

order $\left(\frac{D}{G}\right)^2 \sin^2 2\theta$. Bleaney and Rubins derive the general expression for relative intensity:

$$\left[\frac{3D \sin 2\theta}{4G} \right]^2 \left[1 + \frac{S(S+1)}{3M(M-1)} \right]^2 [I(I+1) - m^2 - m] \quad (5.36)$$

comparing $|M, m\rangle \rightarrow |M-1, m-1\rangle$ with $|M, m\rangle \rightarrow |M-1, m\rangle$,

$ S, \frac{1}{2}\rangle$	$ S, -\frac{1}{2}\rangle$	$ I, \frac{1}{2}\rangle$	$ I, -\frac{1}{2}\rangle$	$ -\frac{1}{2}, \frac{1}{2}\rangle$...
$\frac{1}{2}G + \frac{1}{2}A$ $+\frac{1}{2}D(3\cos^2\theta - 1)$		$-(\sqrt{3}/2)D \sin 2\theta$		$(\sqrt{3}/2)D \sin^2 \theta$	
$\frac{1}{2}G - \frac{1}{2}A$ $+\frac{1}{2}D(3\cos^2\theta - 1)$	$(\sqrt{3}/2)A$	$(\sqrt{3}/2)A$	$-(\sqrt{3}/2)D \sin 2\theta$		
$-(\sqrt{3}/2)D \sin 2\theta$	$(\sqrt{3}/2)A$	$\frac{1}{2}G + \frac{1}{2}A$ $-\frac{1}{2}D(3\cos^2\theta - 1)$			
$-(\sqrt{3}/2)D \sin 2\theta$	$-(\sqrt{3}/2)D \sin 2\theta$	$\frac{1}{2}G - \frac{1}{2}A$ $-\frac{1}{2}D(3\cos^2\theta - 1)$	A		
$(\sqrt{3}/2)D \sin^2 \theta$		A	$-\frac{1}{2}G - \frac{1}{2}A$ $-\frac{1}{2}D(3\cos^2\theta - 1)$		
⋮	⋮	⋮	⋮	⋮	⋮

The forbidden lines have zero intensity at $\theta = 0, \pi/2$ and maximum intensity at $\theta = \pi/4$. They can be of similar intensity to the $\Delta m = 0$ lines for values of $D/G \sim \frac{1}{16}$ as was indeed found to be the case in $V^{2+} - ZnSiF_6 \cdot 6H_2O$.

Bleaney and Rubins also investigated $\Delta m = 2, 3$ transitions in this system while Drumheller and Rubins⁵, and Cavenett⁶ have observed (and explained) $\Delta m = 1$ transitions for Mn^{2+} in cubic lattices. Here, the axial crystal field term is replaced by the cubic term and the angular dependence of the intensities found to depend on $(\sin 4\theta)^2$ rather than $(\sin 2\theta)^2$.

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CHAPTER 6

A Simple Approach to Crystal Field Theory

6.1. Qualitative Outline

It is well known that group theory provides a powerful method of dealing with problems where symmetry plays an important role and the study of crystal field effects has proved one of its most successful applications. Provided the symmetry of the problem is known, group theory gives a detailed qualitative account of the way in which the orbital degeneracy of a magnetic ion is lifted by a crystal field.

The methods of group theory are assumed to be beyond the scope of this book but it is, nevertheless, possible to derive a great many of the results in a very simple way. We need only assume a knowledge of the angular properties of the appropriate (unpaired) electron wavefunctions, i.e. $3d$, $4d$, $4f$, etc. We shall illustrate the idea by applying it to p electrons since they provide a particularly simple case and then apply it to the more important d electrons.

To be specific, we assume a crystal field of intermediate strength (Section 2.3) such that the coupling between spins and orbits is broken down but not that between individual orbitals. Thus the electronic wavefunctions may be described in terms of quantum numbers L and S and, as an electric field may interact only with the orbital motion, our problem is that of calculating how the $(2L+1)$ orbital levels split when a free ion is introduced into a crystal lattice.

Let us first consider the nature of the atomic orbitals involved.¹ If we assume a central field approximation these are hydrogen-like orbits, conveniently written in spherical polar coordinates as:

$$\psi_{nlm}(r, \theta, \varphi) = R_{nl}(r) \cdot \Theta_{lm}(\theta) \cdot \Phi_m(\varphi) \quad (6.1)$$

where n , l , m are the principal, angular momentum and magnetic quantum numbers and the angular functions are:

$$\Theta_{lm}(\theta) = \left[\frac{(2l+1)(l-|m|)!}{2(l+|m|)!} \right]^{\frac{1}{2}} P_l^{|m|}(\cos \theta) \quad (6.2)$$

$$\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}} \exp im\varphi \quad (6.3)$$

The radial function $R_{nl}(r)$, though well known for the free hydrogen atom, is not easy to compute for the transition group orbitals of interest to us. Recent calculations of Freeman and Watson² provide reasonably accurate data for the free ions of the iron group ($3d$ orbitals) and rare earth group ($4f$) but the orbits are sure to be modified when the ion is situated in a crystal lattice. On this count, it is usual to regard $R_{nl}(r)$ as an undetermined function.

The product of the two angular functions is the spherical harmonic of degree l and order m , i.e.

$$(-1)^l \Theta_{lm}(\theta) \Phi_m(\phi) = Y_l^m(\theta, \phi) \quad (6.4)$$

and finally, the function $P_l^m(\cos \theta)$ is the corresponding Legendre polynomial defined as:

$$P_l^m(x) = \frac{(1-x^2)^{m/2}}{2^l l!} \frac{d^{l+m}}{dx^{l+m}} (x^2 - 1)^l \quad (6.5)$$

Values of these angular functions are given in Table 6.1 for p , d and f orbitals ($l = 1, 2, 3$).

Table 6.1. VALUES OF $Y_l^m(\theta, \phi)$ FOR $l = 1, 2, 3$

p	$l = 1$	$m = 0$	$\sqrt{\frac{3}{4\pi}} \cos \theta$
		$m = \pm 1$	$\sqrt{\frac{3}{8\pi}} \sin \theta \exp(\pm i\phi)$
d	$l = 2$	$m = 0$	$\sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)$
		$m = \pm 1$	$\sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta \exp(\pm i\phi)$
		$m = \pm 2$	$\sqrt{\frac{15}{32\pi}} \sin^2 \theta \exp(\pm 2i\phi)$
f	$l = 3$	$m = 0$	$\sqrt{\frac{14}{32\pi}} (5 \cos^2 \theta - 3) \cos \theta$
		$m = \pm 1$	$\sqrt{\frac{21}{64\pi}} (5 \cos^2 \theta - 1) \sin \theta \exp(\pm i\phi)$
		$m = \pm 2$	$\sqrt{\frac{105}{32\pi}} \sin^2 \theta \cos \theta \exp(\pm 2i\phi)$
		$m = \pm 3$	$\sqrt{\frac{35}{64\pi}} \sin^3 \theta \exp(\pm 3i\phi)$

It is convenient to use not the functions of Table 6.1 themselves but suitable linear combinations which give wholly real (or imaginary) functions. Thus, instead of the p states $|1\rangle$, we choose $p_x \equiv \frac{1}{\sqrt{2}}(|1\rangle + | -1\rangle)$ having angular variation $\sqrt{\frac{3}{4\pi}} \sin \theta \cos \varphi$ and

$p_y \equiv \frac{1}{\sqrt{2}}(|1\rangle - | -1\rangle)$ giving $\sqrt{\frac{3}{4\pi}} i \sin \theta \sin \varphi$. In Fig. 6.1 are shown the densities of the functions p_x , p_y and p_z (i.e. $|p_x|^2$, etc.) which represent the probabilities of the electron being found along any specified radius vector.

Each lobe represents a volume of revolution obtained by rotation about the appropriate axis, i.e. p_z about z , p_x about x , p_y about y . Apart from the permutation of axes all three diagrams are identical.

Suppose that we now consider an electron in a p orbital situated within a regular octahedron of negative charges, i.e. charges placed at equal distances along each of the (positive and negative) axes in

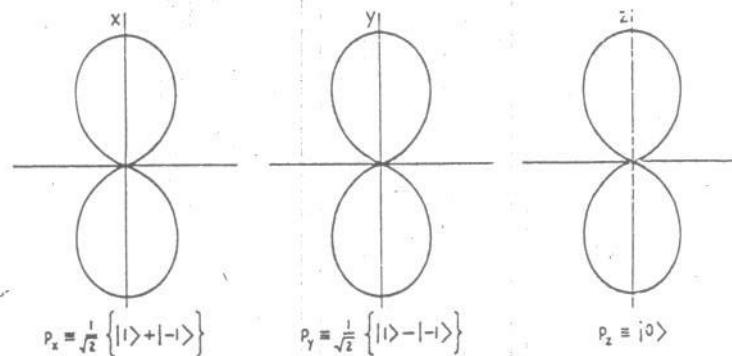


Fig. 6.1. Angular distribution functions for the three p orbitals. The probability of finding the electron along a particular direction is proportional to the length of the corresponding radius vector

Fig. 6.1. For example, these may be the negatively charged oxygen ions in a simple cubic lattice such as magnesium oxide, where the unpaired p electron is bound to an ion at the magnesium site. The negatively charged electron will suffer repulsion from the neighbouring charges and a consequent increase in energy but from symmetry it is apparent that this increase will be the same for each of the three orbitals. The three-fold degeneracy of the p states is not raised by an octahedral crystal field.

If the neighbouring ions along the positive and negative z directions are displaced outwards, giving rise to tetragonal symmetry, it is again apparent that the energy increase of the p_z orbital will be less than that of the other two; the p states are split by a field of tetragonal symmetry. This is represented by the energy level diagram shown in Fig. 6.2.

A simple extension of these ideas indicates that, in a field of rhombic symmetry (each pair of neighbours at different distances from the origin) all degeneracy is lifted. This is a general result which applies to d and f orbitals.

Finally, we note that not only predict that the p energy levels will split but also the sign of splitting—e.g. in Fig. 6.2 we can say with certainty that the level p_z will be higher than the p_x, p_y doublet. What we cannot say, of course, is how large the splitting will be. However, we shall find that more sophisticated treatments can do comparatively little better so this simple pictorial approach is not at a very serious disadvantage.

Having determined the level splitting for a single p electron we can extend our ideas to cover two or more (having the same principal quantum number). To do so we must regard Fig. 6.2 as

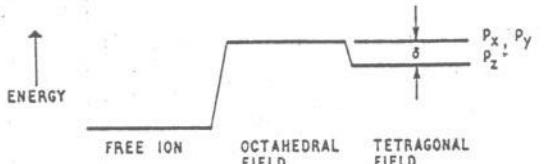


Fig. 6.2. Energy level diagram to show (qualitatively) the change in energy of p orbitals in crystal fields of octahedral and tetrahedral symmetry

representing the splitting of the p orbitals (even when empty) and suppose that we feed electrons into the available levels, bearing in mind Hund's rule that the state of lowest energy is that having maximum total spin. More specifically, we assume that the difference in energy between a parallel and an antiparallel pair of spins is much greater than any crystal field splitting. As we are concerned only with the lowest energy levels, we neglect states having less than maximum spin.

A single p electron may be placed in any one of the three orbitals, p_x, p_y, p_z . For the case we are considering, the lowest energy occurs with the electron in p_z and the energy level diagram for np^1 is simply a copy of Fig. 6.2. Bearing in mind Pauli's exclusion principle, two 'parallel' electrons may be placed in the three orbitals in only three ways, i.e. in configurations $p_z p_x, p_z p_y$, and $p_z p_y$. The first two of these have equal total energy while the third has total energy greater by just the splitting δ . Thus, the energy level diagram for np^2 is similar to Fig. 6.2 but with the singlet lying higher than the doublet. Three electrons can be placed in the three orbitals in only one way and we have a singlet ground state 1S which cannot be split by a crystal field of any symmetry.

At this point we have reached a half-filled shell and the addition of a fourth electron implies that its spin must be antiparallel to those already present. It is easy to see that the energy level diagram will be similar to that for np^1 and that for np^5 with np^2 . This illustrates the general rule that a configuration having one electron less than a filled shell may be regarded as a single positive hole, having energy splittings similar to a single electron but inverted. In the same way $np^2 \equiv -(np^{6-2})$.

6.2. Field Splittings of d States

We can now extend our ideas to discuss crystal field splittings in the iron group. Fig. 6.3 shows the angular variation of the real d wavefunctions formed in the same way as above. Each lobe represents a volume of revolution as before* (except the small lobes of $d_{3z^2-r^2}$,

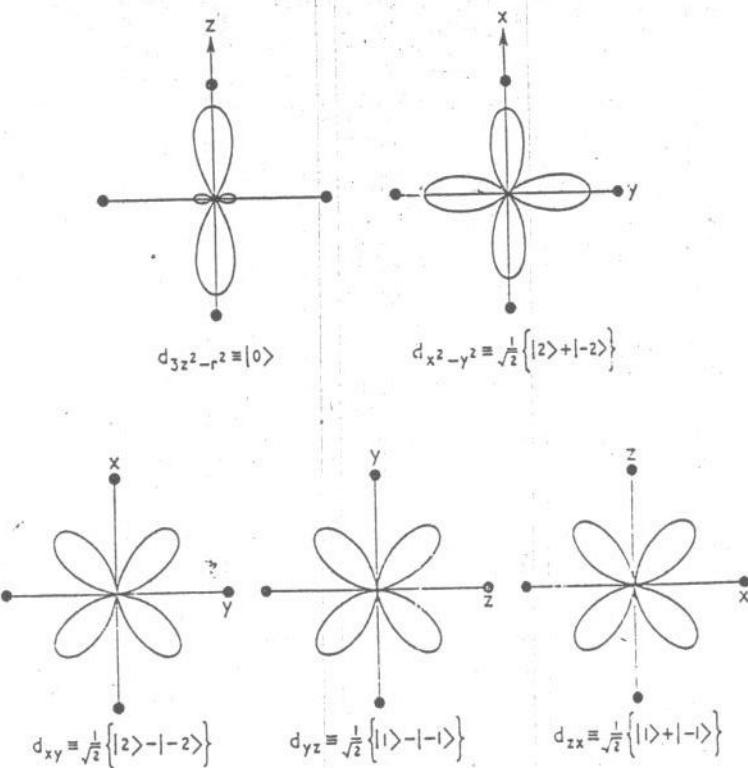


Fig. 6.3. Angular distribution functions for the five d orbitals, cf. Fig. 6.1. The black circles represent neighbouring ions

which are rotated about the z axis and thus form a 'doughnut'). The functions d_{xy}, d_{yz} , and d_{zx} are identical apart from the permutation of axes. The black circles in Fig. 6.3 represent neighbouring, negatively charged ions forming a regular octahedron about the central magnetic ion.

An examination of Fig. 6.3 shows that the functions d_{xy}, d_{yz} , and d_{zx} have the same energy in an octahedral crystal field whereas

* This is strictly true only for the $d_{3z^2-r^2}$ orbital but is an adequate approximation for the qualitative arguments which follow.

$d_{3z^2-r^2}$ and $d_{x^2-y^2}$ have somewhat higher energy. The first three functions are referred to alternatively as d_5 or t_2 states and the second pair as d_7 or e . The t , e nomenclature derives from group theory which is now widely used so we shall adopt it in what follows even though we shall not make use of the theory itself.

The splitting of the d levels in octahedral field is illustrated in Fig. 6.4 (a). It is not, of course, obvious from our simple approach that the two e states have equal energy—this must be taken on trust for the time being. The further splitting produced by moving the neighbouring ions along the z axis further away, to produce a field of tetragonal symmetry is illustrated in Fig. 6.4 (b). The functions d_{xy} and $d_{z^2-y^2}$ which lie close to the xy plane will be very

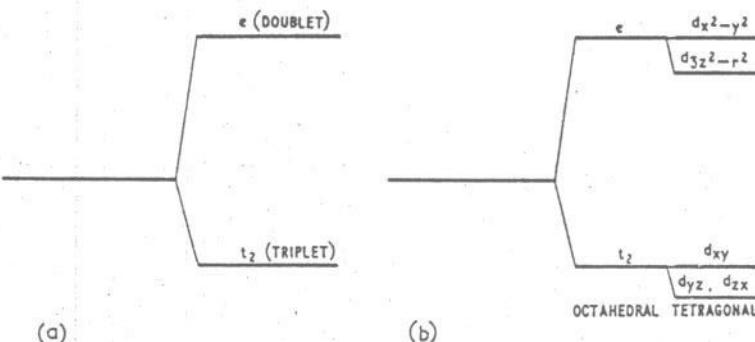


Fig. 6.4. Energy levels of a single d electron in crystal fields of (a) octahedral and (b) tetragonal symmetry

little affected by the change but the energy of $d_{3z^2-r^2}$ will obviously be reduced and (only slightly less obviously) so will those of d_{yz} and d_{zx} by equal amounts.

The further extension of the method to rhombic symmetry is straightforward. The reader may also convince himself that if the magnetic ion is situated at the body centre of a cube, the d states split similarly to Fig. 6.4 (a) but with the doublet lower (with the same reservation concerning the degeneracy of the two e states). Removing ions from alternate corners to leave a tetrahedron of neighbours affects this result only quantitatively.

Having derived (or at least, made plausible) the splittings of the d orbitals we can now work out splittings for all d^n configurations in the same way as we did for p electrons. The case of a single d electron in octahedral field corresponds directly to Fig. 6.4 (a). Two d electrons (with parallel spins) can be placed in the five levels of Fig. 6.4 (a) in ${}^5C_2 = 10$ different ways. The lowest total energy corresponds to both electrons being in the t_2 triplet, there being ${}^3C_2 = 3$ ways of distributing them so this lowest level will be triply degenerate. The maximum total energy occurs when both electrons

are in the e levels. There is only one way of doing this, thus yielding a singlet. Finally, it is also possible to place one electron in a t_2 and the other in an e level which can be done in $3 \times 2 = 6$ ways. However, not all such arrangements yield equal energies as can be understood by considering the repulsive interaction between electrons. For example, an electron in the $d_{3z^2-r^2}$ orbital which lies close to the z axis will interact only slightly with a second one in the $d_{x^2-y^2}$ orbital whose density is confined largely to the xy plane. However, the orbitals $d_{x^2-y^2}$ and d_{xy} will obviously repel one another considerably more. For the case of one electron in e and the other in t_2 states we can construct a table of electron repulsion energies (Table 6.2) from which it is apparent that the six possible d^2 states

Table 6.2

Electron 1	Electron 2	Repulsion
$d_{3z^2-r^2}$	d_{xy}	Small
$d_{3z^2-r^2}$	d_{yz}, d_{zx}	Large
$d_{x^2-y^2}$	d_{xy}	Large
$d_{x^2-y^2}$	d_{yz}, d_{zx}	Small

are split into two groups of three. (Note that the other arrangements where both electrons are in t_2 or e give rise to small repulsion energies.) Collecting together these qualitative results we obtain the result

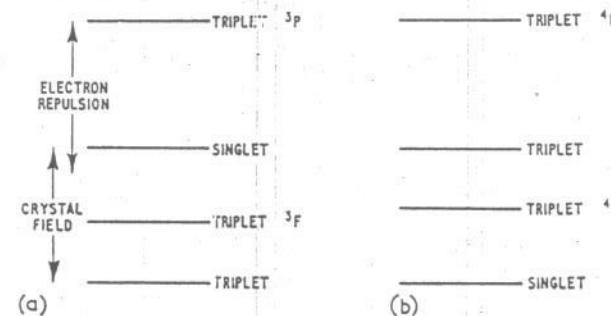


Fig. 6.5. Energy levels of d^2 and d^3 configurations in octahedral crystal field

illustrated in Fig. 6.5 (a) for the energy levels of d^2 in an octahedral field.

The only spin triplet states of the d^2 configuration are 3P and 3F so the assignments on the right of Fig. 6.5 are self-evident. The fact that we find 3F lower is consistent with Hund's rule.

The extension to other d^n configurations is straightforward. We shall briefly outline the argument for d^3 and leave the remaining

examples as an exercise. Three electrons may be distributed among the orbital levels of Fig. 6.4 (a) in the following manner:

1. All in t_2 : one way.
2. Two in e and one in t_2 : three ways.
3. One in e and two in t_2 : six ways.

As above, the third arrangement yields two sets of three levels and suggests the level scheme of Fig. 6.5 (b) where it can be seen that the splitting of the F state is inverted with respect to that of d^2 .

Similar lines of argument can be applied to crystal fields of lower symmetry but sufficient has already been said to give a qualitative picture of the raising of the orbital degeneracy of the free ion by a crystalline electric field. We must now put our ideas on a more formal basis.

6.3. The Crystal Potential, V , and Electron Energies³

Before launching into the mathematical treatment of crystal field effects, let us reiterate the nature of the problem. In the crystal field approximation it reduces to the calculation of the energy of an electric charge (the electron) in an electric field. What raises it above the trivial, is the fact that the electric field has a rather special spatial variation and the electron, being bound in an atom, is also confined to certain regions in space. The electric field arises from the presence of neighbouring charged ions (or electric dipoles) and we have already seen in a qualitative way how the energy of an electron in this field depends on the angular variation of its orbit. The problem of crystal field theory is to calculate the energy associated with each of the possible orbital states in a specific crystal field.

As we wish to calculate electron energies, the obvious way of defining the crystal field is in terms of a potential $V(x, y, z)$ which is a function of space coordinates. If the electron has coordinates (x_1, y_1, z_1) at any instant its energy is simply $eV(x_1, y_1, z_1)$. However, the energy of an electron at a precise point in space is not an experimentally observable quantity: instead we require an average over the whole orbital, i.e. we must calculate the average value of $eV(x, y, z)$, where the range of values of (x, y, z) is determined by the wavefunction in question.

So far we have considered only single electron functions; when we wish to deal with a multi-electron atom, we must sum the potential over all the unpaired electrons. Rather than do this explicitly we shall regard the electrons as coupled together and describe the system in terms of the total angular momentum quantum number L rather than the individual l 's. The effect of the crystal field is then partially to raise the $(2L + 1)$ -fold orbital degeneracy (see Section 6.4).

To illustrate the evaluation of $V(x, y, z)$ we shall consider a special case, that of tetragonal symmetry. The nucleus of the paramagnetic

ion is taken as origin of cartesian coordinates, nearest neighbour ions being situated at $(\pm a, 0, 0)$, $(0, \pm a, 0)$ and $(0, 0, \pm b)$. A section through the zx plane is shown in Fig. 6.6, where R is the distance from the point (x, y, z) to the ion B . The contribution to the potential due to the ion B is simply

$$V_B = \frac{e'}{R} = \frac{e'}{[x^2 + y^2 + (b - z)^2]^{\frac{1}{2}}} = \frac{e'}{[b^2 + r^2 - 2bz]^{\frac{1}{2}}} \quad (6.6)$$

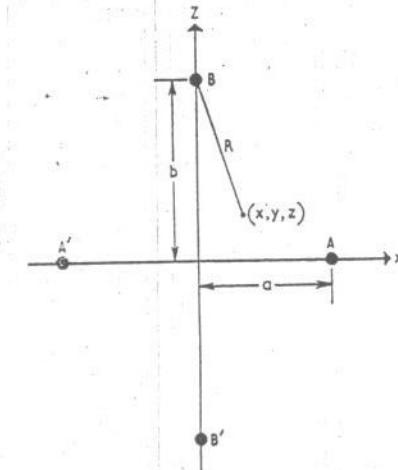


Fig. 6.6. System of axes used in calculating electrostatic potential due to octahedron of negative ions A , A' , etc. Figure represents a cross-section through the zx plane

where e' is the effective charge of B and $r^2 = x^2 + y^2 + z^2$. It is obvious from Fig. 6.6 that the ion B' contributes a similar term

$$V_{B'} = \frac{e'}{[b^2 + r^2 + 2bz]^{\frac{1}{2}}}$$

If we assume there is no overlap of the central ion orbitals onto the neighbours, i.e. we assume $r \ll R$, we may expand these terms using a binomial expansion in terms of the type $\frac{r}{b}$, $\frac{z}{b}$, etc., and it can be seen that odd powers of z cancel in pairs. Similarly, the ions A , A' contribute further terms where b is replaced by a and z by x . Finally the third pair of ions contributes similar terms in y . Expanding all six terms and summing gives the expression:

$$\begin{aligned} V = e' & \left[\left(\frac{4}{a} + \frac{2}{b} \right) - \left(\frac{2r^2}{a^3} + \frac{r^2}{b^3} \right) + 3 \left(\frac{x^2 + y^2}{a^3} + \frac{z^2}{b^3} \right) \right. \\ & + \frac{3}{4} \left(\frac{2r^4}{a^5} + \frac{r^4}{b^5} \right) - \frac{15}{2} \left(\frac{r^2(x^2 + y^2)}{a^5} + \frac{r^2 z^2}{b^5} \right) \\ & \left. + \frac{35}{4} \left(\frac{x^4 + y^4}{a^5} + \frac{z^4}{b^5} \right) + \text{higher order terms} \dots \right] \quad (6.7) \end{aligned}$$

The first term in Equation 6.7 represents an energy which is equal for all orbits (i.e. it shows no angular dependence) and, as we are interested primarily in energy differences, it is usually omitted.

A more convenient form of Equation 6.7 is obtained by dividing it into cubic and axial terms. Setting $a = b$ and using $x^2 + y^2 + z^2 = r^2$ we find

$$V_{\text{cubic}} = \frac{35}{4} \frac{e'}{a^5} \left(x^4 + y^4 + z^4 - \frac{3}{5} r^4 \right) \quad (6.8)$$

correct to fourth order. If we now write $b = a + \delta$, where we assume $\delta \ll a$ (i.e. a small distortion of the octahedron) we can expand each term of Equation 6.7 in powers of δ/a and, retaining only first powers of δ/a obtain:

$$\begin{aligned} V &= \frac{35}{4} \frac{e'}{a^5} \left[x^4 + y^4 + z^4 - \frac{3}{5} r^4 \right] \\ &\quad - 3 \frac{e'}{a^3} [3z^2 - r^2] \frac{\delta}{a} - \frac{e'}{a^5} [35z^4 - 30r^2z^2 + 3r^4] \frac{\delta}{a} \\ &= V_{\text{cubic}} + V_{\text{tetragonal}} \end{aligned} \quad (6.9)$$

The above expressions for V have been obtained on the assumption $r \ll a, b$, implying that the binomial expansion converges rapidly and allows us to neglect higher order terms. This is a rather stringent condition and not likely to be satisfied too well in practice. However, it can be shown that all terms in V of order higher than the fourth do not contribute to the energy of d electrons and may therefore be omitted even when $r \ll a, b$. To understand this, we first note that the various terms in Equation 6.9 can be written as spherical harmonics. The spherical harmonic of degree n and order m is defined as:

$$Y_n^m(\theta, \varphi) = (-1)^n \left[\frac{(2n+1)(n-|m|)!}{2(n+|m|)!} \right]^{\frac{1}{2}} \frac{1}{\sqrt{(2\pi)}} P_n^m(\cos \theta) \exp im\varphi \quad (6.10)$$

where $P_n^m(\cos \theta)$ is defined in Equation 6.5. (The use of n and m here is unfortunate due to possible confusion with quantum numbers appearing in Equations 6.1, et seq. There is, of course, no relation between these two sets of indices.) In Table 6.3 is given a list of the functions $r^n Y_n^m(\theta, \varphi)$ expressed in cartesian coordinates. For example, $P_2^0(\cos \theta) = \frac{1}{2}(3 \cos^2 \theta - 1)$ so $r^2 P_2^0(\cos \theta) = \frac{1}{2}(3z^2 - r^2)$ which we recognise as the second term in our expansion of V (Equation 6.9). The normalisation factor

$$(-1)^n \left[\frac{(2n+1)(n-|m|)!}{4\pi(n+|m|)!} \right]^{\frac{1}{2}}$$

is written in curly brackets in Table 6.3 so as to make clear which part is which.

Referring back to Equation 6.9, it is apparent that the second and

third terms are proportional to $r^2 Y_2^0$ and $r^4 Y_4^0$ respectively. V_{cubic} may be expressed in spherical harmonics by means of the identity: $x^4 + y^4 + z^4 - \frac{3}{5}r^4 = \frac{1}{2}(x^4 - 6x^2y^2 + y^4) + \frac{1}{10}(35z^4 - 30r^2z^2 + 3r^4)$ (6.11)

Therefore:

$$V_{\text{cubic}} = \frac{7\sqrt{\pi}}{3} \frac{e'}{a^5} r^4 \left(Y_4^0 + \sqrt{\left(\frac{5}{14}\right)} [Y_4^4 + Y_4^{-4}] \right) \quad (6.12)$$

The combination $[Y_4^4 + Y_4^{-4}]$ occurs because V is a real potential.

Having written the expansion V in terms of spherical harmonics we can now justify the omission of higher order terms. In calculating the energy of a $3d$ electron in a crystal field we are concerned with evaluating matrix elements of the form $\int \psi_M^* V_n^m \psi_{M'} d\tau$, where ψ_M and $\psi_{M'}$ are two of the functions ψ_{nlm} of Equation 6.1 differing (if at all) only in the value of m , and $V_n^m \propto r^n Y_n^m$. The product $\psi_M^* \psi_{M'}$, being a product of spherical harmonics, may itself be written in terms of spherical harmonics. For example, if we take $\psi_M = \psi_{322}$ and $\psi_{M'} = \psi_{32-1}$ we have

$$\begin{aligned} \psi_M^* \psi_{M'} &\propto \sin^2 \theta \exp -2i\varphi \sin \theta \cos \theta \exp -i\varphi \\ &= \sin^3 \theta \cos \theta \exp -3i\varphi \propto Y_4^{-3} \end{aligned}$$

In general, any product of second order harmonics may be expanded in terms of harmonics of up to fourth order (similarly, for $4f$ electrons, the expansion contains terms up to sixth order). Thus, if V_n^m is also a spherical harmonic, the integral $\int \psi_M^* \psi_{M'} V_n^m d\tau$ will be zero unless $n \leq 4$ (d electrons) or $n \leq 6$ (f electrons) due to the orthogonality of spherical harmonic functions.⁴

Table 6.3

$r^2 Y_2^0$	$= \left\{ \frac{1}{2} \left(\frac{5}{\pi} \right)^{\frac{1}{2}} \right\} \cdot \frac{1}{2} (3z^2 - r^2)$
$r^2 Y_2^{\pm 1}$	$= \left\{ \frac{1}{2} \left(\frac{5}{6\pi} \right)^{\frac{1}{2}} \right\} \cdot 3z(x \pm iy)$
$r^2 Y_2^{\pm 2}$	$= \left\{ \frac{1}{4} \left(\frac{5}{6\pi} \right)^{\frac{1}{2}} \right\} \cdot 3(x^2 - y^2 \pm 2ixy)$
$r^4 Y_4^0$	$= \left\{ \frac{3}{2} \left(\frac{1}{\pi} \right)^{\frac{1}{2}} \right\} \cdot \frac{1}{8} (35z^4 - 30r^2z^2 + 3r^4)$
$r^4 Y_4^{\pm 1}$	$= \left\{ \frac{3}{4} \left(\frac{1}{5\pi} \right)^{\frac{1}{2}} \right\} \cdot \frac{5}{2} z(7z^2 - 3r^2)(x \pm iy)$
$r^4 Y_4^{\pm 2}$	$= \left\{ \frac{1}{4} \left(\frac{1}{10\pi} \right)^{\frac{1}{2}} \right\} \cdot \frac{15}{2} [(y^4 - x^4 - 6y^2z^2 + 6z^2x^2) \pm i(7z^2 - r^2)xy]$
$r^4 Y_4^{\pm 3}$	$= \left\{ \frac{1}{8} \left(\frac{1}{35\pi} \right)^{\frac{1}{2}} \right\} \cdot 105z [(x^3 - 3xy^2) \pm i(3x^2y - y^3)]$
$r^4 Y_4^{\pm 4}$	$= \left\{ \frac{1}{16} \left(\frac{1}{70\pi} \right)^{\frac{1}{2}} \right\} \cdot 105[(x^4 - 6x^2y^2 + y^4) \pm 4i(x^3y - y^3x)]$

For sixth order terms see the review article by Hutchings.³

Thus, provided the potential V can be expanded as a sum of spherical harmonics we can neglect sixth and higher order terms in calculating d electron energies (eighth and higher for f electrons). In general, it is always possible to expand V in this form provided V satisfies Laplace's equation, i.e. provided there is no overlap of the magnetic electron charge cloud onto the neighbouring ions. This is the essence of the crystal field approximation.

It will be noticed that in the example we chose to illustrate the expansion of V only even powers of electron coordinates occur and hence only even spherical harmonics ($n = 0, 2, 4, \dots$). This is because the arrangement of neighbouring ions contains a centre of symmetry. In the absence of this (e.g. in tetrahedral symmetry) odd harmonics will occur in V . However, it is easy to show, on grounds of parity, that these terms have zero matrix element between d (or f) wavefunctions. The principle of parity conservation requires that the integral $\int \psi_M^* V_n \psi_M d\tau$ should be invariant under a change in sign of all three coordinates x, y, z . Since the product $\psi_M^* \psi_M$ remains unchanged (i.e. has even parity) it is necessary that the potential V_n should also have even parity if the matrix element is to be non-zero. We note, in passing, that odd terms give non-zero matrix elements between, for example, d and p functions as the product $\psi_d^* \psi_p$ has odd parity. This property may be important in the theory of magnetic ions in tetrahedral symmetry but we shall not consider it further in this book.

6.4. Crystal Field Operators

Having outlined a method of deriving the potential V , we now consider its use in calculating electron energies. In the first instance we shall confine attention to the iron group, the modifications necessary when considering rare earth ions being described in Section 6.7.

For the simplest case of a single $3d$ electron it is not difficult to calculate matrix elements of V directly. Thus, if we require the diagonal matrix element of $(3z^2 - r^2)$ for the state $|l=2, m=2\rangle$ (see Table 6.1) we need only write the operator as $r^2(3 \cos^2 \theta - 1)$ and evaluate the integral:

$$\langle 2|3z^2 - r^2|2\rangle = \int_0^\infty [R(r)]^2 r^2 \cdot r^2 dr \int_0^\pi \frac{15}{8} \sin^4 \theta (3 \cos^2 \theta - 1) \sin \theta d\theta \int_0^{2\pi} \frac{1}{4\pi} d\varphi \quad (6.13)$$

The radial integral cannot be performed on account of the uncertainty in $R(r)$ so we use the definition of the mean value of r^n :

$$\langle r^n \rangle = \int_0^\infty [R(r)]^2 r^n \cdot r^2 dr \quad (6.14)$$

The angular functions are readily integrated and we find:

$$\langle 2|3z^2 - r^2|2\rangle = -\frac{4}{3}\langle r^2 \rangle (3d^1) \quad (6.15)$$

Other matrix elements may be evaluated similarly. In general, we require matrix elements for multi-electron states and these can be calculated by writing these compound states as determinantal products of single electron functions.⁵ However, there is a much simpler method due to Stevens,⁶ based on operator equivalents, which we now describe.

The individual electrons are considered as coupled together to give a total orbital angular momentum represented by the quantum number L . The crystal field is then taken to interact with this coupled system so as to raise the $(2L+1)$ -fold orbital degeneracy. The method of operator equivalents provides a simple means for calculating matrix elements for states $|M\rangle$, where M is the total orbital magnetic quantum number ($M = L, L-1, \dots, -L$).

Operators are formed from each term in the crystal field expansion $V = \sum A_n V_n$ by replacing coordinates x, y, z by the operators L_x, L_y, L_z (and r^2 by $L(L+1)$). This is complicated by the fact that the L 's do not commute so a term such as xy must be replaced by $\frac{1}{2}(L_x L_y + L_y L_x)$ and so on. Stevens showed that the crystal field operators so formed give matrix elements proportional to those of the original potential functions and that only two constants of proportionality are required, one for second and one for fourth order terms in V (though these are different for each electronic configuration).

Suppose we require matrix elements of $\sum_{\text{electrons}} (3z^2 - r^2)$. The equivalent operator is $K[3L_z^2 - L(L+1)]$ which is taken to operate on the states $|M\rangle$ according to the simple rules previously enumerated for spin momentum (Equations 3.64-3.66), e.g.

$$L_z|M\rangle = M|M\rangle \quad (6.16)$$

$$L_\pm|M\rangle = \{L(L+1) - M(M \pm 1)\}^{\pm}|M \pm 1\rangle \quad (6.17)$$

The method of deriving proportionality constants may be illustrated by returning to the single electron case considered above where L and M are equal to l and m respectively. Using Equation 6.16, it is easy to show:

$$\langle 2|K[3L_z^2 - L(L+1)]|2\rangle = 6K$$

and comparing this with Equation 6.15 we find $K = -\frac{2}{3}\langle r^2 \rangle$. Usually $\langle r^n \rangle$ is written explicitly in the operator, i.e. $(3z^2 - r^2) \rightarrow \alpha \langle r^2 \rangle [3L_z^2 - L(L+1)]$, where α is a pure number ($-\frac{2}{3}$ in this case). Similarly, a potential function $\sum_{\text{electrons}} (35z^4 - 30r^2z^2 + 3r^4)$ is equivalent to the operator

$$\beta \langle r^4 \rangle \{35L_z^4 - 30L(L+1)L_z^2 + 25L_z^2 - 6L(L+1) + 3L^2(L+1)^2\}$$

A number of these equivalent operators are collected together in Table 6.4 together with the appropriate values of α and β .

Let us now summarise the results so far. The crystal field potential is expanded as a sum of spherical harmonics, i.e.

$$V = \sum_{n,m} V_n^m = \sum_{n,m} A_n^m r^n Y_n^m \quad (6.18)$$

and each term in this expansion used to derive an equivalent operator whose matrix elements within a manifold of states $|M\rangle$ are readily calculated. These matrix elements contain the uncertain factors $\langle r^2 \rangle$ and $\langle r^4 \rangle$ so it is fairly common practice to write $A_n^m \langle r^n \rangle \equiv B_n^m$, where B_n^m are parameters obtained directly from experiment (they are not the same as the B_n^m used in Chapter 4 though there is

Table 6.4. SOME OPERATOR EQUIVALENTS TOGETHER WITH VALUES OF α AND β FOR IRON GROUP IONS

$\Sigma(3z^2 - r^2)$	$= \alpha \langle r^2 \rangle \{3L_z^2 - L(L+1)\}$
$\Sigma(35z^4 - 30r^2z^2 + 3r^4)$	$= \beta \langle r^4 \rangle \{35L_z^4 - 30L(L+1)L_z^2 + 25L_z^2 - 6L(L+1) + 3L^2(L+1)^2\}$
$\Sigma(x^4 - 6x^2y^2 + y^4)$	$= \frac{1}{2}\beta \langle r^4 \rangle \{L_+^4 + L_-^4\}$
$\Sigma(x^2y - xy^3)$	$= -\frac{1}{2}i\beta \langle r^4 \rangle \{L_+^4 - L_-^4\}$
$\Sigma z(x^3 - 3xy^2)$	$= \frac{1}{2}\beta \langle r^4 \rangle \{L_z(L_+^3 + L_-^3) + (L_+^3 + L_-^3)L_z\}$
$\Sigma z(y^3 - 3x^2y)$	$= \frac{1}{2}i\beta \langle r^4 \rangle \{L_z(L_+^3 - L_-^3) + (L_+^3 - L_-^3)L_z\}$
$\Sigma(y^4 - x^4 + 6z^2x^2 - 6z^2y^2)$	$= \frac{1}{2}\beta \langle r^4 \rangle \{(7L_z^2 - L(L+1) - 5)(L_+^2 + L_-^2) + (L_+^2 + L_-^2)(7L_z^2 - L(L+1) - 5)\}$
α	$3d^1$
β	$-\frac{2}{3}\frac{1}{3}$
	$3d^2$
	$-\frac{2}{3}\frac{2}{3}$
	$3d^3$
	$\frac{1}{3}\frac{2}{3}$
	$3d^4$
	$\frac{2}{3}\frac{1}{3}$
	$3d^6$
	$-\frac{2}{3}\frac{2}{3}$
	$3d^7$
	$-\frac{2}{3}\frac{1}{3}$
	$3d^8$
	$\frac{1}{3}\frac{2}{3}$
	$3d^9$
	$-\frac{2}{3}\frac{1}{3}$

an obvious correspondence). The A_n^m may be estimated from a 'point charge' calculation as illustrated in Section 6.3 (though a lattice sum over a large number of neighbours is necessary in order to do this properly) but, as we shall see in Chapter 8, no undue reliance should be placed on the result.

6.5. Cubic and Tetragonal Crystal Fields

To illustrate the use of crystal field operators we shall calculate the splitting of the orbital levels by a cubic field of octahedral symmetry when $L = 2$ and $L = 3$. We saw in Chapter 2 that these are the only cases occurring in the iron group.

We write the appropriate potential as:

$$V_{\text{cubic}} = D(x^4 + y^4 + z^4 - \frac{3}{5}r^4) \quad (6.19)$$

which leads to an equivalent operator:

$$\mathcal{H}_{\text{cubic}} = eD\beta \langle r^4 \rangle \left\{ \frac{1}{20} [35L_z^4 - 30L(L+1)L_z^2 + 25L_z^2 - 6L(L+1) + 3L^2(L+1)^2] + \frac{1}{5}(L_+^4 + L_-^4) \right\} \quad (6.20)$$

For $L = 2$ the basic states may be written in their simplest form as $|2\rangle$, $|1\rangle$, $|0\rangle$, $| -1 \rangle$ and $| -2 \rangle$ and the first point to notice is that the operators L_{\pm}^4 couple states $|2\rangle$ and $| -2 \rangle$. All other matrix

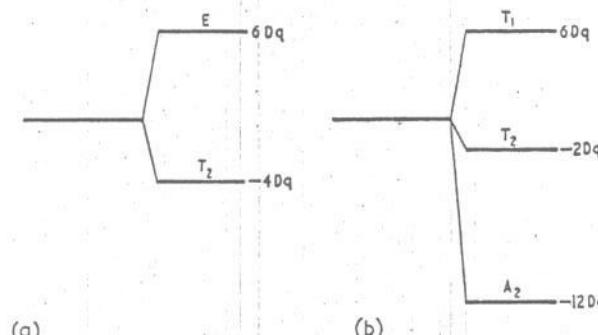


Fig. 6.7. The splitting of D and F states in octahedral crystal field

elements are diagonal. Thus, the energies of states $|1\rangle$, $|0\rangle$ and $| -1 \rangle$ are given directly by the diagonal elements:

$$\begin{aligned} \langle \pm 1 | \mathcal{H}_{\text{cubic}} | \pm 1 \rangle &= -\frac{1}{5}eD\beta \langle r^4 \rangle \\ \langle 0 | \mathcal{H}_{\text{cubic}} | 0 \rangle &= \frac{1}{5}eD\beta \langle r^4 \rangle \end{aligned}$$

To find the energies of the remaining states we must find the roots of the matrix:

	$ 2\rangle$	$ -2 \rangle$
$ 2\rangle$	$\frac{2}{5}eD\beta \langle r^4 \rangle$	$3eD\beta \langle r^4 \rangle$
$ -2 \rangle$	$3eD\beta \langle r^4 \rangle$	$\frac{3}{5}eD\beta \langle r^4 \rangle$

which are $\frac{1}{5}eD\beta \langle r^4 \rangle$ and $-\frac{1}{5}eD\beta \langle r^4 \rangle$. Thus, the five-fold degenerate D state is split into a doublet (E) and triplet (T_2) as illustrated in Fig. 6.7 (a). The separation of these levels is defined as $10Dq$, where $q = \frac{2e}{105} \langle r^4 \rangle \left(\beta = \frac{2}{63} \right)$. The parameter Dq contains

the product ee' which is positive (e and e' both being negative) so the sign of Dq follows that of β . The values of β given in Table 6.4 show that Fig. 6.7 (a) is correct for the configurations $3d^1$ and $3d^9$ but should be inverted for $3d^4$ and $3d^8$. These latter configurations may be thought of as single holes in half-filled and filled d shells, respectively.

For F states the basic kets are $|\pm\downarrow\rangle$, $|\pm 1\rangle$ and $|0\rangle$ where, in addition to the mixing of $|2\rangle$ and $|-\rangle$, L_z^4 operators also couple $|\pm 3\rangle$ with $|\mp 1\rangle$. There are thus three quadratics to be solved in this case. It is easy to show that F states split into a singlet (A_1) and two triplets (T_1 and T_2), where the singlet is lowest for $3d^3$ and $3d^8$ (Fig. 6.7 (b)) while the triplet T_1 is lowest for $3d^2$ and $3d^7$, i.e. Fig. 6.7 (b) should be inverted.

These calculations put on a rather more quantitative footing the results of Section 6.2 (compare Fig. 6.7 with Figs. 6.4 and 6.5) though it is still very difficult to estimate the magnitude of splitting produced. This is due to two factors, the uncertainty in the value of $\langle r^4 \rangle$ and the doubtful validity of the 'point charge' model used. To regard the neighbouring ions purely as point electric charges and to neglect overlap of the d wavefunctions onto these neighbours provides, at best, a crude approximation and gives rise to an uncertainty in the effective value to be used for the inter-ionic distance ' a ' in evaluating D in Equation 6.19. In practice, it is usual to regard Dq as an empirical parameter to be determined by experiment.

Let us now extend the calculation to find the splitting of the orbital levels of the $3d^1$ configuration by a field of tetragonal symmetry. The crystal field potential is given by Equation 6.9 and the equivalent operator may be written:

$$\begin{aligned} \mathcal{H} &= \mathcal{H}_{\text{cubic}} + \mathcal{H}_{\text{tetragonal}} \\ &= \mathcal{H}_{\text{cubic}} + A[3L_z^2 - L(L+1)] \\ &\quad + B[35L_z^4 - 30L(L+1)L_z^2 + 25L_z^2 - 6L(L+1) \\ &\quad \quad \quad + 3L^2(L+1)^2] \end{aligned} \quad (6.21)$$

where, on the point charge model, A and B are given by:

$$\begin{aligned} A &= -\frac{3ee'\delta}{a^4} z\langle r^2 \rangle = \frac{2}{7} \cdot \frac{ee'\delta}{a^4} \langle r^2 \rangle \\ B &= -\frac{ee'\delta}{a^6} \beta\langle r^4 \rangle = -\frac{2}{63} \frac{ee'\delta}{a^6} \langle r^4 \rangle \end{aligned} \quad (6.22)$$

and $\mathcal{H}_{\text{cubic}}$ by Equation 6.20.

Before evaluating matrix elements of $\mathcal{H}_{\text{tetragonal}}$, it is convenient first to diagonalise $\mathcal{H}_{\text{cubic}}$ by choosing appropriate basic states. As we saw above, the only off-diagonal matrix elements of $\mathcal{H}_{\text{cubic}}$ are between $|2\rangle$ and $|-\rangle$ and by examination of the matrix on page 99 it is apparent that the linear combinations of these states which diagonalise $\mathcal{H}_{\text{cubic}}$ are:

$$|+\rangle \equiv \frac{1}{\sqrt{2}} \{ |2\rangle + |-\rangle \} \text{ with energy } 6Dq$$

and

$$|-\rangle \equiv \frac{1}{\sqrt{2}} \{ |2\rangle - |-\rangle \} \text{ with energy } -4Dq$$

to see that $\mathcal{H}_{\text{tetragonal}}$ has only diagonal matrix elements with the basic set of states $|0\rangle$, $|1\rangle$, $|-\rangle$, $|+\rangle$ and $|-\rangle$ and there is no difficulty in evaluating the splittings shown in Fig. 6.8, where we have assumed $Dq \gg A, B$ and $A \gg -B$. This latter condition appears reasonable if we use Equation 6.22 with the values of

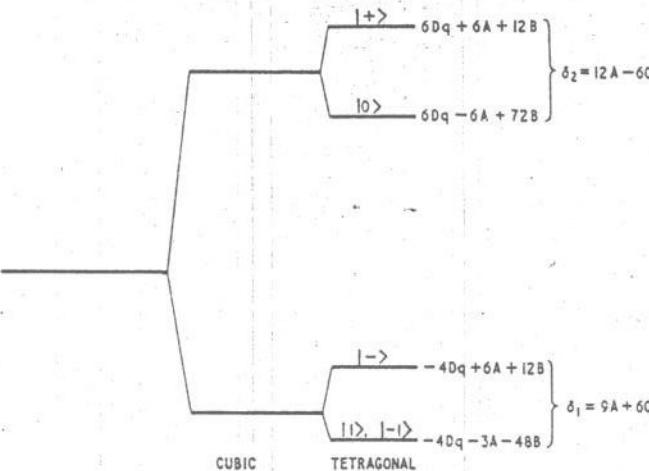


Fig. 6.8. The splitting of the $3d^1$ configuration in octahedral and tetragonal crystal fields

$\langle r^n \rangle$ for the free Ti^{3+} ion obtained from Watson's wavefunctions,² i.e.*

$$\langle r^2 \rangle = 0.531 \text{ \AA}^2, \quad \langle r^4 \rangle = 0.554 \text{ \AA}^4$$

Thus:

$$-\frac{A}{B} = \frac{9a^2\langle r^2 \rangle}{\langle r^4 \rangle} \approx 50$$

where we have taken the inter-ionic separation, $a \approx 2.4 \text{ \AA}$.

Again, the tetragonal splittings δ_1 and δ_2 are usually regarded as parameters to be found experimentally, though, if the condition $A \gg -B$ holds it is easy to see that $\delta_2/\delta_1 \approx \frac{1}{3}$ independently of assumptions about ' a ' or $\langle r^2 \rangle$.

6.6. Other Symmetry Axes

To conclude this chapter we shall discuss a second important example where the crystal field has trigonal symmetry. Suppose again, that the paramagnetic ion is surrounded by an approximately regular octahedron of neighbours which is distorted slightly by

* I am indebted to Dr. M. G. Townsend for these computations.

being extended along a (111) axis parallel to the cubic axes of Fig. 6.6). The geometrical arrangement is illustrated in Fig. 6.9, where the z axis is now chosen to lie along the axis of distortion which is a trigonal (i.e. three-fold symmetry) axis. This situation corresponds approximately to that in the Al_2O_3 lattice where the z axis coincides with the crystalline c axis.

Taking the ligand ions in pairs such as PP' in Fig. 6.9, the potential at the point (x, y, z) may be calculated in the manner of Section 6.3. After some manipulation, the result may be written in the form:

$$\begin{aligned} V = & \frac{3e'}{2R^5}(2c^2 - a^2)(3z^2 - r^2) \\ & + \frac{3e'}{4R^9}[(\frac{2}{3}a^4 - 3a^2c^2 + c^4)(35z^4 - 30r^2z^2 + 3r^4) \\ & + 35a^3c(x^3 - 3xy^2)z] \end{aligned} \quad (6.23)$$

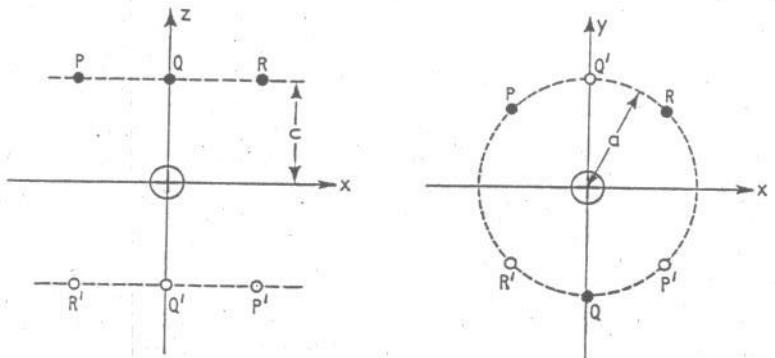


Fig. 6.9. The location of neighbouring ions for the case of a trigonally distorted octahedron. The Z axis is chosen as the trigonal (111) axis

correct to fourth-order terms; where R is the distance between the central ion and each ligand, i.e. $R = \sqrt{(c^2 + a^2)}$. Reference to Table 6.3 shows that V can be written

$$V = A_2^0 r^2 Y_2^0 + A_4^0 r^4 Y_4^0 + A_4^3 r^4 (Y_4^3 + Y_4^{-3}) \quad (6.24)$$

where the A_n^m are calculable in terms of a and c .

Let us first consider the case of regular octahedral symmetry which corresponds to putting $c = \frac{1}{\sqrt{2}}a$. Equation 6.23 reduces to:

$$\begin{aligned} V_{\text{cubic}} = & \frac{e'}{R^5} \left\{ -\frac{7}{24}(35z^4 - 30r^2z^2 + 3r^4) + \frac{35\sqrt{2}}{6}z(x^3 - 3xy^2) \right\} \\ = & -\frac{14\sqrt{\pi}e'}{9R^5}r^4 \left\{ Y_4^0 - \sqrt{\frac{10}{7}}(Y_4^3 + Y_4^{-3}) \right\} \end{aligned} \quad (6.25)$$

which may be compared with Equations 6.8 and 6.12. These two forms of V_{cubic} must, of course, be equivalent as they describe identical crystal fields—they appear different only because of the different choice of axes.

Referring to Table 6.4, the operator equivalent corresponding to Equation 6.25 is seen to be:

$$\begin{aligned} \mathcal{H}_{\text{cubic}} = & -\frac{7ee'}{24R^5}\beta\langle r^4 \rangle \{35L_z^4 - 30L(L+1)L_z^2 + 25L_z^2 \\ & - 6L(L+1) + 3L^2(L+1)^2 \\ & - 5\sqrt{2}[L_z(L_+^3 + L_-^3) + (L_+^3 + L_-^3)L_z]\} \end{aligned} \quad (6.26)$$

The reader should have no difficulty in showing that the eigenvalues of Equation 6.26 are identical with those of Equation 6.20. However,

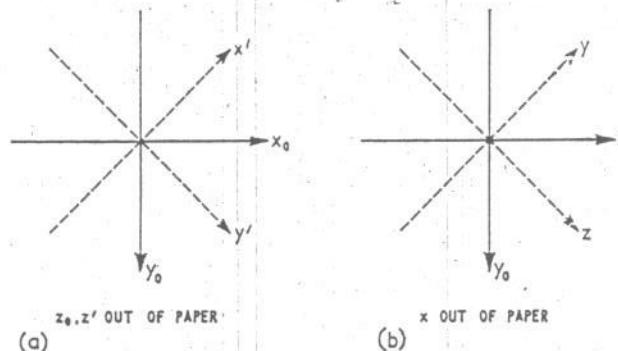


Fig. 6.10. Systems of co-ordinate axes to illustrate the transformation from a tetragonal (four-fold) to an orthorhombic (two fold) principal axis

the different choice of z axis results in different linear combinations of basic states which diagonalise the different forms of $\mathcal{H}_{\text{cubic}}$. These are readily found by the method of Section 3.4 and are given in Table 6.5.

As these two forms of V_{cubic} differ only in the choice of reference frame, they can obviously be obtained from one another by a simple rotation of axes. To illustrate this we consider a simpler example. Suppose we require an expression for V_{cubic} in a system of axes where the z direction coincides with a $\langle 110 \rangle$ direction (referred to the original cubic axes, x_0, y_0, z_0 in Fig. 6.10 (a)). First, rotate the coordinate system by 45° about the z_0 axis as illustrated by Fig. 6.10 (a) which produces the transformations:

$$\begin{aligned} x_0 &\rightarrow \frac{1}{\sqrt{2}}(x' + y') \\ y_0 &\rightarrow \frac{1}{\sqrt{2}}(-x' + y') \\ z_0 &\rightarrow z' \end{aligned}$$

Then, in order to obtain the z axis for $\langle 110 \rangle$ (Fig. 6.10(b)) we simply permute the coordinates, i.e. $y \rightarrow z$, $z' \rightarrow x$ and $x' \rightarrow y$. The complete transformation is given by

$$\begin{aligned}x_0 &\rightarrow \frac{1}{\sqrt{2}} \{y + z\} \\y_0 &\rightarrow \frac{1}{\sqrt{2}} \{-y + z\} \\z_0 &\rightarrow x\end{aligned}\quad (6.27)$$

Table 6.5

	Tetragonal	Trigonal
$L = 2$	$ 0\rangle$ $1/\sqrt{2}(2\rangle + - 2\rangle)$	$\{\sqrt{(1/3) -2\rangle} - \sqrt{(2/3) 1\rangle}$ $\{\sqrt{(1/3) 2\rangle} + \sqrt{(2/3) -1\rangle}$
	$ 1\rangle$ $ - 1\rangle$ $1/\sqrt{2}(2\rangle - - 2\rangle)$	$\{ 0\rangle$ $\{\sqrt{(2/3) -2\rangle} + \sqrt{(1/3) 1\rangle}$ $\{\sqrt{(2/3) 2\rangle} - \sqrt{(1/3) -1\rangle}$
$L = 3$	$\sqrt{(3/8) -1\rangle} + \sqrt{(5/8) 3\rangle}$ $\sqrt{(3/8) 1\rangle} + \sqrt{(5/8) -3\rangle}$ $ 0\rangle$	$\{2/3 0\rangle - 1/3\sqrt{(5/2)}(3\rangle - -3\rangle)$ $\{\sqrt{(5/6) 2\rangle} + \sqrt{(1/6) -1\rangle}$ $\sqrt{(5/6) -2\rangle} - \sqrt{(1/6) 1\rangle}$
	$\sqrt{(5/8) -1\rangle} - \sqrt{(3/8) 3\rangle}$ $\sqrt{(5/8) 1\rangle} - \sqrt{(3/8) -3\rangle}$ $1/(\sqrt{2})(2\rangle + - 2\rangle)$	$\{1/\sqrt{2}(3\rangle + -3\rangle)$ $\{\sqrt{(1/6) 2\rangle} - \sqrt{(5/6) -1\rangle}$ $\sqrt{(1/6) -2\rangle} + \sqrt{(5/6) 1\rangle}$
	$1/\sqrt{2}(2\rangle - - 2\rangle) A_2$	$\sqrt{2/3}(3\rangle - -3\rangle) - \sqrt{5/3} 0\rangle$

Direct substitution of Equations 6.27 into Equation 6.19 yields

$$\begin{aligned}V_{\text{cubic}} &= D[(x^4 + y^4 + z^4 - \frac{3}{8}r^4) - \frac{1}{2}(y^4 + z^4 - 6y^2z^2)] \\&\equiv \frac{1}{8}[(35z^4 - 30r^2z^2 + 3r^4) + 4(y^4 - x^4 + 6z^2x^2 - 6y^2z^2) \\&\quad + (x^4 - 6x^2y^2 + y^4)]\end{aligned}\quad (6.28)$$

where the second step consists of writing V_{cubic} in terms of the functions of Table 6.3. Thus Equation 6.28 is seen to be in the standard form:

$$V_{\text{cubic}} = r^4[A_4^0 Y_4^0 + A_4^2(Y_4^2 + Y_4^{-2}) + A_4^4(Y_4^4 + Y_4^{-4})] \quad (6.29)$$

The occurrence of second order spherical harmonics in Equation 6.29 arises from the choice of a two-fold axis as the z direction. In a similar way, the trigonal axis introduced third-order terms in Equation 6.25.

These different forms of the cubic potential are important because many calculations proceed on the assumption that the cubic part of the crystal field is much greater than lower symmetry terms and may be treated separately, i.e. the crystal field operator \mathcal{H}_c is first

diag for $\mathcal{H}_{\text{cubic}}$ then other terms are treated as small perturbations. The calculation is considerably simplified if the correct choice of axes is made in defining \mathcal{H}_c . The two most important cases are those of tetragonal and trigonal symmetries which occur frequently in practice.

6.7. Application to Rare Earth Ions

So far in our discussion of crystal field effects we have been concerned largely with iron group ions. A rather different situation arises when we consider the rare earths as, here, spin-orbit coupling energies are usually greater than those due to the crystal field and the basic states are described in terms of the quantum number J . However, the calculation of crystal field splittings follows the same form as before, except that now the kets are written as $|M_J\rangle$ instead of $|M_L\rangle$ and $M_J = J, J-1, \dots, -J$. The crystal field potential is determined in precisely the same way as before, though now including sixth-order spherical harmonics, and equivalent operators obtained from them. An important difference lies in the derivation of the proportionality constants corresponding to α and β in Table 6.4. It is first necessary to express the states $|M_J\rangle$ in L, S quantisation, i.e. in the form $|M_L, M_S\rangle$ and then expand the functions $|M_L\rangle$ as products of single electron functions as before. The procedure is explained in detail in Stevens' original paper.⁶ Values of the resulting parameters α , β and γ (the latter for use with sixth-order terms in the expansion of V) may be found in Table V of the book by Low⁷ or Table VI of the article by Hutchings.³

The application of the method to rare earth ions will become clearer when we consider a special case in Section 7.4.

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