l+1)$ independent polynomials.

$l = 1$

The three functions corresponding to (14.3) are (100), (010), (001), which are proportional to x, y, z. They clearly span a three-dimensional representation of the cubic group. A rotation of $\pi/2$ around Oz changes them into $-(010)$, (100), (001), and the trace of the transformation matrix is $\chi(C_4) = 1$, which from Table 1 shows that we are dealing with the representation Γ_4 and not with Γ_5. This can be seen directly from Table 3 since the representation D^1 reduces to Γ_4 under cubic symmetry.

$l = 2$

The functions (011), (101), (110) proportional to yz, zx, xy provide a three-dimensional representation of O that can only be Γ_5 since D^2 is split by O into Γ_3 and Γ_5.

The two-dimensional representation Γ_3 is spanned by the two orthogonal combinations (002) and $(1/\sqrt{(3)})\{(200)-(002)\}$ proportional to $3z^2-r^2$ and $\sqrt{(3)}(x^2-y^2)$. (The $\sqrt{3}$ factor ensures the same normalization for both functions.)

It is quite easy to see how the three wave-functions $\eta_x \propto yz$, $\eta_y \propto zx$, $\eta_z \propto xy$ transform under the cyclic permutations of (x, y, z), R and R^2; that is, under rotations through angles $2\pi/3$ and $4\pi/3$ respectively round the threefold axis (111). It is less easy to see how $\theta \propto (3z^2-r^2)$ and $\varepsilon \propto \sqrt{(3)}(x^2-y^2)$ transform under these conditions; we therefore quote the results

$$\begin{aligned} R\theta &= -\frac{1}{2}\theta+\frac{\sqrt{3}}{2}\varepsilon; & R^2\theta &= -\frac{1}{2}\theta-\frac{\sqrt{3}}{2}\varepsilon; \\ R\varepsilon &= -\frac{\sqrt{3}}{2}\theta-\frac{1}{2}\varepsilon; & R^2\varepsilon &= \frac{\sqrt{3}}{2}\theta-\frac{1}{2}\varepsilon. \end{aligned} \tag{14.4}$$

The first of these can easily be verified, for example, by noting that $(3z^2-r^2) = (2z^2-x^2-y^2)$ transforms into

$$(2x^2-y^2-z^2) = \tfrac{3}{2}(x^2-y^2)-\tfrac{1}{2}(2z^2-x^2-y^2).$$

$l = 3$

(111) proportional to (xyz) provides the unidimensional representation Γ_2. Γ_4 is spanned by the three functions (300), (030), (003) proportional to $x(3y^2+3z^2-2x^2)$, etc.

Γ_5 is spanned by the three orthogonal functions (102)–(120), (210)–(012), (021)–(201), proportional respectively to $x(y^2-z^2)$, etc.

$l = 4$

Here we quote just the results:

$$\Gamma_1 \ \{(x^4+y^4+z^4-\tfrac{3}{5}r^4),$$

$$\Gamma_3 \begin{cases} [z^4-\frac{1}{2}(x^4+y^4)-\frac{6}{7}r^2\sqrt{(5)}\{z^2-\frac{1}{2}(x^2+y^2)\}] \\ \dfrac{\sqrt{3}}{2}\left\{x^4-y^4-\dfrac{6}{7}\dfrac{\sqrt{(15)}}{2}(x^2-y^2)r^2\right\}, \end{cases}$$

$$\Gamma_5 \left\{xy\left(z^2-\frac{r^2}{7}\right)\right. \text{ and two cyclic permutations,}$$

$$\Gamma_4 \ \{xy(x^2-y^2) \text{ and two cyclic permutations.}$$

14.2. The fictitious angular momentum

Let $\mathbf{V}$ be a vector and consider the set of matrix elements $(\xi_i|\ V_k\ |\xi_j)$ where ξ_x, ξ_y, ξ_z are the three wave-functions spanning a representation Γ_4, which transform under O like x, y, z.

The vector components V_x, V_y, V_z that transform under rotations like x, y, z, also transform according to Γ_4 under O. Since the reduction of $\Gamma_4 \times \Gamma_4$ contains Γ_4 only once (see Table 2), it follows that all the matrix elements $(\xi_i|\, V_k\, |\xi_j)$ are uniquely determined within a proportionality factor. The same is true of the matrix elements $(\eta_i|\, V_k\, |\eta_j)$ where η_x, η_y, η_z span Γ_5 and transform like yz, zx, xy, since $\Gamma_5 \times \Gamma_5$ also contains Γ_4 only once. If we introduce the new functions $|\tilde{m}\rangle$ by the formulae

$$|\pm\tilde{1}\rangle = \mp\frac{\xi_x \pm i\xi_y}{\sqrt{2}}, \qquad |\tilde{0}\rangle = \xi_z,$$

or

$$|\pm\tilde{1}\rangle = \mp\frac{\eta_x \pm i\eta_y}{\sqrt{2}}, \qquad |\tilde{0}\rangle = \eta_z, \tag{14.5}$$

the matrix elements of $\langle\tilde{m}|\, A_k\, |\tilde{m}'\rangle$ will be proportional to those of an angular momentum $\tilde{l}$ with $\tilde{l} = 1$, sometimes called the fictitious angular momentum, that is,

$$\langle m|\, A_k\, |\tilde{m}'\rangle = \alpha\langle\tilde{l}, m|\, \tilde{l}_k\, |\tilde{l}, m'\rangle. \tag{14.6}$$

Table 2 shows that the reduction of the direct product $\Gamma_3 \times \Gamma_3$ does not contain Γ_4 and therefore a vector has no matrix elements within the doublet Γ_3, a fact sometimes expressed by saying that this doublet is non-magnetic. As above, we shall denote by θ and ε the two functions that span Γ_3 and transform under O like $3z^2 - r^2$ and $\sqrt{(3)}(x^2 - y^2)$.

For many purposes it is convenient to express the various states $|\tilde{m}\rangle$ that originate in the decomposition of a representation D^J as a linear combination of eigenstates $|J, m\rangle$, where $m = J_z$, the axis Oz being one of the C_2 axes of the cube. Table 4 gives these expressions up to $J = 4$. We have written $|m\rangle$ instead of $|J, m\rangle$ for brevity, since the value of J is indicated unambiguously in the table. Besides each representation Γ_4 and Γ_5 we have written the value α of the proportionality coefficient between $\mathbf{J}$ and the fictitious moment $\tilde{\mathbf{l}}$: that is, $\mathbf{J} = \alpha\tilde{\mathbf{l}}$.

14.3. The multiplets Γ_4 and Γ_5 in trigonal axes

If the cubic environment of an ion is distorted along the direction of one of the C_2 axes of the cube, say Oz, it is fairly obvious that the triplet Γ_4 will be split into a doublet spanned by ξ_x, ξ_y (or $|\tilde{1}\rangle$ and $|-\tilde{1}\rangle$) and a singlet $\xi_z = |\tilde{0}\rangle$. The same will be true for Γ_5, with the functions η instead of ξ. The functions ξ_i for Γ_4 and η_i for Γ_5 (or the functions $|\tilde{m}\rangle$ for both) are thus the 'correct' zero-order wave-functions for this distortion of cubic symmetry. On the other hand, for a trigonal distortion, that is a distortion along a body diagonal, it is preferable to use the following functions which will be the 'correct' zero-order functions:

$$\begin{aligned}|\tilde{1}\rangle_T &= a(\xi_x+\mathrm{e}^{2\pi i/3}\xi_y+\mathrm{e}^{4\pi i/3}\xi_z),\\ |\tilde{0}\rangle_T &= a(\xi_x+\xi_y+\xi_z),\\ |-\tilde{1}\rangle_T &= a(\xi_x+\mathrm{e}^{-2\pi i/3}\xi_y+\mathrm{e}^{-4\pi i/3}\xi_z),\end{aligned} \tag{14.7}$$

where a is a normalization constant (for Γ_5, we use η_x, η_y, η_z instead of ξ_x, ξ_y, ξ_z). The functions (14.7) can be obtained from Table 4, but it is preferable then to quantize J_z along a body diagonal. The results for this are given in Table 5 for the representation Γ_5 contained in $J = 2$, and for both Γ_4 and Γ_5 originating in $J = 3$.

14.4. The double cubic group

In order to find how a half-integer J-level of the free ion splits in an environment of cubic symmetry we must introduce the so-called double cubic group O^+. We recall that D^J with J half-integer is not strictly speaking a representation of the spatial rotation group G but rather a representation of the unimodular group $U = D^{\frac{1}{2}}$, and that to each rotation belonging to G there correspond *two* matrices $\pm u$ of U. The double cubic group is then defined unambiguously as follows: consider the 24 rotations in G that belong to O, subgroup of G; to these correspond twice as many, namely 48, matrices of U, which form a subgroup o^+ of U. The abstract group that has the same multiplication table as o^+ is, by definition, the double cubic group O^+. The group O^+ is obtained by adding to O the element R which is represented in o^+ by the matrix $\begin{pmatrix}-1 & \\ & -1\end{pmatrix}$. R commutes with all the other elements of O^+ and its square is equal to the unit element: $R^2 = E$.

If A is an element of O, every element of O^+ is either A or $RA = AR$. This definition of the double group O^+ can clearly be extended to any finite rotation group.

The irreducible representations Γ_1 to Γ_5 of O are also irreducible representations of O^+. They are representations where R is represented by the unit matrix, but there are others. To elucidate them we must find the classes of O^+. One might think naïvely that as O^+ has twice as many elements as O it has twice as many classes, those already listed for O plus

$$R = RE,\ RC_2,\ RC_2',\ RC_3,\ RC_4.$$

Actually this is not so: C_2 and RC_2 belong to the same class and similarly C_2' and RC_2. This can be shown as follows (Opechowski 1940).

Since the two elements C and RC of a double group have characters of opposite sign it is a necessary condition that these must vanish if C and RC belong to the same class. From (13.16) the rotation that corresponds to these two elements is therefore through an angle π. Let us choose its axis as the z-axis. According to (13.8) with $\alpha = \pi$, $\beta = \gamma = 0$ we can represent C by the matrix $c = \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix}$ and RC by $-c$. If there is in the group a twofold axis perpendicular to the z-axis let us choose it as the y-axis, the corresponding rotation $\alpha = \gamma = 0$, $\beta = \pi$ according to (13.8) can be represented by

$$b = \begin{pmatrix} 0 & -1 \\ +1 & 0 \end{pmatrix}$$

(or by $-b$) and one verifies immediately that $bcb^{-1} = -c$, which means that c and $-c$ belong to the same class.

We have thus shown that in a double group two elements, C and RC, corresponding to a rotation π around a certain axis Z, will belong to the same class provided that the group contains another twofold axis perpendicular to Z. This is clearly the case for the elements of O^+ belonging to C_2 or C_2'. O^+ has then 8 classes and 8 irreducible representations. Since we already know five of them, there must be three more with dimensions l_6, l_7, l_8 given by the relation

$$l_6^2+l_7^2+l_8^2 = 48-(l_1^2+\ldots+l_5^2) = 24, \tag{14.8}$$

which admits of a single solution,

$$l_6 = 2, \qquad l_7 = 2, \qquad l_8 = 4.$$

These representations, known in the literature as Γ_6, Γ_7, Γ_8 or E', E'', U (and possibly many other names), and sometimes called specific representations, differ from the first 5 through the fact that the element R is represented by the negative of the unit matrix. It is therefore clear that D^J for half-integral values of J contains specific representations only. Their characters are given in Table 6. The breakdown of D^J into specific representations is computed in the usual manner and the results are given for $J = \frac{1}{2}$ up to $J = \frac{15}{2}$ in Table 7.

From the character tables we can calculate the decomposition of the direct products. Table 8 contains results for the whole of the double group O^+ and thus incorporates Table 2.

We have not written out explicitly the matrices of the different representations Γ_1 to Γ_8. For the non-specific representations Γ_1 to Γ_5

the fact that xyz is a basis function for Γ_2, x, y, z for Γ_4, xy, yz, zx for Γ_5, $3z^2-r^2$ and $\sqrt{(3)}(x^2-y^2)$ for Γ_3, makes it easy to write them down if desired, using simple geometrical considerations. For the specific representations, we see from Table 7 that $D^{\frac{1}{2}}$ reduces just to Γ_6. The matrices of Γ_6 are thus simply the 48 matrices of $D^{\frac{1}{2}}$ that correspond to the 24 rotations of the cubic group. We shall represent the basis functions of Γ_6 as $|\widetilde{\pm\frac{1}{2}}\rangle$, the tilde being there to remind us that these are *not* actually, except for $J = \frac{1}{2}$, the states $|J, \pm\frac{1}{2}\rangle$. Similarly since $D^{\frac{3}{2}}$ reduces to Γ_8 we can take as the basis functions of Γ_8, the functions $|\widetilde{\pm\frac{3}{2}}\rangle$, $|\widetilde{\pm\frac{1}{2}}\rangle$ that will transform under the rotations S of the cubic group *in the same way as the functions* $|\frac{3}{2}, \pm\frac{3}{2}\rangle$, $|\frac{3}{2}, \pm\frac{1}{2}\rangle$ *would transform* under $D^{\frac{3}{2}}(S)$.

The nature of Γ_7 is less obvious. Since $\Gamma_7 = \Gamma_6 \times \Gamma_2$ let us introduce the functions

$$\begin{aligned} |\alpha\rangle &= |\widetilde{+\tfrac{1}{2}}\rangle\rho, \\ |\beta\rangle &= |\widetilde{-\tfrac{1}{2}}\rangle\rho, \end{aligned} \tag{14.9}$$

where ρ transforms according to Γ_2, that is as the function xyz, and let the functions $|\widetilde{\pm\frac{1}{2}}\rangle$ transform according to Γ_6. α and β will then transform according to Γ_7. The matrices of Γ_7 are $\pm$ those of Γ_6. The matrices of Γ_6, Γ_7, Γ_8 cannot all be made real (see § 15.9, following eqn (15.53)). However, as appears from Table 6, their characters are all real and the Γ_i ($i = 6, 7, 8$) are equivalent to their complex conjugates. *This is why in Table 8 we are able to consider direct products* $\Gamma_i \times \Gamma_j$ rather than $\Gamma_i^* \times \Gamma_j$.

We see in Table 7 that, in the decomposition of D^J, Γ_6 and Γ_7 appear only once up to $J = \frac{15}{2}$, except for $J = \frac{13}{2}$ where Γ_7 appears twice, and that Γ_8 appears only once up to $J = \frac{7}{2}$. We can therefore write *a priori* the corresponding 'good' zero-order wave-functions as linear combinations of $|J, M\rangle$. This is done in Table 9. ($J = \frac{11}{2}$ and $\frac{13}{2}$ are omitted for they do not occur in practice as the ground states of paramagnetic ions.)

The reader perusing Tables 4 and 9 may well ask from what hat these rabbits have been extracted. A brief indication of the method used to obtain these tables will now be given. Consider a ket $|J, M\rangle$ belonging to a representation D^J of the rotation group. If S is an operator belonging to O (or O^+) we know how to calculate the ket $S\,|J, M\rangle$; it will be given by

$$S\,|J, M\rangle = \sum_{M'} |J, M'\rangle\, D^J_{M'M}(S), \tag{14.10}$$

where the $D^J_{M'M}(S)$ are certain matrix elements of the representation D^J of the rotation group, which are known in principle (see § 13.2). We also know in principle the matrices $A^k_{\mu\nu}$ of the various irreducible representations Γ_1 to Γ_8 of the cubic group, as explained above. In the cubic group k stands for the index 1 to 8 of the irreducible representation concerned and μ and ν refer to the various basis functions inside each representation Γ_k. Each representation Γ_k is spanned by l_k functions Ψ^k_μ which, under an operation S of the group, will transform accordingly to

$$S\Psi^k_\mu = \sum_\nu \Psi^k_\nu A^k_{\nu\mu}(S). \tag{14.11}$$

The various Ψ^k_ν will be the linear combinations of the $|J, M\rangle$, given in Tables 4 and 9 for the cubic group, which we wish to obtain. Conversely each ket $|J, M\rangle$ will be a linear combination of the Ψ^k_μ

$$|J, M\rangle = \sum_{k',\mu'} \Psi^{k'}_{\mu'} C^{k'}_{\mu'}(J, M). \tag{14.12}$$

Let us define now the operator

$$P^k_\mu = \frac{l_k}{g} \sum_S A^{k*}_{\mu\mu}(S) \,.\, S, \tag{14.13}$$

where g is the number of elements of the group (48 for O^+) and the sum $\sum_S$ is over all the operations of the group. According to (14.10) we know how to express $P^k_\mu\,|J, M\rangle$ as a sum of $|J, M'\rangle$. On the other hand, if we take for $|J, M\rangle$ the expression (14.12), we get

$$P^k_\mu\,|J, M\rangle = \frac{l_k}{g} \sum_{S,k',\mu'} A^{k*}_{\mu\mu}(S)(S\Psi^{k'}_{\mu'})C^{k'}_{\mu'}(J, M) \tag{14.14}$$

or, using (14.11),

$$P^k_\mu\,|J, M\rangle = \frac{l_k}{g} \sum_{S,k',\mu',\nu'} A^{k*}_{\mu\mu}(S)\Psi^{k'}_{\nu'}A^{k'}_{\nu'\mu'}(S)C^{k'}_{\mu'}(J, M) \tag{14.15}$$

which, taking into account the orthogonality relations (12.9), reduces to

$$P^k_\mu\,|J, M\rangle = \Psi^k_\mu C^k_\mu(J, M). \tag{14.16}$$

We can thus generate all the Ψ^k_μ of Tables 4 and 9 (apart from normalization factors). The operation (14.14) will yield zero if $C^k_\mu(J, M) = 0$, that is if the expansion (14.12) of the ket $|J, M\rangle$ does not contain the function Ψ^k_μ. One then starts from another ket $|J, M'\rangle$ until all the Ψ^k_μ are obtained.

In practice our previous advice is the best: as somebody has prepared the tables, why not use them?

14.5. Groups of lower symmetry

The *tetragonal group*, also known in the literature as the group D_4, is the group that leaves invariant a cube or an octahedron that has been distorted along a C_2 axis called the tetragonal axis.

It contains the following elements and classes:

E, the identity operation,

C_2, rotation by an angle π around the tetragonal axis Oz (1 element),

C_4, rotation by $\pm\pi/2$ around the same axis (2 elements),

C_2', rotation by π around two axes Ox, Oy perpendicular to Oz (2 elements),

C_2'', rotation by π around two axes OX, OY at angles $\pi/4$ to Ox and Oy (2 elements).

Altogether we have 8 elements and 5 classes; whence (see § 12.3) there will be just 5 irreducible representations which we call Γ_1^t, Γ_2^t, Γ_3^t, Γ_4^t, Γ_5^t (the index t is a weak attempt to avoid confusion with the representations of the cubic group), and which are also known in the literature by other names. From eqn (12.14) it is readily apparent that they are all unidimensional except the last, which has two dimensions. The characters are given in Table 10.

We shall not write down the decomposition of D^J into the irreducible representations Γ_k^t of D_4 but be content to indicate the correspondence between the representations Γ_k of the cubic group and those Γ_k^t of the tetragonal group that is a subgroup of O. Using the character tables, it is possible to find, with the help of (12.16), that

$$\begin{cases} \Gamma_1 = \Gamma_1^t, \qquad \Gamma_2 = \Gamma_3^t, \qquad \Gamma_3 = \Gamma_3^t+\Gamma_1^t, \\ \Gamma_4 = \Gamma_2^t+\Gamma_5^t, \qquad \Gamma_5 = \Gamma_4^t+\Gamma_5^t. \end{cases} \tag{14.17}$$

It is apparent that there is no logic whatsoever in this choice of indices (due to Bethe) but we shall not add to the confusion by proposing a new notation of our own differing from the many that already exist.

As far as the 'good' zero-order wave-functions are concerned we can see the following (taking the z-axis to be the tetragonal axis):

For $J = 1$, the cubic triplet Γ_4 spanned by x, y, z is split into the singlet Γ_2^t spanned by z and the doublet Γ_5^t spanned by x and y.

For $J = 2$, the cubic triplet Γ_5 spanned by xy, yz, zx is split into the singlet Γ_4^t spanned by xy and the doublet Γ_5^t spanned by yz and zx.

The cubic doublet Γ_3 is split into the singlet Γ_1^t spanned by $3z^2-r^2$ and the singlet Γ_3^t spanned by x^2-y^2.

For $J = 3$, the cubic singlet Γ_2 becomes the singlet Γ_3 spanned by xyz, the cubic triplet Γ_5 becomes the doublet Γ_5^t spanned by $x(y^2-z^2)$

and $y(z^2-x^2)$, and the singlet Γ_4^t spanned by $z(x^2-y^2)$; the cubic triplet Γ_4 becomes the singlet Γ_2^t spanned by $z(3x^2+3y^2-2z^2)$, and a doublet Γ_5^t spanned by $x(3y^2+3z^2-2x^2)$ and $y(3z^2+3x^2-2y^2)$.

It will be noticed from (14.17) that already in the decomposition of D^3, Γ_5 appears twice and that the correct zero-order functions spanning Γ_5^t cannot be obtained without explicit knowledge of the tetragonal potential. The off-diagonal matrix elements of a tetragonal field between the cubic manifolds Γ_4 and Γ_5 are given explicitly in Fig. 7.5.

The properties of the *double tetragonal group* are obtained in the same manner as for the cubic group. It has 16 elements, twice as many as the simple group, but two more classes only, R and RC_4, since the classes RC_2, RC_2', RC_2'' are not distinct from C_2, C_2', C_2'' in accordance with the theorem in § 14.4. There are two specific representations Γ_6^t and Γ_7^t with dimensions, l_6 and l_7, such that

$$l_6^2+l_7^2 = 16-8 = 8$$

whence $l_6 = l_7 = 2$ showing that both Γ_6 and Γ_7^t are bidimensional. We omit their character table and shall be content to notice that the decomposition of the specific representations of O^+ into those of the double tetragonal group is

$$\Gamma_6 = \Gamma_6^t, \qquad \Gamma_7 = \Gamma_7^t, \qquad \Gamma_8 = \Gamma_6^t+\Gamma_7^t. \tag{14.18}$$

The *rhombic group* or D_2 contains, besides the unit operation, just three binary orthogonal axes x, y, z and thus four classes and four unidimensional representations. For an integral value of J there is no degeneracy left in a rhombic field.

The double group has 8 elements and 5 classes, R being the only extra one. It has one specific representation of dimension 2. A multiplet J of the free ion with half-integral J will thus split into $J+\frac{1}{2}$ doublets.

The *trigonal group* or D_3 leaves invariant a cube distorted along a body-diagonal. Its elements and classes are as follows:

the identity E,

the rotations C_3 of angle $\pm 2\pi/3$ around the threefold axis Oz (2 elements),

the rotations C_2' of angle π around three axes perpendicular to Oz (3 elements).

Altogether we have 3 classes and 6 elements, which shows that there must be two one-dimensional representations that we call Γ_1^T and Γ_2^T and one bidimensional representation Γ_3^T. The characters are given in Table 11. The decomposition of D^J by the trigonal group is given in Table 12.

The connection between cubic and trigonal groups is as follows:

$$\Gamma_1 \to \Gamma_1^T, \qquad \Gamma_2 \to \Gamma_2^T, \qquad \Gamma_3 \to \Gamma_3^T,$$
$$\Gamma_4 \to \Gamma_2^T + \Gamma_3^T, \qquad \Gamma_5 \to \Gamma_1^T + \Gamma_3^T.$$

It is worth noticing that the degeneracy of the cubic doublet Γ_3 is *not* lifted by a trigonal distortion though it is by a tetragonal distortion.

The double trigonal group has 12 elements and 6 classes. (C_2' and RC_2' are distinct since there is no binary axis perpendicular to the binary axes of C_2'.) We find readily that there are two unidimensional specific representations Γ_4^T, Γ_5^T, and one bidimensional Γ_6^T. Their characters are given in Table 13. The decomposition of D^J by the trigonal group for half integer J is given in Table 14.

As the representations Γ_4^T and Γ_5^T are unidimensional one might think that the decomposition of a half-integer J could contain singlets. We shall soon see (§ 15.4), that there is a very general theorem due to Kramers which proves that this can never occur. Therefore the two representations Γ_4^T and Γ_5^T (which are complex conjugates) must always correspond to the same energy of the system.

The decomposition of specific representations of O^+ into those of the trigonal group is the following:

$$\Gamma_6 = \Gamma_6^T, \qquad \Gamma_7 = \Gamma_6^T, \qquad \Gamma_8 = \Gamma_4^T + \Gamma_5^T + \Gamma_6^T. \tag{14.19}$$

14.6. Improper rotations

We have only considered so far symmetry groups containing pure rotations. Another type of symmetry element that occurs in nature is the improper rotation. An improper rotation is a symmetry element resulting from the combination of a rotation with an inversion with respect to a centre situated on the axis of rotation. For instance, reflection in a plane is the product of a rotation by an angle π with an inversion. In ordinary space an inversion corresponds to the reversal of the signs of the three space coordinates and an improper rotation is therefore represented by a real orthogonal matrix with determinant -1. It follows that the product of two improper rotations is a proper rotation and that the product of a proper and improper rotation is an improper rotation. A group G_i that contains at least one improper rotation must therefore contain as many proper as improper rotations and can be represented as the combination of a subgroup G_p of proper rotations with a set of improper rotations of the form $g_\mathrm{i} G_\mathrm{p}$ where g_i is an improper rotation. We write symbolically

$$G_\mathrm{i} = G_\mathrm{p} + g_\mathrm{i} G_\mathrm{p}. \tag{14.20}$$

We shall for brevity call a group such as (14.20) a group of improper rotations, although it contains naturally proper rotations as well. A finite group of improper rotations may or may not contain the inversion operation itself. If it does, we can use for the improper rotation g_i in (14.20) the inversion I itself and write

$$G_i = G_p + IG_p. \tag{14.21}$$

Since I commutes with all the elements of the group G_i, and its square I^2 is just the identity operation, the matrix representing I in an irreducible representation of G_i can be either the unit matrix, for so-called even representations, or its negative for odd representations.

To each representation $\mathscr{D}_p$ of G_p correspond two representations $\mathscr{D}_i^{\pm}$ of G_i such that, if g_p is a proper rotation of G_p,

$$\begin{cases} \mathscr{D}_i^{\pm}(g_p) = \mathscr{D}_p(g_p) \\ \mathscr{D}_i^{\pm}(Ig_p) = \pm\mathscr{D}_p(g_p). \end{cases} \tag{14.22}$$

In particular, if $\mathscr{D}_p$ is irreducible so is $\mathscr{D}_i^{\pm}$.

If $\mathscr{D}_i$ is a *reducible* representation of G_i of given parity there corresponds to it by (14.22) a single reducible representation $\mathscr{D}_p$ of G_p. If we know how to reduce $\mathscr{D}_p$ into its irreducible parts

$$\mathscr{D}_p = \sum a_k \mathscr{D}_p^{(k)}, \tag{14.23}$$

the reduction of $\mathscr{D}_i$ will be

$$\mathscr{D}_i = \sum a_k \mathscr{D}_i^{(k)} \tag{14.24}$$

with the same coefficients a_k.

As an example of a group of improper rotations that contains I, we may take the cubic group of improper rotations O_h defined in accordance with (14.21),

$$O_h = O + IO. \tag{14.25}$$

On the other hand, the tetrahedral group T_d, which is the group of improper rotations that transform a regular tetrahedron into itself, does not contain the inversion I. Since each operation of T_d amounts to a permutation of the vertices of the tetrahedron, T_d is isomorphic with the permutation group S_4 and thus also with O. It has the same set of characters and the same representations as O. Geometrically, however, it is a different group. By adding to T_d the inversion operation we obtain again the full cubic group

$$O_h = T_d + IT_d, \tag{14.26}$$

showing that T_d and O are two isomorphic subgroups of O_h. It should be noticed that in contradistinction to (14.25), (14.26) *is not* a relationship of the type (14.20) since T_d contains improper rotations as well as proper ones.

We examine now how the introduction of improper rotations modifies the splitting of a degenerate level of the free ion by the crystal potential, as studied in the previous sections. If the group of improper rotations G_{i} which describes the environment of the bound ion does contain the inversion element, the crystal field splitting is the same as calculated for the pure rotation group G_{p} associated with G_{i} by (14.21). This follows from the fact that the level J of the free ion has a definite parity and that the wave-functions that span this level provide a reducible representation $\mathscr{D}_{\mathrm{i}}(G_{\mathrm{i}})$ of given parity which, as explained earlier, is reduced in the same manner as the representation $\mathscr{D}_{\mathrm{p}}(G_{\mathrm{p}})$ in the absence of inversion. Thus the splitting pattern of a level of the free ion will be the same in a field of symmetry O_{h} as in symmetry O.

If the group G_{i} does not contain the inversion I we can still predict the splitting pattern as follows. Let us call $V(\mathbf{r})$ the crystalline potential invariant by G_{i} which represents the effects of the environment of the bound ion. We can write

$$V(\mathbf{r}) = \tfrac{1}{2}\{V(\mathbf{r})+V(-\mathbf{r})\}+\tfrac{1}{2}\{V(\mathbf{r})-V(-\mathbf{r})\} = V_{\mathrm{even}}+V_{\mathrm{odd}}. \quad (14.27)$$

Since the states of the free ion have a definite parity the matrix elements of V_{odd} vanish inside their manifold and we can in first approximation replace V by V_{even}. But V_{even} is invariant through I and thus through the group

$$G'_{\mathrm{i}} = G_{\mathrm{i}}+IG_{\mathrm{i}},$$

which can always be rewritten according to (14.20) as

$$G'_{\mathrm{i}} = G'_{\mathrm{p}}+IG'_{\mathrm{p}},$$

where G'_{p} is a certain pure rotation group. The splitting of D^J by a potential of symmetry G_{i} will then be the same as by one with symmetry G'_{i} and therefore, as we saw earlier, the same as by a potential of symmetry G'_{p}. As an example, from (14.26) and (14.25) we deduce that a level D^J will be decomposed in the same manner in a field of tetrahedral symmetry T_{d} as in a cubic field O and we need not repeat the detailed study of the last section.

The foregoing is valid provided we assume that the effects due to the environment are small compared with the distance between two configurations of the free ion with opposite parity.

The absence of a centre of inversion in the environment also modifies drastically the response to an applied electric field as we shall see in § 15.10.