5

Splitting of Atomic Orbitals
in a Crystal Potential

This is the first of several chapters aimed at presenting some *general applications* of group theory while further developing theoretical concepts and amplifying on those given in the first four chapters. The first application of group theory is made to the splitting of atomic energy levels when the atom is placed in a crystal potential, because of the relative simplicity of this application and because it provides a good example of going from higher to lower symmetry, a procedure used very frequently in applications of group theory to solid state physics. In this chapter we also consider irreducible representations of the full rotation group.

5.1 Introduction

The study of crystal field theory is relevant for physics and engineering applications in situations where it is desirable to exploit the sharp, discrete energy levels that are characteristic of atomic systems together with the larger atomic densities that are typical of solids. As an example, consider the variety of powerful lasers whose operation is based on the population inversion of impurity levels of rare earth ions in a transparent host crystal. The energy levels of an electron moving in the field of an ion embedded in such a solid are approximately the same as for an electron moving in the field of a free ion. Thus the interaction between the ion and the host crystal can be treated in perturbation theory. Group theory plays a major role in finding the degeneracy and the symmetry types of the electronic levels in the crystalline field. The topic of crystal field splittings has found many important applications such as in the use of erbium-doped silica-based optical glass fiber amplifiers in optical communications systems. Such applications provide motivation for understanding the splitting of the energy levels of an impurity ion in a crystal field.

In this chapter the point group symmetry of an impurity ion in a crystal is presented. The crystal potential V_{xtal} determines the point group symmetry.

Following the discussion on the form of the crystal potential, some properties of the full rotation group are given, most importantly the characters $\chi^{(\ell)}(\alpha)$ for rotations through an angle α and $\chi^{(\ell)}(i)$ for inversions. Irreducible representations of the full

rotation group are generally found to be reducible representations of a point group of lower symmetry which is a subgroup of the higher symmetry group. If the representation is reducible, then crystal field splittings of the energy levels occur. If, however, the representation is irreducible, then no crystal field splittings occur. Examples of each type of representation are presented. We focus explicitly on giving examples of going from higher to lower symmetry. In so doing, we consider the

(a) Splitting of the energy levels,
(b) Symmetry types of the split levels,
(c) Choice of basis functions to bring the Hamiltonian $\mathcal{H}$ into block diagonal form. Spherical symmetry results in spherical harmonics $Y_{\ell m}(\theta, \phi)$ for basis functions. Proper linear combinations of the spherical harmonics $Y_{\ell m}(\theta, \phi)$ are taken to make appropriate basis functions for the point group of lower symmetry.

In crystal field theory we write down the Hamiltonian for the impurity ion in a crystalline solid as

$$\mathcal{H} = \sum_i \left\{ \frac{p_i^2}{2m} - \frac{Ze^2}{r_{i\mu}} + \sum_j \frac{e^2}{r_{ij}} + \sum_j \xi_{ij} \boldsymbol{\ell}_i \cdot \boldsymbol{s}_j + \gamma_{i\mu} \boldsymbol{j}_i \cdot \boldsymbol{I}_\mu \right\} + V_{\text{xtal}}, \quad (5.1)$$

where the first term is the kinetic energy of the electrons associated with the ion, the second term represents the Coulomb attraction of the electrons of the ion to their nucleus, the third term represents the mutual Coulomb repulsion of the electrons associated with the impurity ion, and the sum on j denotes a sum on pairs of electrons. These three quantities are denoted by $\mathcal{H}_0$ the electronic Hamiltonian of the free atom without spin–orbit interaction. $\mathcal{H}_0$ is the dominant term in the total Hamiltonian $\mathcal{H}$. The remaining terms are treated in perturbation theory in some order. Here $\xi_{ij} \boldsymbol{\ell}_i \cdot \boldsymbol{s}_j$ is the spin–orbit interaction of electrons on the impurity ion and $\gamma_{i\mu} \boldsymbol{j}_i \cdot \boldsymbol{I}_\mu$ is the hyperfine interaction between the electrons on the ion and the nuclear spin. The perturbing crystal potential V_{xtal} of the host ions acts on the impurity ion and lowers its spherical symmetry.

Because of the various perturbation terms appearing in (5.1), it is important to distinguish the two limiting cases of weak and strong crystal fields.

(a) *Weak field case.* In this case, the perturbing crystal field V_{xtal} is considered to be small compared with the spin–orbit interaction. In this limit, we find the energy levels of the free impurity ion with spin–orbit interaction and at this point we consider the crystal field as an additional perturbation. These approximations are appropriate to rare earth ions in ionic host

crystals. We will deal with the group theoretical aspects of this case in Chap. 14, after we have learned how to deal with the spin on the electron in the context of group theory.

(b) *Strong field case.* In this case, the perturbing crystal field V_{xtal} is strong compared with the spin–orbit interaction. We now consider V_{xtal} as the major perturbation on the energy levels of $\mathcal{H}_0$. Examples of the strong crystal field case are transition metal ions (Fe, Ni, Co, Cr, etc.) in a host crystal. It is this limit that we will consider first, and is the focus of this chapter.

We note that the crystal potential V_{xtal} lowers the full rotational symmetry of the free atom to cause level splittings relative to those of the free atom.

We now consider in Sect. 5.2 some of the fundamental properties of the full rotation group. These results are liberally used in later chapters.

5.2 Characters for the Full Rotation Group

The free atom has full rotational symmetry and the number of symmetry operations which commute with the Hamiltonian is infinite. That is, all C_ϕ rotations about any axis are symmetry operations of the full rotation group. We are not going to discuss infinite or continuous groups in any detail, but we will adopt results that we use frequently in quantum mechanics without rigorous proofs.

Let us then recall the form of the spherical harmonics $Y_{\ell m}(\theta, \phi)$ which are the basis functions for the full rotation group:

$$Y_{\ell m}(\theta, \phi) = \left[\frac{2\ell + 1}{4\pi} \frac{(\ell - |m|)!}{(\ell + |m|)!}\right]^{1/2} P_\ell^m(\cos\theta) e^{im\phi}, \tag{5.2}$$

in which

$$Y_{\ell,-m}(\theta, \phi) = (-1)^m Y_{\ell,m}(\theta, \phi)^*, \tag{5.3}$$

and the symbol $*$ denotes the complex conjugate. The associated Legendre polynomial in (5.2) is written as

$$P_\ell^m(x) = (1 - x^2)^{1/2|m|} \frac{d^{|m|}}{dx^{|m|}} P_\ell(x), \tag{5.4}$$

in which $x = \cos\theta$, while

$$P_\ell^{-m}(x) = [(-1)^m (\ell - m)!/(\ell + m)!] P_\ell^m(x),$$

and the Legendre polynomial $P_\ell(x)$ is generated by

$$1/\sqrt{1 - 2sx + s^2} = \sum_{\ell=0}^{\infty} P_\ell(x) s^\ell. \tag{5.5}$$

It is shown above that the spherical harmonics (angular momentum eigenfunctions) can be written in the form

$$Y_{\ell,m}(\theta, \phi) = C P_\ell^m(\theta)\, e^{im\phi}\,, \tag{5.6}$$

where C is a normalization constant and $P_\ell^m(\theta)$ is an associated Legendre polynomial given explicitly in (5.4). The coordinate system used to define the polar and azimuthal angles is shown in Fig. 5.1. The $Y_{\ell,m}(\theta, \phi)$ spherical harmonics generate odd-dimensional representations of the rotation group and these representations are irreducible representations. For $\ell = 0$, we have a one-dimensional representation; $\ell = 1$ ($m = 1, 0, -1$) gives a three-dimensional irreducible representation; $\ell = 2$ ($m = 2, 1, 0, -1, -2$) gives a five-dimensional representation, etc. So for each value of the angular momentum, the spherical harmonics provide us with a representation of the proper $2\ell+1$ dimensionality.

These irreducible representations are found from the so-called *addition theorem for spherical harmonics* which tells us that if we change the polar axis (i.e., the axis of quantization), then the "old" spherical harmonics $Y_{\ell,m}(\theta, \phi)$ and the "new" $Y_{\ell',m'}(\theta', \phi')$ are related by a *linear transformation* of basis functions when $\ell' = \ell$:

$$\hat{P}_{\mathrm{R}} Y_{\ell,m}(\theta', \phi') = \sum_{m'} D^{(\ell)}(R)_{m'm} Y_{\ell,m'}(\theta, \phi)\,, \tag{5.7}$$

where $\hat{P}_{\mathrm{R}}$ denotes a rotation operator that changes the polar axis, and the matrix $D^{(\ell)}(R)_{m'm}$ provides an ℓ-dimensional matrix representation of element R in the full rotation group. Let us assume that the reader has previously
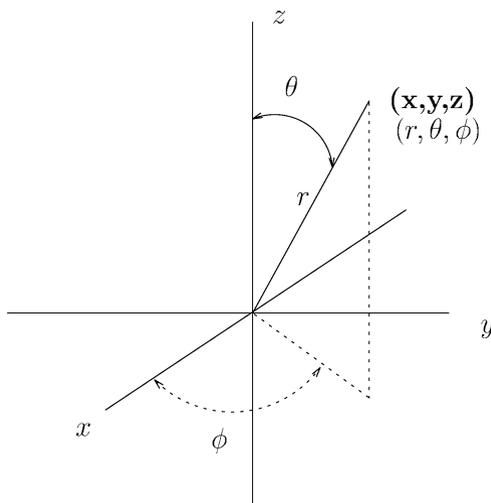

Fig. 5.1. Polar coordinate system defining the polar angle θ and the azimuthal angle ϕ

seen this expansion for spherical harmonics which is a major point in the development of the irreducible representations of the rotation group. From the similarity between (5.7) and (4.1), the reader can see the connection between the group theory mathematical background given in Chap. 4 and the application discussed here.

In any system with full rotational symmetry, the choice of the z-axis is arbitrary. We thus choose the z-axis as the axis about which the operator $\hat{P}_\alpha$ makes the rotation α. Because of the form of the spherical harmonics $Y_{\ell,m}(\theta, \phi)$ [see (5.6)] and the choice of the z-axis, the action of $\hat{P}_\alpha$ on the $Y_{\ell m}(\theta, \phi)$ basis functions only affects the ϕ dependence of the spherical harmonic (not the θ dependence). The effect of this rotation on the function $Y_{\ell,m}(\theta, \phi)$ is equivalent to a rotation of the axes in the opposite sense by the angle $-\alpha$

$$\hat{P}_\alpha Y_{\ell,m}(\theta, \phi) = Y_{\ell,m}(\theta, \phi - \alpha) = \mathrm{e}^{-\mathrm{i}m\alpha} Y_{\ell,m}(\theta, \phi), \tag{5.8}$$

in which the second equality results from the explicit form of $Y_{\ell,m}(\theta, \phi)$. But (5.8) gives the linear transformation of $Y_{\ell,m}(\theta, \phi)$ resulting from the action by the operator $\hat{P}_\alpha$. Thus by comparing (5.7) and (5.8), we see that the matrix $D^{(\ell)}(\alpha)_{m'm}$ is diagonal in m so that we can write $D^{(\ell)}(\alpha)_{m'm} = \mathrm{e}^{-\mathrm{i}m\alpha}\delta_{m'm}$, where $-\ell \le m \le \ell$, yielding

$$D^{(\ell)}(\alpha) = \begin{pmatrix} \mathrm{e}^{-\mathrm{i}\ell\alpha} & & & \mathcal{O} \\ & \mathrm{e}^{-\mathrm{i}(\ell-1)\alpha} & & \\ & & \ddots & \\ \mathcal{O} & & & \mathrm{e}^{\mathrm{i}\ell\alpha} \end{pmatrix}, \tag{5.9}$$

where $\mathcal{O}$ represents all the zero entries in the off-diagonal positions. The character of the rotations C_α is thus given by the geometric series

$$\begin{aligned} \chi^{(\ell)}(\alpha) = \operatorname{trace} D^{(\ell)}(\alpha) &= \mathrm{e}^{-\mathrm{i}\ell\alpha} + \cdots + \mathrm{e}^{\mathrm{i}\ell\alpha} \\ &= \mathrm{e}^{-\mathrm{i}\ell\alpha}\left[1 + \mathrm{e}^{\mathrm{i}\alpha} + \cdots + \mathrm{e}^{2\mathrm{i}\ell\alpha}\right] \\ &= \mathrm{e}^{-\mathrm{i}\ell\alpha}\sum_{k=0}^{2\ell}(\mathrm{e}^{\mathrm{i}k\alpha}) \\ &= \mathrm{e}^{-\mathrm{i}\ell\alpha}\left[\frac{\mathrm{e}^{\mathrm{i}(2\ell+1)\alpha} - 1}{\mathrm{e}^{\mathrm{i}\alpha} - 1}\right] \\ &= \frac{\mathrm{e}^{\mathrm{i}(\ell+1/2)\alpha} - \mathrm{e}^{-\mathrm{i}(\ell+1/2)\alpha}}{\mathrm{e}^{\mathrm{i}\alpha/2} - \mathrm{e}^{-\mathrm{i}\alpha/2}} = \frac{\sin[(\ell + \frac{1}{2})\alpha]}{\sin[(\frac{1}{2})\alpha]}. \end{aligned} \tag{5.10}$$

Thus we show that the character for rotations α about the z-axis is

$$\chi^{(\ell)}(\alpha) = \frac{\sin[(\ell + \frac{1}{2})\alpha]}{\sin[\alpha/2]}. \tag{5.11}$$

To obtain the character for the inversion operator i, we have

$$iY_{\ell m}(\theta, \phi) = Y_{\ell m}(\pi - \theta, \pi + \phi) = (-1)^\ell Y_{\ell m}(\theta, \phi) \tag{5.12}$$

and therefore

$$\chi^{(\ell)}(i) = \sum_{m=-\ell}^{m=\ell} (-1)^\ell = (-1)^\ell (2\ell + 1), \tag{5.13}$$

where $Y_{\ell m}(\theta, \phi)$ are the spherical harmonics, while ℓ and m denote the total and z-component angular momentum quantum numbers, respectively.

The dimensionalities of the representations for $\ell = 0, 1, 2, \ldots$ are $1, 3, 5, \ldots$. In dealing with the symmetry operations of the full rotation group, the inversion operation frequently occurs. This operation also occurs in the lower symmetry point groups either as a separate operation i or in conjunction with other compound operations (e.g., $S_6 = i \otimes C_3^{-1}$). A compound operation (like an improper rotation or a mirror plane) can be represented as a product of a proper rotation followed by inversion. The character for the inversion operation is $+(2\ell + 1)$ for *even* angular momentum states ($\ell = $ even in $Y_{\ell,m}(\theta, \phi)$) and $-(2\ell + 1)$ for *odd* angular momentum states (see (5.13)). This idea of compound operations will become clearer after we have discussed in Chap. 6 the direct product groups and direct product representations.

We now give a general result for an improper rotation defined by

$$S_n = C_n \otimes \sigma_h \tag{5.14}$$

and $S_3 = C_3 \otimes \sigma_h$ is an example of (5.14) (for an odd integer n). Also S_n can be written as a product of $C_{n/2} \otimes i$, as for example, $S_6 = C_3 \otimes i$, for n an even integer, where $\otimes$ denotes the direct product of the two symmetry operations appearing at the left and right of the symbol $\otimes$, which is discussed in Chap. 6. If we now apply (5.11) and (5.12), we obtain

$$\chi^{(\ell)}(S_n) = \chi^{(\ell)}(C_{n/2} \otimes i) = (-1)^\ell \frac{\sin[(\ell + \frac{1}{2})\alpha]}{\sin[\alpha/2]} . \tag{5.15}$$

In the case of mirror planes, such as σ_h, σ_d, or σ_v we can make use of relations such as

$$\sigma_h = C_2 \otimes i \tag{5.16}$$

to obtain the character for mirror planes in the full rotation group.

Now we are going to place our free ion into a crystal field which does not have full rotational symmetry operations, but rather has the symmetry operations of a crystal which may include rotations about finite angles, inversions and a finite number of reflections. The *full rotation group contains all these symmetry operations.* Therefore, the representation $D^{(\ell)}(\alpha)$ given above is a representation of the crystal point group if α is a symmetry operation in that point group. But $D^{(\ell)}(\alpha)$ is, in general, a *reducible* representation of the lower

symmetry group. Therefore the $(2\ell + 1)$-fold degeneracy of each level will in general be partially lifted.

We can find out how the degeneracy of each level is lifted by asking what are the irreducible representations contained in $D^{(\ell)}(\alpha)$ in terms of the group of lower symmetry for the crystal. The actual calculation of the crystal field splittings depends on setting up a suitable Hamiltonian and solving it, usually in some approximation scheme. But the energy level *degeneracy* does not depend on the detailed Hamiltonian, but only on its symmetry. Thus, the decomposition of the level degeneracies in a crystal field is a consequence of the symmetry of the crystal field.

5.3 Cubic Crystal Field Environment
for a Paramagnetic Transition Metal Ion

As an example of a crystal field environment, suppose that we place our
paramagnetic ion (e.g., an iron impurity) in a cubic host crystal. Assume further that this impurity goes into a substitutional lattice site, and is surrounded by a regular octahedron of negative ions (see Fig. 5.2). A regular octahedron has O_h symmetry, but since we have not yet discussed the inversion operation and direct product groups (see Chap. 6), we will simplify the symmetry operations and work with the point group O. The character table for O is shown in Table 5.1 (see also Table A.30). From all possible rotations on a sphere, only 24 symmetry operations of the full rotation group remain in the group O.

Reviewing the *notation* in Table 5.1, the Γ notations for the irreducible representations are the usual ones used in solid-state physics and are due to Bouckaert, Smoluchowski and Wigner [1].

The second column in Table 5.1 follows the notation usually found in molecular physics and chemistry applications, which are two research fields that also make lots of use of symmetry and group theory. The key
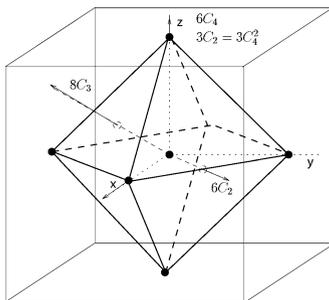

Fig. 5.2. A regular octahedron inscribed in a cube, illustrating the symmetry operations of group O

Table 5.1. Character table for O and decomposition of the angular momenta representations into the irreducible representations of group O

O		E	$8C_3$	$3C_2 = 3C_4^2$	$6C_2'$	$6C_4$
Γ_1	A_1	1	1	1	1	1
Γ_2	A_2	1	1	1	-1	-1
Γ_{12}	E	2	-1	2	0	0
$\Gamma_{15'}$	T_1	3	0	-1	-1	1
$\Gamma_{25'}$	T_2	3	0	-1	1	-1
$\Gamma_{\ell=0}$	A_1	1	1	1	1	1
$\Gamma_{\ell=1}$	T_1	3	0	-1	1	-1
$\Gamma_{\ell=2}$	$E + T_2$	5	-1	1	1	-1
$\Gamma_{\ell=3}$	$A_2 + T_1 + T_2$	7	1	-1	-1	-1
$\Gamma_{\ell=4}$	$A_1 + E + T_1 + T_2$	9	0	1	1	1
$\Gamma_{\ell=5}$	$E + 2T_1 + T_2$	11	-1	-1	-1	1

to the notation is that A denotes one-dimensional representations, E denotes two-dimensional representations, and T denotes three-dimensional representations. Papers on lattice dynamics of solids often use the A, E, T symmetry notation to make contact with the molecular analog. The subscripts in Table 5.1 refer to the conventional indexing of the representations of the group O (see Table A.30). The pertinent symmetry operations can be found from Fig. 5.2, and the classes associated with these symmetry operations label the various columns where the characters in Table 5.1 appear.

The various types of rotational symmetry operations are listed as

- the $8C_3$ rotations are about the axes through the triangular face centroids of the octahedron,
- the $6C_4$ rotations are about the corners of the octahedron,
- the $3C_2$ rotations are also about the corners of the octahedron, with $C_2 = C_4^2$,
- the $6C_2'$ rotations are twofold rotations about a (110) axis passing through the midpoint of the edges (along the 110 directions of the cube).

To be specific, suppose that we have a magnetic impurity atom with angular momentum $\ell = 2$. We first find the characters for all the symmetry operations which occur in the O group for an irreducible representation of the full rotation group. The representation of the full rotation group will be a representation of group O, but in general this representation will be *reducible*.

Since the character for a general rotation α in the full rotation group is found using (5.11), the identity class (or $\alpha = 0$) yields the characters

$$\chi^{(\ell)}(0) = \frac{\ell + \frac{1}{2}}{1/2} = 2\ell + 1 \,. \tag{5.17}$$

Table 5.2. Classes and characters for the group O

class	α	$\chi^{(2)}(\alpha)$
$8C_3$	$2\pi/3$	$\dfrac{\sin(5/2)\cdot(2\pi/3)}{\sin((2\pi)/(2\cdot3))} = (-\sqrt{3}/2)/(\sqrt{3}/2) = -1$
$6C_4$	$2\pi/4$	$\dfrac{\sin(5/2)\cdot(\pi/2)}{\sin(\pi/4)} = (-1/\sqrt{2})/(1/\sqrt{2}) = -1$
$3C_2$ and $6C_2$	$2\pi/2$	$\dfrac{\sin(5/2)\pi}{\sin(\pi/2)} = 1$

Table 5.3. Characters found in Table 5.2 for the $\Gamma_{\text{rot}}^{(2)}$ of the full rotation group ($\ell = 2$)

	E	$8C_3$	$3C_2$	$6C_2'$	$6C_4$
$\Gamma_{\text{rot}}^{(2)}$	5	-1	1	1	-1

For our case $\ell = 2$ ($\chi^{(2)}(E) = 5$), and by applying (5.11) to the symmetry operations in each class we obtain the results summarized in Table 5.2. To compare with the character table for group O (Table 5.1), we list in Table 5.3 the characters found in Table 5.2 for the $\Gamma_{\text{rot}}^{(2)}$ of the full rotation group ($\ell = 2$) according to the classes listed in the character table for gr oup O (see Tables 5.1 and A.30).

We note that $\Gamma_{\text{rot}}^{(2)}$ is a reducible representation of group O because group O has no irreducible representations with dimensions $\ell_n > 3$. To find the irreducible representations contained in $\Gamma_{\text{rot}}^{(2)}$ we use the decomposition formula for reducible representations (3.20):

$$a_j = \frac{1}{h} \sum_k N_k \chi^{(\Gamma_j)}(\mathcal{C}_k)^* \chi^{\text{reducible}}(\mathcal{C}_k), \qquad (5.18)$$

where we have used (3.16)

$$\chi^{\text{reducible}}(\mathcal{C}_k) = \sum_{\Gamma_j} a_j \chi^{(\Gamma_j)}(\mathcal{C}_k), \qquad (5.19)$$

in which $\chi^{(\Gamma_j)}$ is an irreducible representation and the characters for the reducible representation $\Gamma_{\text{rot}}^{(2)}$ are written as $\chi^{\text{reducible}}(\mathcal{C}_k) \equiv \chi^{\Gamma_{\text{rot}}^{(2)}}(\mathcal{C}_k)$. We now ask how many times is A_1 contained in $\Gamma_{\text{rot}}^{(2)}$? Using (5.18) we obtain

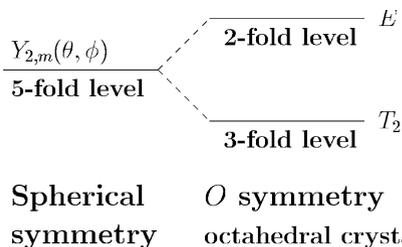$$a_{A_1} = \frac{1}{24}[5 - 8 + 3 + 6 - 6] = 0, \qquad (5.20)$$

Fig. 5.3. The splitting of the d-Levels (fivefold) in an octahedral crystal field

which shows that the irreducible representation A_1 is not contained in $\Gamma_{\rm rot}^{(2)}$. We then apply (5.18) to the other irreducible representations of group O:

$$A_2: \quad a_{A_2} = \frac{1}{24}[5 - 8 + 3 - 6 + 6] = 0$$

$$E: \quad a_E = \frac{1}{24}[10 + 8 + 6 + 0 - 0] = 1$$

$$T_1: \quad a_{T_1} = \frac{1}{24}[15 + 0 - 3 - 6 - 6] = 0$$

$$T_2: \quad a_{T_2} = \frac{1}{24}[15 + 0 - 3 + 6 + 6] = 1\,,$$

so that finally we write

$$\Gamma_{\rm rot}^{(2)} = E + T_2\,,$$

which means that the reducible representation $\Gamma_{\rm rot}^{(2)}$ breaks into the irreducible representations E and T_2 in cubic symmetry. In other words, an atomic d-level in a cubic O crystal field splits into an E and a T_2 level. Similarly, an atomic d-level in a cubic O_h crystal field splits into an E_g and a T_{2g} level, where the g denotes evenness under inversion. Group theory does not provide any information about the ordering of the levels (see Fig. 5.3). For general utility, we have included in Table 5.1 the characters for the angular momentum states $\ell = 0, 1, 2, 3, 4, 5$ for the full rotation group expressed as reducible representations of the group O. The splittings of these angular momentum states in cubic group O symmetry are also included in Table 5.1.

We can now carry out the passage from higher to lower symmetry by going one step further. Suppose that the presence of the impurity strains the crystal. Let us further imagine (for the sake of argument) that the new local symmetry of the impurity site is D_4 (see Table 5.4 and Table A.18), which is a proper subgroup of the full rotation group. Then the levels E and T_2 given above may be split further in D_4 (tetragonal) symmetry (for example by stretching the molecule along the fourfold axis). We now apply the same technique to investigate this tetragonal field splitting. We start again by writing the character table for the group D_4 which is of order 8. We then consider the representations E and T_2 of the group O as reducible representations of group D_4
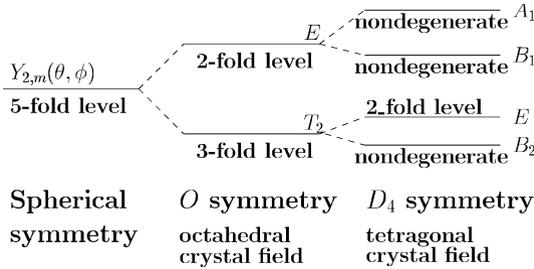
Fig. 5.4. d-Level splitting in octahedral and D_4 crystal fields

Table 5.4. Character table for D_4 and the decomposition of the irreducible representations of group O into representations for group D_4

character table for D_4		E	$C_2 = C_4^2$	$2C_4$	$2C_2'$	$2C_2''$	
Γ_1	A_1	1	1	1	1	1	
$\Gamma_{1'}$	A_2	1	1	1	-1	-1	
Γ_2	B_1	1	1	-1	1	-1	
$\Gamma_{2'}$	B_2	1	1	-1	-1	1	
Γ_3	E	2	-2	0	0	0	
reducible representations from O group							
	E	2	2	0	2	0	$\equiv A_1 + B_1$
	T_2	3	-1	-1	-1	1	$\equiv E + B_2$

Table 5.5. Decomposition of the $\ell = 2$ angular momentum level into the irreducible representations of group D_4

	E	C_2	$2C_4$	$2C_2'$	$2C_2''$	
$\Gamma_{\text{rot}}^{(2)}$	5	1	-1	1	1	$A_1 + B_1 + B_2 + E$

and write down the characters for the E, C_4, C_4^2, C_2' and C_2'' operations from the character table for O given above, noting that the C_2'' in the group D_4 refers to three of the (110) axes $6C_2'$ of the cubic group O (Table 5.4). Using the decomposition theorem, (3.20), we find that E splits into the irreducible representations $A_1 + B_1$ in the group D_4 while T_2 splits into the irreducible representations $E + B_2$ in the group D_4, as summarized in Fig. 5.4.

We note that the C_2 operations in D_4 is a π rotation about the z-axis and the $2C_2'$ are π rotations about the x- and y-axes. The C_2 and the $2C_2'$ come from the $3C_2 = 3C_4^2$ in group O. The $2C_2''$ are π rotations about (110) axes and come from the $6C_2'$ in group O. To check the decomposition of the $\ell = 2$ level in D_4 symmetry, we add up the characters for $A_1 + B_1 + B_2 + E$ for group D_4 (see Table 5.5), which are the characters for the spherical harmonics considered as a reducible representation of group D_4, so that this result checks.
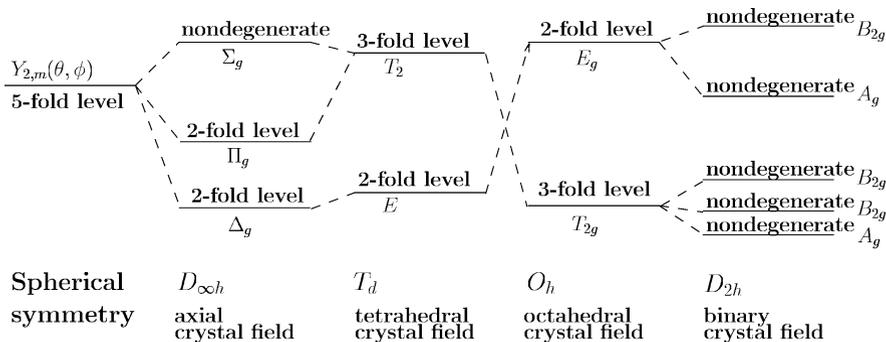
Fig. 5.5. d-Level splitting in various crystal fields

Suppose now that instead of applying a stress along a (001) direction, we apply a stress along a (110) direction (see Problem 5.4). You will see that the crystal field pattern is somewhat altered, so that the crystal field pattern provides symmetry information about the crystal field. Figure 5.5 shows the splitting of the $\ell = 2$ level in going from full rotational symmetry to various lower symmetries, including $D_{\infty h}$, T_d, O_h, and D_{2h}, showing in agreement with the above discussion, the lifting of all the degeneracy of the $\ell = 2$ level in D_{2h} symmetry.

5.4 Comments on Basis Functions

Although group theory tells us how the impurity ion energy levels are split by the crystal field, it does not tell us the ordering of these levels. Often a simple physical argument can be given to decide which levels ought to lie lower. Consider the case of a d-electron in a cubic field, where the host ions are at $x = \pm a$, $y = \pm a$, $z = \pm a$. Assume that the impurity ion enters the lattice substitutionally, so that it is replacing one of the cations. Then the nearest neighbor host ions are all anions. The charge distributions for the d-states are shown in Fig. 5.6. Referring to the basis functions for O, which can be obtained from Table A.30, we see that for the irreducible representation E we have basis functions $(x^2 - y^2, 3z^2 - r^2)$ and for T_2 we have basis functions (xy, yz, zx). For the basis functions which transform as the T_2 representation, the charge distributions do not point to the host ions and hence the crystal field interaction is relatively weak.

However, for the d-functions which transform as E, the interaction will be stronger since the charge distributions now *do* point to the host ion sites. If, however, the interaction is repulsive, then the E level will lie higher than the T_2 level. A more quantitative way to determine the ordering of the levels is to solve the eigenvalue problem explicitly. In carrying out this solution it is con-
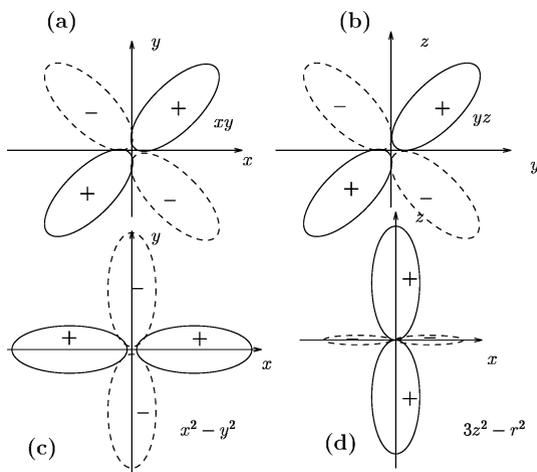
Fig. 5.6. The angular parts of d-wave functions in cubic crystals are shown as labeled by the basis functions for the partners of their irreducible representations. (**a**) $xy/r^2 \Rightarrow (T_2)$, (**b**) $yz/r^2 \Rightarrow (T_2)$, (**c**) $(x^2-y^2)/r^2 \Rightarrow (E)$, (**d**) $(3z^2-r^2)/r^2 \Rightarrow (E)$

venient to use basis functions that transform as the irreducible representations of the crystal field group.

We now look at the basis functions which provide irreducible representations for these cases of lower symmetry. In going from the full rotation group to the cubic group O, we obtain the irreducible representations E and T_2 shown in Fig. 5.3, which can be expressed in terms of the basis functions for these irreducible representations. The basis functions for the twofold level are $(x^2 - y^2)$ and $(3z^2 - r^2)$, while the basis functions for the threefold level are (xy), (yz), and (zx). We note that these basis functions bring the crystal field potential into block form, but need not completely diagonalize the Hamiltonian. There are various forms of the crystal field potential that have O_h symmetry (e.g., octahedral sites, cubic sites, etc.), and in each case the appropriate set of basis functions that transform as irreducible representations of the group will bring the secular equation into block form.

Upon lowering the symmetry further to D_4 symmetry, the T_2 and E levels split further according to $T_2 \rightarrow E + B_2$ and $E \rightarrow A_1 + B_1$ (see Fig. 5.4). The appropriate basis functions for these levels can be identified with the help of the character table for group D_4 in Table A.18:

$$E\begin{Bmatrix} yz \\ zx \end{Bmatrix}, \quad B_2\{xy\}, \quad B_1\{x^2 - y^2\}, \quad A_1\{z^2\}. \tag{5.21}$$

In Sects. 5.3 and 5.4 we consider the spherical harmonics for $\ell = 2$ as reducible representations of the point groups O_h, O, and D_4. In this connection, Table 5.6 gives the decomposition of the various spherical harmonics for angular

Table 5.6. Splitting of angular momentum in cubic symmetry O_h

ℓ	A_{1g}	A_{2g}	E_g	T_{1g}	T_{2g}	A_{1u}	A_{2u}	E_u	T_{1u}	T_{2u}
0	1									
1									1	
2			1		1					
3							1		1	1
4	1		1	1	1					
5								1	2	1
6	1	1	1	1	2					
7							1	1	2	2
8	1		2	2	2					
9						1	1	1	3	2
10	1	1	2	2	3					
11							1	2	3	3
12	2	1	2	3	3					
13						1	1	2	4	3
14	1	1	3	3	4					
15						1	2	2	4	4

momentum $\ell \leq 15$ into irreducible representations of the full cubic group O_h, which will be further discussed in Chap. 6 when direct product groups are discussed.

5.5 Comments on the Form of Crystal Fields

Any function (e.g., any arbitrary V_{xtal}) can be written in terms of a complete set of basis functions, such as the spherical harmonics. In the case of the crystal field problem, group theory can greatly simplify the search for the spherical harmonics $Y_{\ell,m}(\theta,\phi)$ pertaining to V_{xtal}. Consider, for example, V_{cubic} and Table 5.6. The spherical harmonics in V_{xtal} must exhibit all the symmetry operations of the physical system. We note that the lowest angular momentum state to contain the totally symmetric A_{1g} irreducible representation of O_h is $\ell = 4$, and must, therefore be the lowest angular momentum state in the crystal field for a cubic crystal V_{cubic} when written in terms of spherical harmonics.

We can check the predictions from group theory by obtaining the crystal field analytically. To construct the crystal field, we consider the electrostatic interaction of the neighboring host ions at the impurity site. To illustrate how this is done, consider the highly symmetric case of an impurity ion in a cubic environment provided by ions at $x = \pm a$, $y = \pm a$, $z = \pm a$. The contribution from an ion at $x = -a$ at the field point $\boldsymbol{r}$ denoted by (x,y,z) is

$$V_{x=-a} = \frac{e}{|\boldsymbol{r}|} = \frac{e}{a\sqrt{(1+x/a)^2 + (y/a)^2 + (z/a)^2}} = \frac{e}{a\sqrt{1+\varepsilon}}, \qquad (5.22)$$

where e is the charge on the electron and ε is a small dimensionless quantity if considering (x, y, z) in the neighborhood of the origin 0. Then using the binomial expansion:

$$(1 + \varepsilon)^{-1/2} = 1 - \frac{1}{2}\varepsilon + \frac{3}{8}\varepsilon^2 - \frac{5}{16}\varepsilon^3 + \frac{35}{128}\varepsilon^4 + \cdots, \qquad (5.23)$$

we obtain the contribution to the potential for charges e at $x = a$ and $x = -a$:

$$V_{x=-a} + V_{x=a} = \frac{2e}{a}\left[1 - \frac{1}{2}(r^2/a^2) + \frac{3}{2}(x^2/a^2) + \frac{3}{8}(r^4/a^4) \right.$$

$$\left. - \frac{15}{4}(x^2/a^2)(r^2/a^2) + \frac{35}{8}(x^4/a^4) + \cdots \right]. \qquad (5.24)$$

For a cubic field with charges e at $x = \pm a$, $y = \pm a$, $z = \pm a$ we get for $V_{\text{total}} = V_{\text{xtal}}$:

$$V_{\text{total}} = \frac{2e}{a}\left[3 + \frac{35}{8a^4}(x^4 + y^4 + z^4) - \frac{21}{8}(r^4/a^4) + \cdots \right], \qquad (5.25)$$

so that the perturbation that will lift the degeneracy of the free atom is of the form

$$V_{\text{cubic}} = \frac{35e}{4a^5}\left[(x^4 + y^4 + z^4) - \frac{3}{5}r^4 \right]. \qquad (5.26)$$

From these expressions it also follows that for a orthorhombic field where the charges are at $x = \pm a$, $y = \pm b$, $z = \pm c$ (and $a \neq b \neq c$). The crystal potential becomes

$$V_{\text{total}} = \frac{2e}{a} + \frac{2e}{b} + \frac{2e}{c} + ex^2\left[\frac{2}{a^3} - \frac{1}{b^3} - \frac{1}{c^3} \right]$$

$$+ ey^2\left[\frac{2}{b^3} - \frac{1}{a^3} - \frac{1}{c^3} \right] + ez^2\left[\frac{2}{c^3} - \frac{1}{a^3} - \frac{1}{b^3} \right], \qquad (5.27)$$

so that the orthorhombic perturbation V_{ortho} that will lift the degeneracy of the free atom is of the form

$$V_{\text{ortho}} = Ax^2 + By^2 - (A + B)z^2, \qquad (5.28)$$

where the values for the coefficients A and B can be found from (5.27).

We note that V_{cubic} contains no terms of order x^2, whereas V_{ortho} does. Let us now express the crystal field potential in terms of spherical harmonics since the unperturbed states for the free impurity ion are expressed in that way. Here we make use of the fact that the crystal field potential is generated by a collection of point sources and in the intervening space we are "outside" the field sources so that the potential must satisfy the Laplace equation $\nabla^2 V = 0$.

Solutions to Laplace's equation [5] are of the form $r^\ell Y_{\ell m}(\theta, \phi)$. From the definitions for the spherical harmonics (5.2) it is clear that for a cubic field (5.26), the only spherical harmonics that will enter V_{cubic} are $Y_{4,0}, Y_{4,4}$ and $Y_{4,-4}$ since $(z/4)^4$ involves only $Y_{4,0}$ while $[(x/4)^4 + (y/4)^4]$ involves only $Y_{4,4}$ and $Y_{4,-4}$.

The crystal field potential V_{xtal} can therefore be written in terms of spherical harmonics, the basis functions normally used to describe the potential of the free ion which has full spherical symmetry. One important role of group theory in the solution of quantum mechanical problems is to determine the degeneracy of the eigenvalues and which choice of basis functions yields the eigenvalues most directly. This information is available without the explicit diagonalization of the Hamiltonian. In the case of the crystal field problem, we determine V_{xtal} for a specific crystal symmetry using the appropriate basis functions for the relevant point group.

Selected Problems

**5.1.** Consider the hydrogen atom, described by the Schrödinger equation

$$\mathcal{H}\Psi_{n\ell m} = \left\{ -\frac{\hbar^2}{2m}\nabla_r^2 - \frac{L^2}{r^2} + V(r) \right\} \Psi_{n\ell m} = E_{n\ell}\Psi_{n\ell m}.$$

(a) Does $\mathcal{H}$ commute with any arbitrary rotation about the origin? Explain your answer.
(b) If the electron is in a d-orbital ($\ell = 2$) described by the eigenfunction

$$\Psi_{n2m}(r, \theta, \phi) = R_n(r)Y_{2,m}(\theta, \phi),$$

where $Y_{2,m}(\theta, \phi)$ is a spherical harmonic for $\ell = 2$, what is the effect on $\Psi_{n2m}(r, \theta, \phi)$ of rotating the coordinate system by a polar angle α. Is the new wave function still an eigenfunction of the Hamiltonian with the same eigenvalue? Explain.

5.2. Suppose that an iron (Fe) impurity is introduced into a two-dimensional honeycomb lattice of an insulating host material. A honeycomb lattice is a hexagonal lattice with atoms at the hexagon corners but not at the center. Suppose that the Fe impurity is placed first in a substitutional location and second in an interstitial location at the center of the hexagon.

substitutional   interstitial
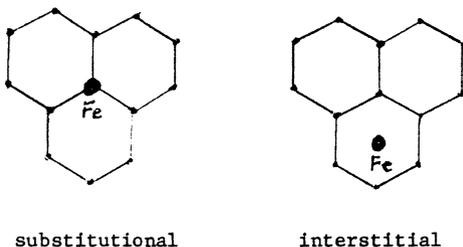
(a) What is the difference in crystal potential (include only nearest neighbors) between the substitutional and interstitial locations?
(b) For the interstitial case, express your result in part (a) in terms of spherical harmonics for the lowest order terms with angular dependencies.
(c) What is the proper point group symmetry and character table in each case?
(d) Give the crystal field splitting of the fivefold d-levels of the Fe impurity in the crystal fields for the two locations of the Fe ion in part (a).
(e) Identify the basis functions associated with each of the levels in part (d).
(f) Since the bonding orbitals lie lower in energy than the antibonding orbitals, indicate how the ordering of the levels might indicate whether the Fe impurity is located substitutionally or interstitially in the honeycomb lattice.

5.3. Show (by finding the characters of the rotation group) that the d-level for a transition metal impurity in a metal cluster with I_h point symmetry is not split by the icosahedral crystal field.

5.4. Suppose that a stress is applied along a (110) axis of a cubic crystal, thereby lowering its symmetry from O to D_2.

(a) What are the symmetry operations of D_2? Identify each symmetry axis of D_2 with a particular (xyz) direction of the high symmetry group O.
(b) Considering the irreducible representation $\Gamma_{\rm rot}^{(2)}$ for the full rotation group as a reducible representation of D_2, find the irreducible representations of D_2 contained in $\Gamma_{\rm rot}^{(2)}$.
(c) How do the T_2 and E levels corresponding to $\Gamma_{\rm rot}^{(2)}$ in the cubic group split by the application of a force along the (110) direction, giving the irreducible representations of the group D_2 contained in the T_2 and E levels.
(d) What is the physical interpretation of the occurrence of a particular irreducible representation Γ_j of group D_2 more than once when the fivefold degeneracy of $\Gamma_{\rm rot}^{(2)}$ is lifted by applying a force in the (110) direction?

5.5. What is the form of the crystal field of a hexagonal semiconductor like ZnO? Which are the lowest order $Y_{\ell,m}(\theta, \phi)$ spherical harmonics that describe the crystal field potential?