

## ELEMENTARY THEORY OF THE CRYSTAL FIELD

IN this chapter we gather together some mathematical results useful for the calculation of the matrix elements of the crystal field and the determination of the wave-functions of the bound ion, in the framework of the elementary crystal-field theory. It should be made clear at the outset that this theory is a model that may or may not be an adequate description of the physical reality. It is probably quite good for rare-earth salts and rather bad for some complexes of the iron group, but we shall not discuss this point now.

### 16.1. The crystal field (or crystal potential)

Once the assumptions describing the model are stated, the rest is algebra. These assumptions can be formulated as follows. Let  $\mathcal{H}_0$  be the Hamiltonian of the free ion. The Hamiltonian  $\mathcal{H}$  of the bound ion is then assumed to be of the form  $\mathcal{H} = \mathcal{H}_0 + V$  where  $V$  is an electrostatic potential energy that satisfies the Laplace equation  $\Delta V = 0$  and has the symmetry of the surroundings of the ion. The potential  $V$  can then be expanded as a sum of spherical harmonics,

$$V = \sum_{k=0}^{\infty} \sum_{q=-k}^k B_k^q Y_k^q(\theta, \varphi) = \sum V_k^q, \quad (16.1)$$

with the sign convention,  $Y_k^{q*} = (-1)^q Y_k^{-q}$ . Certain limitations are imposed on the  $B_k^q$  by the symmetry of the surroundings. For instance, if there is a centre of inversion there will be no harmonics of odd  $k$  in the expansion (16.1); also the reality of  $V$  requires  $B_k^q = (-1)^q B_k^{-q*}$ .

The potential energy  $V$  is assumed to arise from the electronic and nuclear charges of the atoms and ions surrounding the paramagnetic ion under study. To calculate this potential the simplest method is the so-called point charge approximation where each ion is replaced by a point charge equal to the total charge of the ion and located at its centre. For a monatomic ion the position of the centre is naturally that of its nucleus but it is not so clear what its position should be for, say, a negative ion such as  $(\text{NO}_3)^-$ .

As soon as one tries to improve on this approximation, difficulties arise. Even if one does take into account the spatial extension of the charge distribution producing  $V$ , there are still polarization effects, large and difficult to estimate. This comes from the fact that the closed

shells of the paramagnetic ion are distorted by the potential  $V$  and under this distortion create a modified potential 'seen' by the magnetic electrons of the unfilled shells, which does not have the spherical symmetry of the self-consistent Hartree potential of the free ion anymore. Be it as it may, we start from (16.1), whatever its origin, and proceed to carry out some algebra with it, postponing discussion of the physics until later.

We are not interested in the absolute displacements of the energy levels but only in their splittings by the crystal potential. We can then without loss of generality omit the term  $k = 0$  in the expansion (16.1).

The most important approximation we make is to take the electronic configuration as defined in § 11.4, as a good quantum number. This has the following implications. The wave-functions  $\Psi$  between which we calculate matrix elements of the crystal potential will be Slater determinants or linear combinations of Slater determinants. Each determinant will be of the form  $(\chi_1, \dots, \chi_N, \varphi_1, \dots, \varphi_p)$  in which the first  $N$  one-electron functions  $\chi_1, \dots, \chi_N$  represent closed shells and unless stated otherwise will be the same for all the Slater determinants appearing in the expansion of the states  $\Psi$  of the paramagnetic ion. The remaining one-electron wave-functions  $\varphi_1, \dots, \varphi_p$  are those of the magnetic electrons of the unfilled shells,  $d$ - or  $f$ -electrons, depending on the transition group considered; they are therefore of the form  $|l, m_l, m_s\rangle$  where  $l = 2$  for  $d$ -electrons and 3 for  $f$ -electrons. The crystal potential  $V$  is a sum of one-electron operators  $V = \sum V_p$  where  $V_p$  is obtained by replacing in (16.1)  $r, \theta, \varphi$  by the coordinates  $r_p, \theta_p, \varphi_p$  of the  $p$ th electron. According to the rules given in § 11.6, any matrix element  $(\Psi | V | \Psi')$  will be a sum of one-electron matrix elements of the form  $(\psi_a | V | \psi_b)$ , where  $\psi_a$  and  $\psi_b$  are functions  $\chi$  from the filled shells and  $\varphi$  from the unfilled shells. The contribution of the closed shells to a

matrix element  $(\Psi | V | \Psi')$  will be  $\sum_{i=1}^N (\chi_i | V | \chi_i)$ , which vanishes if the term  $k = 0$  is omitted in the expansion (16.1). We can then omit closed shells altogether and write our Slater determinant as  $(\varphi_1, \dots, \varphi_p)$ , building it solely from wave-functions of magnetic electrons (it should not be forgotten that we are only able to do this because we deal with one-electron operators such as  $V$ ; it would not be quite correct for two-electron operators). A one-electron matrix element then takes the form

$$\sum_{k,q} \langle l, m_l, m_s | V_k^q | l, m'_l, m'_s \rangle = \sum_k \langle r^k \rangle \sum_q B_k^q(l, m_l) Y_k^q(l, m'_l) \delta(m_s, m'_s), \quad (16.2)$$

where

$$\langle r^k \rangle = \int_0^\infty |f_i(r)|^2 r^k r^2 dr \quad (16.3)$$

and  $f_i(r)$  is the radial wave-function of the Hartree-Fock approximation.  $V_k^q$  is a component of an irreducible tensor and the corresponding matrix element vanishes unless

$$k \leq 2l \text{ and } m_i = q + m'_i. \quad (16.4)$$

The selection rule  $k \leq 2l$  decreases considerably the number of parameters that are needed for the description of the crystal potential. Furthermore, even in the absence of a centre of symmetry, terms  $V_k^q$  with odd  $k$  can be omitted because the corresponding matrix elements vanish. (These terms will, however, admix excited configurations.)

The number of terms in (16.1) is further reduced by the symmetry of the surroundings. Only even values of  $q$  are admissible if the surroundings have either a twofold axis of symmetry parallel to the axis of quantization or a plane of symmetry perpendicular to it. If there is a threefold axis, only values of  $q$  that are multiples of 3 appear.

Pairs of terms in (16.1) with values of  $q$  of opposite sign can be rewritten in the form

$$\begin{aligned} B_k^{[q]} Y_k^{[q]} + B_k^{[q]*} Y_k^{[q]*} &= \frac{(B_k^{[q]} + B_k^{[q]*})}{2} (Y_k^{[q]} + Y_k^{[q]*}) - \frac{(B_k^{[q]} - B_k^{[q]*})}{2i} \frac{(Y_k^{[q]} - Y_k^{[q]*})}{i} \\ &= f(\theta) \cos\{|q| \varphi\} + g(\theta) \sin\{|q| \varphi\}. \end{aligned} \quad (16.5)$$

If there is a plane of symmetry passing through the axis of quantization we take it as the plane  $xOz$ ; the term  $\sin\{|q| \varphi\}$  must vanish and  $B_k^{[q]}$  is real.

If there is a plane of symmetry perpendicular to a threefold axis of quantization (symmetry  $C_{3h}$ ),  $B_k^{[q]}$  can also be made real by a suitable choice of the  $xOz$  plane. For symmetry  $C_{3h}$  there is no term with  $q \neq 0$  for  $l = 2$  and a single one  $B_6^6 Y_6^6 + B_6^{-6} Y_6^{-6}$  for  $l = 3$  where it is always possible to make  $B_6^6 - B_6^{6*}$  vanish by a rotation around the  $z$ -axis.

By a parallel argument similar relations are obtained for symmetry  $C_{4h}$  or  $D_4$ , where only  $|q| = 0$  and  $|q| = 4$  are possible.

We consider finally a potential of cubic symmetry. Being invariant under all transformations of the cubic group, this potential provides the representation  $\Gamma_1$  of this group. We see in Table 3 that this representation appears once for  $k = 4$  and once for  $k = 6$ . Hence there

must be a single combination of spherical harmonics of fourth-order invariant by the cubic group and a single one of sixth order.

For  $k = 4$  it is just the function corresponding to  $J = 4$ ,  $\Gamma_1$  in Table 4, that is,

$$V_4 = b_4 r^4 \left\{ \frac{\sqrt{(14)}}{\sqrt{(24)}} Y_4^0 + \frac{\sqrt{(5)}}{\sqrt{(24)}} (Y_4^4 + Y_4^{-4}) \right\}. \quad (16.6)$$

For  $k = 6$  it can be computed in the same way and is given by

$$V_6 = b_6 r^6 \left\{ \frac{2}{\sqrt{(32)}} Y_6^0 - \frac{\sqrt{(14)}}{\sqrt{(32)}} (Y_6^4 + Y_6^{-4}) \right\}. \quad (16.7)$$

The coefficients  $b_4$  and  $b_6$  are defined in such a way that  $V_4/b_4$  and  $V_6/b_6$  should be normalized to unity over the unit sphere.

The reader will observe that there is a positive sign within the bracket in (16.6) but a negative sign in (16.7); this is not an accident. It is important, in calculations where both occur, to preserve these signs, since only then will (16.7) correspond to the use of the same set of axes as (16.6). A rotation through an angle  $\phi$  about the polar axis multiplies a spherical harmonic  $Y_k^q$  by  $\exp(-iq\phi)$ ; thus a rotation through  $\pi/4$  just changes all the signs of the  $Y_k^{\pm 4}$  terms giving

$$V_4 = b_4 r^4 \left\{ \frac{\sqrt{(14)}}{\sqrt{(24)}} Y_4^0 - \frac{\sqrt{(5)}}{\sqrt{(24)}} (Y_4^4 + Y_4^{-4}) \right\} \quad (16.6a)$$

$$V_6 = b_6 r^6 \left\{ \frac{2}{\sqrt{(32)}} Y_6^0 + \frac{\sqrt{(14)}}{\sqrt{(32)}} (Y_6^4 + Y_6^{-4}) \right\}. \quad (16.7a)$$

These are equally valid with (16.6) and (16.7), but one must not take a combination of one of these and one of (16.6) or (16.7).

These equations express the cubic potential in spherical harmonics such that the polar axis is one of the fourfold axes of the cube. It is sometimes convenient to have the corresponding expressions in the form of a set of spherical harmonics whose polar axis is one of the threefold axes (a body diagonal of the cube). With the same values of  $b_4$  and  $b_6$ , the corresponding expressions for  $V_4$  and  $V_6$  are then

$$V_4 = -b_4 r^4 \left\{ \sqrt{\left(\frac{7}{27}\right)} Y_4^0 + \sqrt{\left(\frac{10}{27}\right)} (Y_4^3 - Y_4^{-3}) \right\} \quad (16.8)$$

$$V_6 = +b_6 r^6 \frac{\sqrt{(2)}}{18} \left\{ 8 Y_6^0 + \sqrt{\left(\frac{70}{3}\right)} (Y_6^3 - Y_6^{-3}) + \sqrt{\left(\frac{77}{3}\right)} (Y_6^6 + Y_6^{-6}) \right\}. \quad (16.9)$$

Note that rotation of the coordinate system through an angle  $\phi$  about the threefold axis multiplies each spherical harmonic  $Y_k^q$  by  $\exp(-iq\phi)$ , so that rotation through  $\pi$  changes the signs of the coefficients of the  $Y_k^{\pm 3}$  but not those of the  $Y_k^{\pm 6}$ .

Although an expansion such as (16.1) for the crystal potential is the more natural one, it has been customary in the literature to expand it into homogeneous polynomials of degree  $k$ , each one a certain combination of spherical harmonics, without paying much attention to the normalization of these polynomials. When the symmetry is such that the coefficients  $B_k^q$  of the expansion (16.1) are real, this new expansion is of the form

$$V = \sum_{k,q>0} A_k^q P_k^q(x, y, z), \quad (16.10)$$

where the  $P_k^q$  are unnormalized homogeneous polynomials proportional to  $r^k(Y_k^q + Y_k^{q*})$  but which, in spite of the symbol, should not be confused with Legendre polynomials. A list of those that occur most frequently in the literature are given in Table 15 together with the relationship between the  $A_k^q$  of (16.10) and the  $B_k^q$  of (16.1).

For cubic symmetry one introduces the polynomials

$$P_4 = P_4^0 + 5P_4^4 = 20(x^4 + y^4 + z^4 - \frac{2}{3}r^4), \quad (16.11)$$

$$P_6 = P_6^0 - 21P_6^4 = -14 \times 16 \times \\ \times \{x^6 + y^6 + z^6 + \frac{1}{4}x^4y^2 + y^4x^2 + x^4z^2 + z^4x^2 + y^4z^2 + z^4y^2\} - \frac{1}{4}r^6\} \quad (16.12)$$

and the cubic potential can be written

$$V \text{ (cubic)} = A_4 P_4 + A_6 P_6, \quad (16.13)$$

where  $A_4$  and  $A_6$  are related to  $b_4$  and  $b_6$  of (16.6) and (16.7) by

$$\begin{cases} A_4 = \frac{1}{\sqrt{(2\pi)}} \frac{3}{16} \sqrt{\left(\frac{7}{6}\right)} b_4, \\ A_6 = \frac{1}{\sqrt{(2\pi)}} \frac{\sqrt{(13)}}{64} b_6. \end{cases} \quad (16.14)$$

In the point charge approximation the coefficients  $A_4$  and  $A_6$  can be computed by an expansion of  $\sum_i |\mathbf{r} - \mathbf{R}_i|^{-1}$  where  $\mathbf{R}_i$  are the positions of the charges that produce the potential. The electrostatic energy of an electron of charge  $-e$  in the potential produced by 6 charges  $-Ze$  situated at the six vertices of a regular octahedron is given by (16.11)–(16.14) with

$$\begin{cases} A_4 \text{ (octahedron)} = \frac{7}{16} \frac{Ze^2}{R^5}, \\ A_6 \text{ (octahedron)} = \frac{3}{64} \frac{Ze^2}{R^7}. \end{cases} \quad (16.15)$$

Here  $R$  is the distance of each charge  $-Ze$  from the centre of the octahedron.

For 8 charges at the vertices of a cube one finds

$$\begin{cases} A_4 (\text{cube}) = -\frac{7}{18} \frac{Ze^2}{R^5}, \\ A_6 (\text{cube}) = \frac{1}{9} \frac{Ze^2}{R^7}, \end{cases} \quad (16.16)$$

where  $R$  is again the distance of each charge  $-Ze$  from the centre of the cube.

For a regular tetrahedron whose vertices are 4 of the 8 apexes of the cube, the even part of the potential is half of that of the cube and

$$A_{4,6} (\text{tetrahedron}) = \frac{1}{2} A_{4,6} (\text{cube}). \quad (16.17)$$

Since the tetrahedron (unlike the cube or octahedron) does not possess a centre of inversion symmetry, its potential includes also terms of odd degree involving spherical harmonics  $Y_k^q$  of odd  $k$ . These have no matrix elements within a manifold of electrons of a given value of  $l$  (see the remarks following eqn (16.4)).

More detailed evaluations of these expansions can be found in Hutchings (1964).

## 16.2. Equivalent operators

Having written down the expansions (16.1) or (16.10) for the crystal field, the next problem is to calculate the matrix elements  $\langle \Psi | V | \Psi' \rangle$ . A simple pedestrian approach would involve expanding  $\Psi$  and  $\Psi'$  into Slater determinants, thus reducing  $\langle \Psi | V | \Psi' \rangle$  to a sum of one-electron matrix elements of the type  $\langle l, m_l | V | l, m'_l \rangle \delta(m_s, m'_s)$ .

It is very much preferable to use for  $\Psi$  and  $\Psi'$  eigenstates of  $L, S, M_L, M_S$  or  $L, S, J, M_J$  and apply the Wigner-Eckart theorem as has been explained in § 13.5. The  $L, S, M_L, M_S$  representation is suitable for crystal fields of intermediate strength (iron group) and the  $J, M_J$  representation for weak crystal fields (rare-earth group).

For matrix elements within a manifold  $L$  or  $J$  such as

$$\langle L, M_L | V | L, M'_L \rangle \text{ or } \langle J, M_J | V | J, M'_J \rangle$$

the best procedure is to use the equivalent operators mentioned in § 13.5. With the components  $L_x, L_y, L_z$  of  $\mathbf{L}$  or  $J_x, J_y, J_z$  of  $\mathbf{J}$ , tensor operators  $O_k^q$  are constructed which have the same transformation

properties as the polynomials  $P_k^q$  defined in Table 15. Thus, within each manifold  $L$  we shall be able to write

$$\langle L, M_L | \sum_i P_k^q(\mathbf{r}_i) | L, M_L' \rangle = a_k \langle r^k \rangle \langle L, M_L | O_k^q(\mathbf{L}) | L, M_L' \rangle \quad (16.18)$$

where the summation  $\sum_i$  is over all the electrons.

For the  $|J, M_J\rangle$  representation,  $L$  is to be replaced throughout by  $J$ . The value of the constant  $a_k$  depends on the structure of the level  $L$  or  $J$  under consideration and has to be determined in each case by a direct calculation. The current and unfortunate practice is to write  $\alpha, \beta, \gamma$  instead of  $a_2, a_4, a_6$ , and we shall write  $\langle l \| \alpha \| l \rangle, \langle L \| \alpha \| L \rangle, \langle J \| \alpha \| J \rangle$ , etc. to make it clear whether we are dealing with single electrons or representations in terms of  $L$  or  $J$ .

The construction of the polynomials  $O_k^q$  is not trivial because the various components  $J_x, J_y, J_z$  do not commute with each other. As a result, whenever an expression  $x^\lambda y^\mu z^\nu$  appears in  $P_k^q$  it should not be replaced by  $J_x^\lambda J_y^\mu J_z^\nu$  in  $O_k^q$  but rather by the symmetrized product, average of all the products where  $J_x, J_y, J_z$  appear respectively  $\lambda, \mu, \nu$  times. This average can then be simplified using the commutation rules of  $J_x, J_y, J_z$ . A list of the  $O_k^q$  is given in Table 16, where we use the notation  $\{A, B\}_S = \frac{1}{2}(AB + BA)$ . The non vanishing matrix elements of these operators  $O_k^q$  are given in Tables 17 for values of  $J$  varying from  $\frac{1}{2}$  to  $\frac{1}{2}^5$  and from 0 to 8.

To show how  $\alpha, \beta, \gamma$  are calculated we start first with a single electron with orbital angular momentum  $l$ , for which the parameters we require can be written as  $\langle l \| \alpha \| l \rangle$ , etc. We take as an example the operator  $P_4^0$ . In the state  $l, m_l = l$  the expectation value of  $P_4^0$  can be found by direct calculation:

$$\begin{aligned} \langle l; l | P_4^0 | l, l \rangle &= \langle r^4 \rangle \{ (2l+1)/4\pi \} \int (Y_l^0)^2 (P_4^0/r^4) d\Omega \\ &= \langle r^4 \rangle \frac{12l(l-1)}{(2l+3)(2l+5)}. \end{aligned} \quad (16.19)$$

On the other hand, the value of  $\langle l, l | O_4^0 | l, l \rangle$  is found from Table 16 by writing  $J_z = J = l$  to be

$$\langle l, l | O_4^0 | l, l \rangle = 2l(2l-1)(l-1)(2l-3), \quad (16.20)$$

which incidentally shows that the matrix element of this operator vanishes for all quantum numbers less than 2. Hence we have, since  $\langle l, l | P_4^0 | l, l \rangle = \langle r^4 \rangle \langle l \| \beta \| l \rangle \langle l, l | O_4^0 | l, l \rangle$ ,

$$\langle l \| \beta \| l \rangle = \frac{6}{(2l-1)(2l-3)(2l+3)(2l+5)}. \quad (16.21)$$

Similar calculations can be carried out for  $\alpha$ ,  $\gamma$  and the results are tabulated in Table 18, together with the numerical values for  $p$ -,  $d$ -, and  $f$ -electrons ( $l = 1, 2, 3$ ).

To proceed to the next step we must describe the structure of the spectral terms ( $L, S$ ) and multiplets ( $L, S, J$ ) of the ground levels of the free ion, encountered in the transition group; we begin with the ions of the iron group listed in Table 19.

We notice in Table 19 that the values of  $L$  and  $S$  given by Hund's rule are symmetrical with respect to the middle of the  $3d$  shell and the values of  $\alpha$  and  $\beta$  (there is no  $\gamma$  for  $l = 2$ ) antisymmetrical. This is a consequence of a general rule that we derive as follows.

Consider two complementary configurations  $\mathcal{C}$  and  $\mathcal{C}'$  containing respectively  $x$  and  $2(2l+1)-x$  electrons outside closed shells. It is possible to establish a one-to-one correspondence between a function  $\Psi$  of  $\mathcal{C}$  and  $\Psi'$  of  $\mathcal{C}'$  such that

$$\begin{cases} \langle \Psi | L_z | \Psi \rangle = \langle \Psi' | L_z | \Psi' \rangle, \\ \langle \Psi | S_z | \Psi \rangle = \langle \Psi' | S_z | \Psi' \rangle. \end{cases} \quad (16.22)$$

More generally, given a tensor operator  $\mathcal{T}_k = \sum_i \mathcal{T}_k(l_i, \mathbf{s}_i)$  with  $k > 0$ ,

$$\langle \Psi | \mathcal{T}_k | \Psi \rangle = \pm \langle \Psi' | \mathcal{T}_k | \Psi' \rangle, \quad (16.23)$$

where the  $+$  sign applies when  $\mathcal{T}_k$  is time-odd and the negative sign when it is time-even; that is, odd or even through inversion of all  $l_i$  and  $\mathbf{s}_i$ .

The correspondence between  $\Psi$  and  $\Psi'$  is as follows. To each determinant of  $\mathcal{C}$ ,  $\Phi = (m_l^1, m_s^1; \dots, m_l^x, m_s^x)$  we associate the determinant of  $\mathcal{C}'$ ,

$$\Phi' = (-m_l'^1, -m_s'^1; \dots; -m_l'^{2(2l+1)-x}, -m_s'^{2(2l+1)-x}),$$

where  $m_l'^1, m_s'^1, \dots$ , etc. are the one-electron states *unoccupied* in  $\Phi$ . The proof of (16.23) then goes as follows.

We introduce also the Slater determinant

$$\Phi'' = (m_l'^1, m_s'^1; \dots; m_l'^{2(2l+1)-x}, m_s'^{2(2l+1)-x})$$

which (apart from possible phase factors) is the time-reversed of  $\Phi'$ . The sum  $\langle \Phi | \mathcal{T}_k | \Phi \rangle + \langle \Phi'' | \mathcal{T}_k | \Phi'' \rangle$  vanishes, since, from the rules given in § 11.6 for the calculation of diagonal matrix elements of Slater determinants this sum is a trace over a closed shell of one-electron tensor operators

$$\sum_{\substack{m_l, m_s \\ \text{closed shell}}} (m_l, m_s | \mathcal{T}_k | m_l, m_s).$$



Hence  $\langle \Phi | \mathcal{T}_k | \Phi \rangle = -\langle \Phi'' | \mathcal{T}_k | \Phi'' \rangle = \mp \langle \Phi' | \mathcal{T}_k | \Phi' \rangle$  where the negative sign applies for time-even operators. One says sometimes that the configuration  $\mathcal{C}'$  consists of holes. According to (16.22), (16.23) the holes must be treated as positive charges for time-even operators such as the crystal field or the spin-orbit coupling, but as negative charges for the coupling with a magnetic field either applied or produced by the nuclear magnetic moment.

As a consequence, the order in energy of the various terms  $(L, S)$  of the free ion, which is determined by the electrostatic repulsion between the particles, whether electrons or holes, is the same for  $\mathcal{C}$  and  $\mathcal{C}'$  (we have not really *proved* this since our reasoning applied only to one-electron operators, but it turns out to be true). On the other hand, the spin-orbit coupling constant  $\lambda$  in  $\lambda(\mathbf{L} \cdot \mathbf{S})$ , and the constants  $\alpha$ ,  $\beta$ , have opposite signs and the order of sub-levels in the splitting of a term  $(L, S)$  is reversed.

We now extend our previous calculation of  $\langle l \| \alpha \| l \rangle$ ,  $\langle l \| \beta \| l \rangle$  to find the equivalent factors for a term  $(L, S)$ , and consider first  $\langle L \| \alpha \| L \rangle$ , for which an explicit formula can be obtained rather easily. Essentially we wish to replace the operator  $\langle l \| \alpha \| l \rangle \sum \{3l_z^2 - l(l+1)\}$  summed over all electrons, by the operator

$$\langle L \| \alpha \| L \rangle \{3L_z^2 - L(L+1)\}.$$

To find the value of  $\langle L \| \alpha \| L \rangle$  we consider a term  $(L, S)$  originating from a configuration with  $r$  electrons of orbital momentum  $l$ , and obeying Hund's rule so that the state  $L_z = L$ ,  $S_z = S$  is a single Slater determinant. Assume first that we are in the first half of the shell, so that  $r \leq 2l+1$  and  $r = 2S$ . According to Hund's rule,

$$L = l + (l-1) + \dots + (l-r+1) = \frac{1}{2}r(2l-r+1) = S(2l+1-2S) \quad (16.24)$$

and

$$\begin{aligned} \sum \{3l_z^2 - l(l+1)\} &= 3\{l^2 + (l-1)^2 + \dots + (l-r+1)^2\} - 2Sl(l+1) \\ &= S(2l+1-r)(2l+1-2r) = L(2l+1-4S) \end{aligned}$$

while  $\{3L_z^2 - L(L+1)\}_{L_z=L} = L(2L-1)$ . Hence, remembering that the sign of  $\langle L \| \alpha \| L \rangle$  must be reversed for a shell that is more than half-filled, we have

$$\begin{aligned} \langle L \| \alpha \| L \rangle &= \pm \frac{(2l+1-4S)}{2L-1} \langle l \| \alpha \| l \rangle \\ &= \mp \frac{2(2l+1-4S)}{(2l-1)(2l+3)(2L-1)}, \end{aligned} \quad (16.25)$$

where the upper sign applies to a shell less than half-full, and the lower sign to a shell more than half-full.

Similar methods are used to find the values of  $\langle L \| \beta \| L \rangle$  and  $\langle L \| \gamma \| L \rangle$ , but in these cases it is often as simple to carry out the calculation numerically for each ion as to use a general formula. As an example we calculate the value of  $\beta$  for the term  ${}^4F$  of the configuration  $3d^3$ . The state  $L = 3$ ,  $L_z = 3$ ,  $S = \frac{3}{2}$ ,  $S_z = \frac{3}{2}$  of this term is a single Slater determinant  $|\xi\rangle = (2^+, 1^+, 0^+)$ , for which

$$\begin{aligned} \langle l \| \beta \| l \rangle & \{ \langle 2, 2 | O_4^0(\mathbf{l}) | 2, 2 \rangle + \langle 2, 1 | O_4^0(\mathbf{l}) | 2, 1 \rangle + \langle 2, 0 | O_4^0(\mathbf{l}) | 2, 0 \rangle \} \\ & = \langle L \| \beta \| L \rangle \langle 3, 3 | O_4^0(\mathbf{L}) | 3, 3 \rangle, \end{aligned}$$

whence, using Tables 17 and 18, we have

$$\langle L \| \beta \| L \rangle = \frac{1}{5} \langle l \| \beta \| l \rangle = \frac{2}{315}$$

for this particular ion.

The numerical values of  $\langle L \| \alpha \| L \rangle$  and  $\langle L \| \beta \| L \rangle$  for the ground states of the iron-group ions are listed in Table 19, together with general formulae for these quantities.

We pass on now to the rare-earth group where the various terms are given together with the values of the constants  $\alpha$ ,  $\beta$ ,  $\gamma$  in Table 20. The calculation of  $\alpha$ ,  $\beta$ ,  $\gamma$  is more complicated than in the iron group because not only do we couple the individual  $\mathbf{l}$  and  $\mathbf{s}$  to a total  $\mathbf{L}$  and  $\mathbf{S}$  but we then couple  $\mathbf{L}$  and  $\mathbf{S}$  to a total  $\mathbf{J}$ . However the problem is much simpler in the second half of the rare-earth group, where the ground multiplet is a state not only of maximum  $S$  and  $L$  but also of maximum  $J = L + S$ . It follows that the state  $J_z = J$  is a single Slater determinant and we can use the same method as for the iron group: first we calculate  $\alpha$ ,  $\beta$ ,  $\gamma$  for a single  $f$ -electron by the same procedure as before (the results are listed in Table 18) and find, for example, that

$$\langle l \| \alpha \| l \rangle = -\frac{2}{45}.$$

Consider then, for instance,  $\text{Tm}^{3+}(4f^{12}, {}^3H_6)$ . The state  $J = 6$ ,  $J_z = 6$ , or  $|6, 6\rangle$  is also a state  $L = L_z = 5$ ;  $S = S_z = 1$  and therefore a single Slater determinant of holes  $(3^+, 2^+)$ . Hence

$$\begin{aligned} \langle J \| \alpha \| J \rangle & (4f^{12}, {}^3H_6) \langle 6, 6 | O_2^0(\mathbf{J}) | 6, 6 \rangle \\ & = -\langle J \| \alpha \| J \rangle (4f^2, {}^3H_6) \langle 6, 6 | O_2^0(\mathbf{J}) | 6, 6 \rangle \\ & = -\langle l \| \alpha \| l \rangle \{ \langle 3, 3 | O_2^0(\mathbf{l}) | 3, 3 \rangle + \langle 3, 2 | O_2^0(\mathbf{l}) | 3, 2 \rangle \} \quad (16.26) \end{aligned}$$

and, using Tables 17, we obtain for  $(4f^{12}, {}^3H_6)$

$$\langle J \| \alpha \| J \rangle = \frac{1}{9}.$$

The first half of the shell is more difficult to handle for in the ground multiplet  $(J, L, S)$ ,  $J$  is not  $L+S$  but  $|L-S|$  and no substate of this multiplet is a single Slater determinant. We can, however, expand any substate of this multiplet into eigenstates of  $|L, M_L\rangle$  and  $|S, M_S\rangle$  using Clebsch-Gordan coefficients,

$$|L, S, J, M_J\rangle = \sum_{\substack{M_L+M_S \\ =M_J}} \langle L, M_L; S, M_S | L, S; J, M_J \rangle |L, M_L\rangle |S, M_S\rangle. \quad (16.27)$$

Let us assume we wish to calculate  $\langle J \| \alpha \| J \rangle$ . We find first the expectation value of  $\sum_i P_2^0(\mathbf{r}_i)$  in the state (16.27). In the state  $|L, S, J, M_J\rangle$  it is equal to

$$\langle J \| \alpha \| J \rangle \langle J, M_J | O_2^0(\mathbf{J}) | J, M_J \rangle,$$

and in a state  $|L, M_L\rangle |S, M_S\rangle$  to

$$\langle L \| \alpha \| L \rangle \langle L, M_L | O_2^0(\mathbf{L}) | L, M_L \rangle.$$

Equation (16.27) then yields

$$\left\{ \begin{aligned} &\langle J \| \alpha \| J \rangle \langle J, M_J | O_2^0(\mathbf{J}) | J, M_J \rangle \\ &= \langle L \| \alpha \| L \rangle \sum_{\substack{M_L+M_S \\ =M_J}} |\langle L, M_L; S, M_S | L, S; J, M_J \rangle|^2 \times \\ &\quad \times \langle L, M_L | O_2^0(\mathbf{L}) | L, M_L \rangle, \end{aligned} \right. \quad (16.28)$$

where the  $\langle L \| \alpha \| L \rangle$  can be calculated by the same method as in the iron group.

Actually, as we explained in § 13.5 dealing with the coupling of angular momenta, the use of equivalent operators is a paraphrase of the fundamental formula (13.38) which expresses the Wigner-Eckart theorem, and the Tables 17 of the matrix elements of the  $O_k^a$  are nothing but tables of Clebsch-Gordan coefficients apart from normalization constants. The quantities  $\langle J \| \alpha \| J \rangle$ ,  $\langle J \| \beta \| J \rangle$ ,  $\langle J \| \gamma \| J \rangle$  that we have tabulated are proportional to the diagonal values of reduced matrix elements in formula (13.38),

$$\frac{1}{\sqrt{(2J+1)}} (J \| T_k \| J).$$

Similarly  $\langle L \| \alpha \| L \rangle$ ,  $\langle L \| \beta \| L \rangle$ ,  $\langle L \| \gamma \| L \rangle$  are proportional to reduced matrix elements  $(1/\sqrt{(2L+1)})(L \| T_k \| L)$  and a relation between them can be obtained in a closed form by means of the vector recoupling 6j-symbol of Racah.

Indeed the passage from  $(L \| T_k \| L)$  to  $(J \| T_k \| J)$  involves two

vector coupling schemes: on one hand,

$$\mathbf{L} + \mathbf{S} = \mathbf{J}, \quad \mathbf{J} + \mathbf{k} = \mathbf{J};$$

and on the other hand,

$$\mathbf{L} + \mathbf{k} = \mathbf{L}, \quad \mathbf{L} + \mathbf{S} = \mathbf{J},$$

which, from the vector coupling properties of the  $6j$ -symbol described in § 13.5 leads to the formula

$$(J \| T_k \| J) = (-1)^{L+S+J+k}(2J+1) \begin{pmatrix} J & k & J \\ L & S & L \end{pmatrix} (SL \| T_k \| SL). \quad (16.29)$$

This enables us to rewrite formula (16.28) in a closed form,

$$(J \| \alpha, \beta, \gamma \| J) = (L, S \| \alpha, \beta, \gamma \| L, S) (-1)^{L+S+J+k} \times \\ \times \frac{\sqrt{(2J+1)}}{\sqrt{(2L+1)}} \begin{pmatrix} J & k & J \\ L & S & L \end{pmatrix}. \quad (16.30)$$

### 16.3. Off-diagonal matrix elements of the crystal field

The approximation of the intermediate crystal field implies that its magnitude is small compared to the distance between two terms  $(L, S)$  and  $(L', S)$  between which it has matrix elements. A few calculations have been made in the iron group taking into account off-diagonal effects of the crystal field. Even more important is the coupling through the crystal field between two multiplets  $(L, S, J)$  and  $(L, S, J')$  in the rare earths. The method of equivalent operators becomes inadequate in that case and one must go back to the Wigner-Eckart formula (13.38). One of the advantages of this more powerful approach is that the calculation of a reduced off-diagonal matrix element  $(J \| T_k \| J')$ , knowing  $(L, S \| T_k \| L, S)$  or  $(L, S \| T_k \| L', S)$ , is no more difficult than that of the diagonal elements  $(J \| T_k \| J)$  which are proportional to the  $(J \| \alpha, \beta, \gamma \| J)$ .

The formula generalizing (16.29) is

$$(J \| T_k \| J') = (-1)^{L+S+J'+k} \sqrt{(2J+1)} \sqrt{(2J'+1)} \begin{pmatrix} J & k & J' \\ L' & S & L \end{pmatrix} \times \\ \times (SL \| T_k \| SL'). \quad (16.31)$$

This formula (16.31) combined with the fundamental formula (13.38) enables one to calculate all the matrix elements

$$\langle L, S, J, M_J | T_k^q | L, S, J', M_J' \rangle \quad (16.32)$$

in closed form once the constants  $\langle SL \| T_k \| SL \rangle$  have been computed.

It is in a way unfortunate that the pioneer work of Stevens (1952a) has not been expressed in the more rational formalism of Racah which culminates in the powerful formulae (13.38) and (16.31). However, so much of the published work in paramagnetic resonance has been couched in the Stevens language that more would be lost than gained by attempting to translate it all into Racah's language. Therefore even for off-diagonal elements we shall keep the normalization (or lack of it) of Stevens and give the following formulae useful in the theory of magnetic resonance for rare-earth ions.

$$\langle J+1, J_z | \sum_i P_2^0(\mathbf{r}_i) | J, J_z \rangle = \langle r^2 \rangle \langle J+1 \| \alpha \| J \rangle J_z \sqrt{\{(J+1)^2 - J_z^2\}} \quad (16.33)$$

$$\begin{aligned} \langle J+1, J_z | \sum_i P_4^0(\mathbf{r}_i) | J, J_z \rangle \\ = \langle r^4 \rangle \langle J+1 \| \beta \| J \rangle J_z (7J_z^2 - 3J^2 - 6J + 2) \sqrt{\{(J+1)^2 - J_z^2\}} \end{aligned} \quad (16.34)$$

$$\begin{aligned} \langle J+1, J_z | \sum_i P_6^0(\mathbf{r}_i) | J, J_z \rangle = \langle r^6 \rangle \langle J+1 \| \gamma \| J \rangle \times \\ \times J_z \{33J_z^4 - 5J_z^2(6J^2 + 12J - 15) + 5J^4 + 20J^3 - 5J^2 - 50J + 12\} \end{aligned} \quad (16.35)$$

$$\begin{aligned} \langle J+1, J_z \pm 6 | \sum_i P_6^6(\mathbf{r}_i) | J, J_z \rangle \\ = \pm \frac{\langle r^6 \rangle}{14} \langle J+1 \| \gamma \| J \rangle \sqrt{\frac{(J \pm J_z + 7)! (J \mp J_z)!}{(J \mp J_z - 5)! (J \pm J_z)!}}. \end{aligned} \quad (16.36)$$

The coefficients  $\langle J+1 \| \alpha \| J \rangle$ ,  $\langle J+1 \| \beta \| J \rangle$ ,  $\langle J+1 \| \gamma \| J \rangle$  are listed for the rare earths in Table 20.

#### 16.4. The electronic Zeeman interaction

We continue the list of electronic interactions by including first the equivalent operators for the electronic Zeeman interaction. The magnetic moment operator is  $\mu = -\beta(\mathbf{L} + 2\mathbf{S})$  and inside a manifold  $(J, L, S)$  we can write

$$\mathbf{L} + 2\mathbf{S} = \langle J \| \Lambda \| J \rangle \mathbf{J}, \quad (16.37)$$

where  $\langle J \| \Lambda \| J \rangle$  is just the Landé factor. It is given by eqn (11.12b) in the approximation we have made of taking  $g_s = 2$ , and numerical values for the ground states of the rare-earth ions are listed in Table 20.

There are also off-diagonal elements  $\langle JM | \mathbf{L} + 2\mathbf{S} | J'M' \rangle$ . Here it is useful to note that the matrix elements of  $\mathbf{J} = \mathbf{L} + \mathbf{S}$ , being diagonal in  $\mathbf{J}$ , are zero between two manifolds for which  $J \neq J'$ . Hence

$$\langle JM | \mathbf{S} | J'M' \rangle = -\langle JM | \mathbf{L} | J'M' \rangle = \langle JM | \mathbf{L} + 2\mathbf{S} | J'M' \rangle \quad (16.38)$$

and these matrix elements vanish except for  $|J-J'| = 1$ . The matrix elements we require are

$$\langle J+1, J_z | L_z + 2S_z | J, J_z \rangle = \langle J+1 \| \Lambda \| J \rangle \{ (J+1)^2 - J_z^2 \}^{\frac{1}{2}} \quad (16.39)$$

$$\begin{aligned} \langle J+1, J_z \pm 1 | L_x + 2S_x | J, J_z \rangle \\ = \mp \langle J+1 \| \Lambda \| J \rangle \frac{1}{2} \{ (J \pm J_z + 1)(J \pm J_z + 2) \}^{\frac{1}{2}}, \end{aligned} \quad (16.40)$$

where the reduced matrix element is given by

$$\begin{aligned} \langle J+1 \| \Lambda \| J \rangle \\ = \left\{ \frac{(J+L+S+2)(-J+S+L)(J+S-L+1)(L+J-S+1)}{4(J+1)^2(2J+1)(2J+3)} \right\}^{\frac{1}{2}}, \end{aligned} \quad (16.41)$$

whose values are also listed in Table 20.

### 16.5. Electron spin-spin interactions

In addition to the magnetic interaction between the electrons and the external magnetic field, there are also spin-spin interactions between electrons which may contribute to the fine structure of the resonance line.

As shown by Breit (1929), the magnetic interaction between two electrons can be written:

$$\mathcal{H}_{ss} = 4\beta^2 \left\{ \frac{\mathbf{s}_1 \cdot \mathbf{s}_2}{r_{12}^3} - \frac{3(\mathbf{s}_1 \cdot \mathbf{r}_{12})(\mathbf{s}_2 \cdot \mathbf{r}_{12})}{r_{12}^5} \right\} - \frac{32\pi\beta^2}{3} (\mathbf{s}_1 \cdot \mathbf{s}_2) \delta(\mathbf{r}_{12}). \quad (16.42)$$

The last term of (16.42) is invariant under rotations of both spin and orbital coordinates. It commutes therefore with  $\mathbf{L}^2$  and  $\mathbf{S}^2$ , and within a term  $(L, S)$  behaves as an additive constant. This constant vanishes for a term obeying Hund's rule which, being completely symmetrical with respect to spin coordinates, is completely antisymmetrical with respect to orbital coordinates. The first term of (16.42), by arguments (see § 17.4) similar to those that lead to eqn (17.45), can be rewritten within a term  $(L, S)$  as

$$\begin{aligned} W_{ss} &= -\rho \sum_{p,q} \left\{ \frac{1}{2}(L_p L_q + L_q L_p) - \frac{1}{3}L(L+1) \delta_{pq} \right\} S_p S_q \\ &= -\rho \{ (\mathbf{L} \cdot \mathbf{S})^2 + \frac{1}{2}(\mathbf{L} \cdot \mathbf{S}) - \frac{1}{3}L(L+1)S(S+1) \}. \end{aligned} \quad (16.43)$$

The constant  $\rho$  can be evaluated by the usual methods of operator equivalents. For an  $(L, S)$  term that obeys Hund's rule and is built from  $d$ -electrons,  $\rho$  is given by (Pryce 1950)

$$\rho = \frac{-4}{7(2L-1)} \left\{ \left( \frac{5}{S} - 4 \right) p + \frac{1}{7} \left( 62 - \frac{100}{S} \right) q \right\}^2 \beta^2, \quad (16.44)$$

where

$$p = \int_0^\infty \frac{1}{r} R^2(r) \, dr \int_0^r r'^2 R^2(r') \, dr',$$

$$q = \int_0^\infty \frac{1}{r^3} R^2(r) \, dr \int_0^r r'^4 R^2(r') \, dr',$$

in which  $R(r)$  is the radial wave-function of the  $d$ -electrons. For free ions,  $\rho$  can be estimated from the departure from the Landé interval rule, leading to values of  $\rho$  of the order of  $0.5 \text{ cm}^{-1}$  in the iron group (Pryce 1950), but, as pointed out by Trees (1951), this includes contributions from second-order effects of the spin-orbit coupling. Later calculations by Watson and Blume (1965) give rather smaller values, which are listed in Table 7.6 for ions of the  $3d$  group. Just what value should be used in interpreting a paramagnetic resonance experiment is rather complicated. If an interaction of the form  $W_{ss}$  is present, its magnitude should include contributions from all sources, including second-order effects of the spin-orbit coupling. However the latter may not be the same as for the free ion, just as the spin-orbit coupling itself is modified through bonding effects.