4

Basis Functions

In the previous chapters we have discussed symmetry elements, their matrix representations and the properties of the characters of these representations. In this discussion we saw that the matrix representations are not unique though their characters are unique. Because of the uniqueness of the characters of each irreducible representation, the characters for each group are tabulated in character tables. Also associated with each irreducible representation are "basis functions" which can be used to generate the matrices that represent the symmetry elements of a particular irreducible representation. Because of the importance of basis functions, it is customary to list the most important basis functions in the character tables.

4.1 Symmetry Operations and Basis Functions

Suppose that we have a group G with symmetry elements R and symmetry operators $\hat{P}_R$. We denote the irreducible representations by Γ_n, where n labels the representation. We can then define a set of basis vectors denoted by $|\Gamma_n j\rangle$. Each vector $|\Gamma_n j\rangle$ of an irreducible representation Γ_n is called a component or partner and j labels the component or partner of the representation, so that if we have a two-dimensional representation, then $j = 1, 2$. All partners collectively generate the matrix representation denoted by $D^{(\Gamma_n)}(R)$. These basis vectors relate the symmetry operator $\hat{P}_R$ with its matrix representation $D^{(\Gamma_n)}(R)$ through the relation

$$\hat{P}_R|\Gamma_n \alpha\rangle = \sum_j D^{(\Gamma_n)}(R)_{j\alpha}|\Gamma_n j\rangle \,. \tag{4.1}$$

The basis vectors can be abstract vectors; a very important type of basis vector is a *basis function* which we define here as a basis vector expressed explicitly in coordinate space. *Wave functions* in quantum mechanics, which are basis functions for symmetry operators, are a special but important example of such basis functions.

In quantum mechanics, each energy eigenvalue of Schrödinger's equation is labeled according to its symmetry classification, which is specified according to an irreducible representation of a symmetry group. If the dimensionality of the representation is $j > 1$, the energy eigenvalue will correspond to a j-fold degenerate state, with j linearly independent wave-functions. The effect of the symmetry operator $\hat{P}_R$ on one of these wave functions (e.g., the αth wave function) will generally be the formation of a linear combination of the j wave functions, as is seen in (4.1).

Like the matrix representations and the characters, the basis vectors also satisfy orthogonality relations

$$\langle \Gamma_n j | \Gamma_{n'} j' \rangle = \delta_{nn'} \delta_{jj'} \ , \tag{4.2}$$

and this relation is proved in Sect. 6.2 in connection with selection rules. In quantum (wave) mechanics, this orthogonality relation would be written in terms of the orthogonality for the wave functions

$$\int \psi^*_{n,j}(\boldsymbol{r}) \psi_{n',j'}(\boldsymbol{r}) \mathrm{d}^3 r = \delta_{nn'} \delta_{jj'} \ , \tag{4.3}$$

where the wave functions $\psi_{n,j}$ and $\psi_{n',j'}$ correspond to different energy eigenvalues (n, n') and to different components (j, j') of a particular degenerate state, and the integration is usually performed in 3D space. The orthogonality relation (4.3) allows us to generate matrices for an irreducible representation from a complete set of basis vectors, as is demonstrated in Sect. 4.2.

4.2 Use of Basis Functions to Generate Irreducible Representations

In this section we demonstrate how basis functions can be used to generate the matrices for an irreducible representation.

Multiplying (4.1) on the left by the basis vector $\langle \Gamma_{n'} j' |$ (corresponding in wave mechanics to $\psi^*_{n',j'}(\boldsymbol{r})$), we obtain using the orthogonality relation for basis functions (4.2):

$$\langle \Gamma_{n'} j' | \hat{P}_R | \Gamma_n \alpha \rangle = \sum_j D^{(\Gamma_n)}(R)_{j\alpha} \langle \Gamma_{n'} j' | \Gamma_n j \rangle = D^{(\Gamma_{n'})}(R)_{j'\alpha} \delta_{nn'} \ . \tag{4.4}$$

From (4.4) we obtain a relation between each matrix element of $D^{(\Gamma_n)}(R)_{j\alpha}$ and the effect of the symmetry operation on the basis functions:

$$D^{(\Gamma_n)}(R)_{j\alpha} = \langle \Gamma_n j | \hat{P}_R | \Gamma_n \alpha \rangle \ . \tag{4.5}$$

Thus by taking matrix elements of a symmetry operator $\hat{P}_R$ between all possible partners of an irreducible representation as shown by (4.5) the matrix

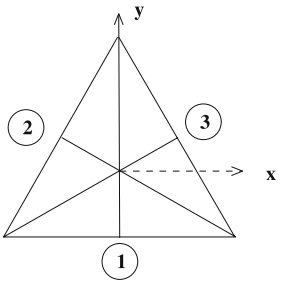

Fig. 4.1. Symmetry operations of an equilateral triangle. The notation of this diagram defines the symmetry operations in Table 4.1. Each vertex is labeled by the same number as its axis

representation $D^{\Gamma_n}(R)_{j\alpha}$ can be generated. In practice, this turns out to be the easiest way to obtain these matrix representations for the symmetry elements.

As an example of how basis vectors or basis functions can generate the matrices for an irreducible representation, consider a planar molecule with threefold symmetry such that the symmetry operations are isomorphic to those of an equilateral triangle and also isomorphic to $P(3)$ (see Chap. 1). Thus there are six symmetry operations and six operators $\hat{P}_R$ (see Sect. 1.2). The proper point group to describe all the symmetry operations of a regular planar triangle could be $D_{3h} = D_3 \otimes \sigma_h$. However, since the triangle is a 2D object, the horizontal mirror plane may not be an important symmetry operation and we can here simplify the algebra by using the group D_3 which has six symmetry elements. Group theory tells us that the energy levels can never be more than twofold degenerate. Thus no threefold or sixfold degenerate levels can occur because the largest dimensionality of an irreducible representation of $P(3)$ is 2 (see Problem 2.2). For the one-dimensional representation Γ_1, the operator $\hat{P}_R$ leaves every basis vector invariant. Thus any constant such as the number one forms a suitable basis function. For many practical problems we like to express our basis functions in terms of functions of the coordinates (x, y, z). Some explanation is needed here about the meaning of (x, y, z) as a basis function. To satisfy the orthonormality requirement, the basis functions are vectors with unit length and the matrices which represent the symmetry operations are unitary matrices. The transformation properties of the x, y, and z components of an arbitrary vector under the symmetry operations of the group are the same as those for the unit vectors x, y, and z.

In this connection it is convenient to write out a basis function table such as Table 4.1. On the top row we list the functions to be investigated; in the first column we list all the symmetry operations of the group (see Fig. 4.1 for notation). If we denote the entries in the table by $f'(x, y, z)$, then Table 4.1 can be summarized as

$$\hat{P}_R f(x, y, z) = f'(x, y, z) \,, \tag{4.6}$$

Table 4.1. Symmetry operations $\hat{P}_R$ of the group of the equilateral triangle on basis functions taking (x, y, z) into (x', y', z')

$\hat{P}_R$	x'	y'	z'	x'^2	y'^2	z'^2
$E = E$	x	y	z	x^2	y^2	z^2
$C_3 = F$	$\frac{1}{2}(-x + \sqrt{3}y)$	$\frac{1}{2}(-y - \sqrt{3}x)$	z	$\frac{1}{4}(x^2 + 3y^2 - 2\sqrt{3}xy)$	$\frac{1}{4}(y^2 + 3x^2 + 2\sqrt{3}xy)$	z^2
$C_3^{-1} = D$	$\frac{1}{2}(-x - \sqrt{3}y)$	$\frac{1}{2}(-y + \sqrt{3}x)$	z	$\frac{1}{4}(x^2 + 3y^2 + 2\sqrt{3}xy)$	$\frac{1}{4}(y^2 + 3x^2 - 2\sqrt{3}xy)$	z^2
$C_{2(1)} = A$	$-x$	y	$-z$	x^2	y^2	z^2
$C_{2(2)} = B$	$\frac{1}{2}(x - \sqrt{3}y)$	$\frac{1}{2}(-y - \sqrt{3}x)$	$-z$	$\frac{1}{4}(x^2 + 3y^2 - 2\sqrt{3}xy)$	$\frac{1}{4}(y^2 + 3x^2 + 2\sqrt{3}xy)$	z^2
$C_{2(3)} = C$	$\frac{1}{2}(x + \sqrt{3}y)$	$\frac{1}{2}(-y + \sqrt{3}x)$	$-z$	$\frac{1}{4}(x^2 + 3y^2 + 2\sqrt{3}xy)$	$\frac{1}{4}(y^2 + 3x^2 - 2\sqrt{3}xy)$	z^2

where the symmetry operations $\hat{P}_R$ label the rows. From Table 4.1 we can then write down the matrix representations for entries on each irreducible representation. In the trivial case of the identity representation, the (1×1) matrix 1 satisfies $\hat{P}_R 1 = 1$ for all $\hat{P}_R$ so that this homomorphic representation always applies, i.e., $|\Gamma_1\rangle = 1$.

To find the basis functions for the $\Gamma_{1'}$ representation (i.e., the representation of the factor group for $P(3)$), we note that (E, D, F) leaves z invariant while (A, B, C) takes z into $-z$, so that z forms a suitable basis function for $\Gamma_{1'}$, which we write as $|\Gamma_{1'}\rangle = z$. Then application of (4.5) yields the matrices for the irreducible representation $\Gamma_{1'}$

$$\langle z|(E, D, F)|z\rangle = 1 \ , \quad \langle z|(A, B, C)|z\rangle = -1 \ . \tag{4.7}$$

Thus the characters (1) and (-1) for the (1×1) irreducible representations are obtained for $\Gamma_{1'}$. We note that *in the case of* (1×1) *representations, the characters and the representations are identical.*

To find the two-dimensional representation Γ_2 we note that all the group operations take (x, y) into (x', y'). Table 4.1 shows the results of each $\hat{P}_R$ operator acting on x, y, z to yield x', y', z' and $\hat{P}_R$ acting on x^2, y^2, z^2 to yield x'^2, y'^2, z'^2. Table 4.1 thus can be used to find the matrix representation for Γ_2 by taking as basis functions $|\Gamma_2, 1\rangle = |x\rangle$ and $|\Gamma_2, 2\rangle = |y\rangle$. We now illustrate the use of Table 4.1 to generate the matrix $D^{(\Gamma_2)}(C_3^{-1} = D)$ where D is a clockwise rotation of $2\pi/3$ about the z-axis:

$$D|x\rangle = -1/2(x + \sqrt{3}y) \quad \text{yields first column of matrix representation}$$
$$D|y\rangle = 1/2(\sqrt{3}x - y) \quad \text{yields second column of matrix representation}$$

so that

$$D^{(\Gamma_2)}(C_3^{-1} = D) = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \ . \tag{4.8}$$

To clarify how we obtain all the matrices for the irreducible representations with Γ_2 symmetry, we repeat the operations leading to (4.8) for each of the symmetry operations $\hat{P}_R$. We thus obtain for the other five symmetry operations of the group $\hat{P}_R$ using the same basis functions (x, y) and the notation of Fig. 4.1:

$$D^{(\Gamma_2)}(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \ , \tag{4.9}$$

$$D^{(\Gamma_2)}(C_2(2) = B) = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \ , \tag{4.10}$$

$$D^{(\Gamma_2)}(C_3 = F) = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} , \tag{4.11}$$

$$D^{(\Gamma_2)}(C_2(1) = A) = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} , \tag{4.12}$$

$$D^{(\Gamma_2)}(C_2(3) = C) = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} . \tag{4.13}$$

As mentioned before, x and y are both basis functions for representation Γ_2 and are called the *partners* of this irreducible representation. The number of partners is equal to the dimensionality of the representation.

In Table 4.1 we have included entries for $\hat{P}_R x^2$, $\hat{P}_R y^2$, $\hat{P}_R z^2$ and these entries are obtained as illustrated below by the operation $D = C_3^{-1}$:

$$Dx^2 = \left(-\frac{x}{2} - \frac{\sqrt{3}}{2} y \right)^2 = \left(\frac{x^2}{4} + \frac{\sqrt{3}}{2} xy + \frac{3}{4} y^2 \right) , \tag{4.14}$$

$$Dy^2 = \left(-\frac{y}{2} + \frac{\sqrt{3}}{2} x \right)^2 = \left(\frac{y^2}{4} - \frac{\sqrt{3}}{2} xy + \frac{3}{4} x^2 \right) , \tag{4.15}$$

$$D(x^2 + y^2) = x^2 + y^2 , \tag{4.16}$$

$$\begin{aligned} D(xy) &= \left(-\frac{x}{2} - \frac{\sqrt{3}}{2} y \right) \left(-\frac{y}{2} + \frac{\sqrt{3}}{2} x \right) \\ &= \frac{1}{4} \left(-2xy - \sqrt{3}[x^2 - y^2] \right) , \end{aligned} \tag{4.17}$$

$$D(x^2 - y^2) = -\frac{1}{4} \left(2[x^2 - y^2] - 4\sqrt{3} xy \right) , \tag{4.18}$$

$$D(xz) = \left(-\frac{x}{2} - \frac{\sqrt{3}}{2} y \right) z , \tag{4.19}$$

$$D(yz) = \left(-\frac{y}{2} + \frac{\sqrt{3}}{2} x \right) z . \tag{4.20}$$

Using (4.1) we see that $\hat{P}_R(x^2+y^2) = (x^2+y^2)$ for all $\hat{P}_R$ so that (x^2+y^2) is a basis function for Γ_1 or as we often say transforms according to the irreducible representation Γ_1. Correspondingly $z(x^2+y^2)$ transforms as $\Gamma_{1'}$ and z^2

transforms as Γ_1. These transformation properties will be used extensively for many applications of group theory. It is found that many important basis functions are given directly in the published character tables. Like the matrix representations, the basis functions are not unique. However, corresponding to a given set of basis functions, the matrix representation which is generated by these basis functions will be unique.

As before, the characters for a given representation are found by taking the sum of the diagonal elements of each matrix in a given representation:

$$\chi^{(\Gamma_n)}(R) \equiv tr\ D^{(\Gamma_n)}(R) = \sum_j D^{(\Gamma_n)}(R)_{jj} = \sum_j \langle \Gamma_n j | \hat{P}_R | \Gamma_n j \rangle \ . \qquad (4.21)$$

Since the trace is invariant under a similarity transformation, the character is independent of the particular choice of basis functions or matrix representations.

If instead of a basis function (which generates irreducible representations) we use an arbitrary function f, then a reducible representation will result, in general. We can express an arbitrary function as a linear combination of the basis functions. For example, any linear function of x, y, z such as $f(x, y, z)$ can be expressed in terms of linear combinations of basis vectors x, y, z and likewise any quadratic function is expressed in terms of quadratic basis functions which transform as irreducible representations of the group. For example for the group $P(3)$ (see Table 4.1), quadratic forms which serve as basis functions are $(x^2 + y^2)$ and z^2 which both transform as Γ_1; z transforms as $\Gamma_{1'}$; (xz, yz) and $(xy, x^2 - y^2)$ both transform as Γ_2.

If we now inspect the character table $D_3(32)$ found in Table A.12 (and reproduced below in Table 4.2), we find that these basis functions are listed in this character table. The basis functions labeled R_α represent the angular momentum component around axis α (e.g., $R_x = yp_z - zp_y$). For the two dimensional irreducible representations both partners of the basis functions are listed, for example (xz, xy) and $(x^2 - y^2, xy)$, etc. The reason why (x, y, z) and (R_x, R_y, R_z) often transform as different irreducible representations (not the case for the group $D_3(32)$) is that x, y, z transforms as a radial vector (such as coordinate, momentum) while R_x, R_y, R_z transforms as an axial vector (such as angular momentum $\boldsymbol{r} \times \boldsymbol{p}$).

Table 4.2. Character Table for Group D_3 (rhombohedral)

$D_3(32)$			E	$2C_3$	$3C_2'$
$x^2 + y^2, z^2$		A_1	1	1	1
	R_z, z	A_2	1	1	−1
(xz, yz) $(x^2 - y^2, xy)$	(x, y) (R_x, R_y)	E	2	−1	0

4.3 Projection Operators $\hat{P}_{kl}^{(\Gamma_n)}$

The previous discussion of basis vectors assumed that we already knew how to write down the basis vectors. In many cases, representative basis functions are tabulated in the character tables. However, suppose that we have to find basis functions for the following cases:

(a) An irreducible representation for which no basis functions are listed in the character table; or
(b) An arbitrary function.

In such cases the basis functions can often be found using *projection operators* $\hat{P}_{k\ell}$, not to be confused with the symmetry operators $\hat{P}_R$. We define the projection operator $\hat{P}_{k\ell}^{(\Gamma_n)}$ as transforming one basis vector $|\Gamma_n \ell\rangle$ into another basis vector $|\Gamma_n k\rangle$ of the same irreducible representation Γ_n:

$$\hat{P}_{k\ell}^{(\Gamma_n)} |\Gamma_n \ell\rangle \equiv |\Gamma_n k\rangle \; . \tag{4.22}$$

The utility of projection operators is mainly to project out basis functions for a given partner of a given irreducible representation from an arbitrary function. The discussion of this topic focuses on the following issues:

(a) The relation of the projection operator to symmetry operators of the group and to the matrix representation of these symmetry operators for an irreducible representation (see Sect. 4.4).
(b) The effect of projection operators on an arbitrary function (see Sect. 4.5).

As an example, we illustrate in Sect. 4.6 how to find basis functions from an arbitrary function for the case of the group of the equilateral triangle (see Sect. 4.2).

4.4 Derivation of an Explicit Expression for $\hat{P}_{k\ell}^{(\Gamma_n)}$

In this section we find an explicit expression for the projection operators $\hat{P}_{kl}^{(\Gamma_n)}$ by considering the relation of the projection operator to symmetry operators of the group. We will find that the coefficients of this expression give the matrix representations of each of the symmetry elements.

Let the projection operator $\hat{P}_{k\ell}^{(\Gamma_n)}$ be written as a linear combination of the symmetry operators $\hat{P}_R$:

$$\hat{P}_{k\ell}^{(\Gamma_n)} = \sum_R A_{k\ell}(R) \hat{P}_R \; , \tag{4.23}$$

where the $A_{k\ell}(R)$ are arbitrary expansion coefficients to be determined. Substitution of (4.23) into (4.22) yields

$$\hat{P}_{k\ell}^{(\Gamma_n)}|\Gamma_n\ell\rangle \equiv |\Gamma_n k\rangle = \sum_R A_{k\ell}(R)\hat{P}_R|\Gamma_n\ell\rangle \ . \tag{4.24}$$

Multiply (4.24) on the left by $\langle\Gamma_n k|$ to yield

$$\langle\Gamma_n k|\Gamma_n k\rangle = 1 = \sum_R A_{k\ell}(R)\underbrace{\langle\Gamma_n k|\hat{P}_R|\Gamma_n\ell\rangle}_{D^{(\Gamma_n)}(R)_{k\ell}} \ . \tag{4.25}$$

But the Wonderful Orthogonality Theorem (2.51) specifies that

$$\sum_R D^{(\Gamma_n)}(R)^*_{k\ell}D^{(\Gamma_n)}(R)_{k\ell} = \frac{h}{\ell_n} \ , \tag{4.26}$$

where h is the number of symmetry operators in the group and ℓ_n is the dimensionality of the irreducible representation Γ_n, so that we can identify $A_{k\ell}(R)$ with the matrix element of the representation for the symmetry element R:

$$A_{k\ell}(R) = \frac{\ell_n}{h}D^{(\Gamma_n)}(R)^*_{k\ell} \ . \tag{4.27}$$

Thus the projection operator is explicitly given in terms of the symmetry operators of the group by the relation:

$$\hat{P}_{k\ell}^{(\Gamma_n)} = \frac{\ell_n}{h}\sum_R D^{(\Gamma_n)}(R)^*_{k\ell}\hat{P}_R \ . \tag{4.28}$$

From the explicit form for $\hat{P}_{k\ell}^{(\Gamma_n)}$ in (4.28) and from (4.22) we see how to find the partners of an irreducible representation Γ_n from any single known basis vector, provided that the matrix representation for all the symmetry operators $D^{(\Gamma_n)}(R)$ is known.

As a special case, the projection operator $\hat{P}_{kk}^{(\Gamma_n)}$ transforms $|\Gamma_n k\rangle$ into itself and can be used to check that $|\Gamma_n k\rangle$ is indeed a basis function. We note that the relation of $\hat{P}_{kk}^{(\Gamma_n)}$ to the symmetry operators $\hat{P}_R$ involves only the *diagonal elements of the matrix representations* (though not the trace):

$$\hat{P}_{kk}^{(\Gamma_n)} = \frac{\ell_n}{h}\sum_R D^{(\Gamma_n)}(R)^*_{kk}\hat{P}_R \ , \tag{4.29}$$

where

$$\hat{P}_{kk}^{(\Gamma_n)}|\Gamma_n k\rangle \equiv |\Gamma_n k\rangle \ . \tag{4.30}$$

4.5 The Effect of Projection Operations on an Arbitrary Function

The projection operators $\hat{P}_{kk}^{(\Gamma_n)}$ defined in (4.30) are of special importance because they can project the kth partner of irreducible representation Γ_n

from an arbitrary function. Any arbitrary function F can be written as a linear combination of a complete set of basis functions $|\Gamma_{n'} j'\rangle$:

$$F = \sum_{\Gamma_{n'}} \sum_{j'} f_{j'}^{(\Gamma_{n'})} |\Gamma_{n'} j'\rangle \ . \tag{4.31}$$

We can then write from (4.29):

$$\hat{P}_{kk}^{(\Gamma_n)} F = \frac{\ell_n}{h} \sum_R D^{(\Gamma_n)}(R)_{kk}^* \hat{P}_R F \tag{4.32}$$

and substitution of (4.31) into (4.32) then yields

$$\hat{P}_{kk}^{(\Gamma_n)} F = \frac{\ell_n}{h} \sum_R \sum_{\Gamma_{n'}} \sum_{j'} f_{j'}^{(\Gamma_{n'})} D^{(\Gamma_n)}(R)_{kk}^* \ \hat{P}_R |\Gamma_{n'} j'\rangle \ . \tag{4.33}$$

But substitution of (4.1) into (4.33) and use of the Wonderful Orthogonality Theorem (2.51):

$$\sum_R D^{(\Gamma_{n'})}(R)_{jj'} D^{(\Gamma_n)}(R)_{kk}^* = \frac{h}{\ell_n} \delta_{\Gamma_n \Gamma_{n'}} \delta_{jk} \delta_{j'k} \tag{4.34}$$

yields

$$\hat{P}_{kk}^{(\Gamma_n)} F = f_k^{(\Gamma_n)} |\Gamma_n k\rangle \ , \tag{4.35}$$

where

$$\hat{P}_{kk}^{(\Gamma_n)} = \frac{\ell_n}{h} \sum_R D^{(\Gamma_n)}(R)_{kk}^* \hat{P}_R \ . \tag{4.36}$$

We note that the projection operator does not yield normalized basis functions. One strategy to find basis functions is to start with an arbitrary function F.

(a) We then use $\hat{P}_{kk}^{(\Gamma_n)}$ to project out one basis function $|\Gamma_n k\rangle$.
(b) We can then use the projection operator $\hat{P}_{k\ell}^{(\Gamma_n)}$ to project out all other partners $|\Gamma_n \ell\rangle$ orthogonal to $|\Gamma_n k\rangle$ in irreducible representation Γ_n. Or alternatively we can use $\hat{P}_{\ell\ell}^{(\Gamma_n)}$ to project out each of the partners ℓ of the representation, whichever method works most easily in a given case.

If we do not know the explicit representations $D_{k\ell}^{(\Gamma_n)}(R)^*$, but only know the characters, then we can still project out basis functions which transform according to the irreducible representations (using the argument given in the next paragraph), though we cannot in this case project out specific partners but only linear combinations of the partners of these irreducible representations.

If we only know the characters of an irreducible representation Γ_n, we define the projection operator for this irreducible representation as $\hat{P}^{(\Gamma_n)}$:

$$\hat{P}^{(\Gamma_n)} \equiv \sum_k \hat{P}_{kk}^{(\Gamma_n)} = \frac{\ell_n}{h} \sum_R \sum_k D^{(\Gamma_n)}(R)^*_{kk} \hat{P}_R \,, \tag{4.37}$$

so that

$$\hat{P}^{(\Gamma_n)} = \frac{\ell_n}{h} \sum_R \chi^{(\Gamma_n)}(R)^* \hat{P}_R \tag{4.38}$$

and using (4.35) we then obtain

$$\hat{P}^{(\Gamma_n)} F = \sum_k \hat{P}_{kk}^{(\Gamma_n)} F = \sum_k f_k^{(\Gamma_n)} |\Gamma_n k\rangle \,, \tag{4.39}$$

which projects out a function transforming as Γ_n but not a specific partner of Γ_n.

In dealing with physical problems it is useful to use physical insight in guessing at an appropriate "arbitrary function" to initiate this process for finding the basis functions and matrix representations for specific problems. This is the strategy to pursue when you do not know either the matrix representations or the basis functions *a priori*.

4.6 Linear Combinations of Atomic Orbitals for Three Equivalent Atoms at the Corners of an Equilateral Triangle

As an example of finding basis functions from an arbitrary function, we here consider forming linear combinations of atomic orbitals which transform as irreducible representations of the symmetry group.

In many of the applications that we will be making of group theory to solid-state physics, we will have equivalent atoms at different sites. We use the symmetry operations of the group to show which irreducible representations result when the equivalent atoms transform into each other under the symmetry operations of the group. The discussion of projection operators of an arbitrary function applies to this very important case.

As an example of this application, suppose that we have three equivalent atoms at the three corners of an equilateral triangle (see Fig. 4.2) and that each atom is in the same spherically symmetric ground state described by a wave function $\psi_0(\boldsymbol{r}_i)$, where the subscript i is a site index, which can apply to any of the three sites. As a short-hand notation for $\psi_0(\boldsymbol{r}_a)$, $\psi_0(\boldsymbol{r}_b)$, $\psi_0(\boldsymbol{r}_c)$ we will here use a, b, c.

We now want to combine these atomic orbitals to make a molecular orbital that transforms according to the irreducible representations of the group. We will see that only the Γ_1 and Γ_2 irreducible representations are contained in the linear combination of atomic orbitals for a, b, c. This makes sense since we have

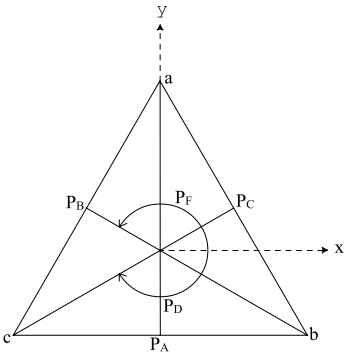

Fig. 4.2. Equilateral triangle and arbitrary functions a, b, c for atomic orbitals at corners of an equilateral triangle, defining the notation used in Sect. 4.6

three atomic orbitals which split into a nondegenerate and a two-dimensional representation in trigonal symmetry through the symmetry operations $\hat{P}_R$ on the equivalent site functions a, b, c.

To generate the proper linear combination of atomic orbitals that transform as irreducible representations of the symmetry group, we use the results on the projection operator to find out which irreducible representations are contained in the function F. According to the above discussion, we can project out a basis function for representation Γ_n by considering the action of $\hat{P}_{kk}^{(\Gamma_n)}$ on one of the atomic orbitals, as for example orbital $F = a$:

$$\hat{P}_{kk}^{(\Gamma_n)} a = \frac{\ell_n}{h} \sum_R D^{(\Gamma_n)}(R)_{kk}^* \, \hat{P}_R a = f_k^{(\Gamma_n)} |\Gamma_n k\rangle \; , \tag{4.40}$$

in which we have used the definition for $\hat{P}_{kk}^{(\Gamma_n)}$ given by (4.35) and the expression for $\hat{P}_{kk}^{(\Gamma_n)}$ given by (4.36). If the representation Γ_n is one-dimensional, then we can obtain $D^{(\Gamma_n)}(R)$ directly from the character table, and (4.40) then becomes

$$\hat{P}^{(\Gamma_n)} a = \frac{\ell_n}{h} \sum_R \chi^{(\Gamma_n)}(R)^* \hat{P}_R a = f^{(\Gamma_n)} |\Gamma_n\rangle \; . \tag{4.41}$$

For the appropriate symmetry operators for this problem we refer to Sect. 1.2 where we have defined: $E \equiv$ identity; $(A, B, C) \equiv \pi$ rotations about twofold axes in the plane of triangle; $(D, F) \equiv 2\pi/3$ rotations about the threefold axis $\perp$ to the plane of the triangle. These symmetry operations are also indicated in Fig. 4.2.

For the identity representation Γ_1 the characters and matrix representations are all unity so that

$$\begin{aligned}\hat{P}^{(\Gamma_1)}a &= \frac{1}{6}(\hat{P}_E a + \hat{P}_A a + \hat{P}_B a + \hat{P}_C a + \hat{P}_D a + \hat{P}_F a) \\ &= \frac{1}{6}(a + a + c + b + b + c) \\ &= \frac{1}{3}(a + b + c)\ , \end{aligned} \tag{4.42}$$

a result which is intuitively obvious. Each atom site must contribute equally to the perfectly symmetrical molecular representation Γ_1. This example illustrates how starting with an arbitrary function a (or $\psi(\boldsymbol{r}_a)$) we have found a linear combination that transforms as Γ_1. Likewise, we obtain the same result by selecting b or c as the arbitrary function

$$\hat{P}^{(\Gamma_1)}b = \hat{P}^{(\Gamma_1)}c = \frac{1}{3}(a + b + c)\ . \tag{4.43}$$

We now apply a similar analysis for representation $\Gamma_{1'}$ to illustrate another important point. In this case the matrix representations and characters are $+1$ for (E, D, F), and -1 for (A, B, C). Thus

$$\begin{aligned}\hat{P}^{(\Gamma_{1'})}a &= \frac{1}{6}(\hat{P}_E a - \hat{P}_A a - \hat{P}_B a - \hat{P}_C a + \hat{P}_D a + \hat{P}_F a) \\ &= \frac{1}{6}(a - a - c - b + b + c) = 0\ , \end{aligned} \tag{4.44}$$

which states that no molecular orbital with $\Gamma_{1'}$ symmetry can be made by taking a linear combination of the a, b, c orbitals. This is verified by considering

$$\hat{P}^{(\Gamma_{1'})}b = \hat{P}^{(\Gamma_{1'})}c = 0\ . \tag{4.45}$$

The same approach can be used to obtain the two-dimensional irreducible representations, but it does not result in a simple set of linear combinations of atomic orbitals with a set of unitary matrices for the representation of the symmetry operations of the group (see Problem 4.6).

To obtain a symmetrical set of basis functions for higher dimensional representations it is useful to start with an arbitrary function that takes account of the dominant symmetry operations of the group (e.g., a threefold rotation $\hat{P}_D$)

$$|\Gamma_2\alpha\rangle = a + \omega b + \omega^2 c\ , \tag{4.46}$$

where $\omega = \mathrm{e}^{2\pi\mathrm{i}/3}$ and we note here from symmetry that $\hat{P}_D|\Gamma_2\alpha\rangle = \omega^2|\Gamma_2\alpha\rangle$ and $\hat{P}_F|\Gamma_2\alpha\rangle = \omega|\Gamma_2\alpha\rangle$.

Thus $|\Gamma_2\alpha\rangle$ is already a basis function. Clearly the partner of $|\Gamma_2\alpha\rangle$ is $|\Gamma_2\alpha\rangle^*$ since $\hat{P}_D|\Gamma_2\alpha\rangle^* = \hat{P}_D(a + \omega^2 b + \omega c) = \omega(a + \omega^2 b + \omega c) = \omega|\Gamma_2\beta\rangle$, where we have used the notation (α, β) to denote the two partners of the Γ_2 representation:

$$|\Gamma_2\alpha\rangle = a + \omega b + \omega^2 c\ , \quad |\Gamma_2\beta\rangle = a + \omega^2 b + \omega c\ . \tag{4.47}$$

The two partners in (4.47) are complex conjugates of each other. Corresponding to these basis functions, the matrix representation for each of the group elements is simple and symmetrical

$$E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad A = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad B = \begin{pmatrix} 0 & \omega^2 \\ \omega & 0 \end{pmatrix} \tag{4.48}$$

$$C = \begin{pmatrix} 0 & \omega \\ \omega^2 & 0 \end{pmatrix} \quad D = \begin{pmatrix} \omega^2 & 0 \\ 0 & \omega \end{pmatrix} \quad F = \begin{pmatrix} \omega & 0 \\ 0 & \omega^2 \end{pmatrix} .$$

By inspection, the representation given by (4.48) is *unitary*.

4.7 The Application of Group Theory to Quantum Mechanics

Suppose E_n is a k-fold degenerate level of the group of Schrödinger's equation (see Sect. 1.8). Then any linear combination of the eigenfunctions $\psi_{n1}, \psi_{n2}, \ldots, \psi_{nk}$ is also a solution of Schrödinger's equation. We can write the operation $\hat{P}_R \psi_{n\alpha}$ on one of these eigenfunctions as

$$\hat{P}_R \psi_{n\alpha} = \sum_j D^{(n)}(R)_{j\alpha} \psi_{nj} \ , \tag{4.49}$$

where $D^{(n)}(R)_{j\alpha}$ is an irreducible matrix which defines the linear combination, n labels the energy index, α labels the degeneracy index.

Equation (4.49) is identical with the more general equation for a basis function (4.1) where the states $|\Gamma_n \alpha\rangle$ and $|\Gamma_n j\rangle$ are written symbolically rather than explicitly as they are in (4.49).

We show here that the matrices $D^{(n)}(R)$ form an ℓ_n dimensional irreducible representation of the group of Schrödinger's equation where ℓ_n denotes the degeneracy of the energy eigenvalue E_n. Let R and S be two symmetry operations which commute with the Hamiltonian and let RS be their product. Then from (4.49) we can write

$$\begin{aligned} \hat{P}_{RS} \psi_{n\alpha} &= \hat{P}_R \hat{P}_S \psi_{n\alpha} = \hat{P}_R \sum_j D^{(n)}(S)_{j\alpha} \psi_{nj} \\ &= \sum_{jk} D^{(n)}(R)_{kj} D^{(n)}(S)_{j\alpha} \psi_{nk} = \sum_k \left[D^{(n)}(R) D^{(n)}(S) \right]_{k\alpha} \psi_{nk} \end{aligned} \tag{4.50}$$

after carrying out the indicated matrix multiplication. But by definition, the product operator RS can be written as

$$\hat{P}_{RS} \psi_{n\alpha} = \sum_k D^{(n)}(RS)_{k\alpha} \psi_{nk} \ , \tag{4.51}$$

so that

$$D^{(n)}(RS) = D^{(n)}(R)D^{(n)}(S) \tag{4.52}$$

and the matrices $D^{(n)}(R)$ form a representation for the group. We label quantum mechanical states typically by a state vector (basis vector) $|\alpha, \Gamma_n, j\rangle$ where Γ_n labels the irreducible representation, j the component or partner of the irreducible representation, and α labels the other quantum numbers that do not involve the symmetry of the $\hat{P}_R$ operators.

The dimension of the irreducible representation is equal to the degeneracy of the eigenvalue E_n. The representation $D^{(n)}(R)$ generated by $\hat{P}_R\psi_{n\alpha}$ is an irreducible representation if all the ψ_{nk} correspond to a single eigenvalue E_n. For otherwise it would be possible to form linear combinations of the type

$$\underbrace{\psi'_{n1}, \psi'_{n2}, \ldots, \psi'_{ns}}_{\text{subset 1}} \underbrace{\psi'_{n,s+1}, \ldots, \psi'_{nk}}_{\text{subset 2}} , \tag{4.53}$$

whereby the linear combinations within the subsets would transform amongst themselves. But if this happened, then the eigenvalues for the two subsets would be different, except for the rare case of accidental degeneracy. Thus, the transformation matrices for the symmetry operations form an *irreducible* representation for the group of Schrödinger's equation.

The rest of the book discusses several applications of the group theory introduced up to this point to problems of solid state physics. It is convenient at this point to classify the ways that group theory is used to solve quantum mechanical problems. Group theory is used both to obtain exact results and in applications of perturbation theory. In the category of exact results, we have as examples:

(a) Irreducible representations of the symmetry group of Schrödinger's equation *label the states and specify their degeneracies* (e.g., an atom in a crystal field).

(b) Group theory is useful in following the changes in the degeneracies of the energy levels as the *symmetry* is lowered. This case can be thought of in terms of a Hamiltonian

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}' , \tag{4.54}$$

where $\mathcal{H}_0$ has high symmetry corresponding to the group G, and $\mathcal{H}'$ is a perturbation having lower symmetry and corresponding to a group G' of lower order (fewer symmetry elements). Normally group G' is a subgroup of group G. Here we find first which symmetry operations of G are contained in G'; the irreducible representations of G' label the states of the lower symmetry situation exactly. In going to lower symmetry we want to know what happens to the degeneracy of the various states in the initial higher symmetry situation (see Fig. 4.3). We say that in general the irreducible representation of the *higher symmetry group forms reducible representations for the lower symmetry group.*

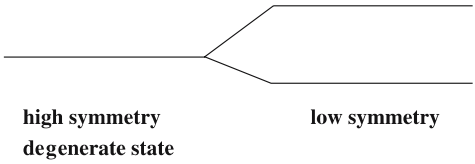

Fig. 4.3. The effect of lowering the symmetry often results in a lowering of the degeneracy of degenerate energy states

The degeneracy of states may either be lowered as the symmetry is lowered or the degeneracy may be unchanged. Group theory tells us exactly what happens to these degeneracies. We are also interested in finding the basis functions for the lower symmetry group G'. For those states where the degeneracy is unchanged, the basis functions are generally unchanged. When the degeneracy is reduced, then by proper choice of the form of the partners, the basis functions for the degenerate state will also be basis functions for the states in the lower symmetry situation.
An example of going from higher to lower symmetry is the following: If (x, y, z) are basis functions for a three-dimensional representation in the cubic group, then lowering the symmetry to tetragonal with z as the main symmetry direction will give a two-dimensional representation with basis functions (x, y) and a one-dimensional representation with basis function z. However, if the symmetry is lowered to tetragonal along a z' direction (different from z), then linear combinations of (x, y, z) must be taken to obtain a vector along z' and two others that are mutually orthogonal. The lowering of degeneracy is a very general topic and will enter the discussion of many applications of group theory (see Chap. 5).

(c) Group theory is helpful in finding the correct *linear combination of wavefunctions* that is needed to diagonalize the Hamiltonian. This procedure involves the concept of equivalence which applies to situations where equivalent atoms sit at symmetrically equivalent sites (see Chap. 7).

Selected Problems

4.1. (a) What are the matrix representations for $(2xy, x^2 - y^2)$ and (R_x, R_y) in the point group D_3?

(b) Using the results in (a), find the unitary transformation which transforms the matrices for the representation corresponding to the basis functions $(xy, x^2 - y^2)$ into the representation corresponding to the basis functions (x, y).

(c) Using projection operators, check that xy forms a proper basis function of the two-dimensional irreducible representation Γ_2 in point group D_3. Using the matrix representation found in (a) and projection operators, find the partner of xy.

(d) Using the basis functions in the character table for D_{3h}, write a set of (2×2) matrices for the two two-dimensional representations E' and E''. Give some examples of molecular clusters that require D_{3h} symmetry.

4.2. (a) Explain the Hermann–Manguin notation $T_d(\bar{4}3\,m)$.
(b) What are the irreducible representations and partners of the following basis functions in T_d symmetry? (i) $\omega x^2+\omega^2 y^2+z^2$, where $\omega = \exp(2\pi \mathrm{i}/3)$; (ii) xyz; and (iii) x^2yz.
(c) Using the results of (b) and the basis functions in the character table for the point group T_d, give one set of basis functions for each irreducible representation of T_d.
(d) Using the basis function $\omega x^2 + \omega^2 y^2 + z^2$ and its partner (or partners), find the matrix for an S_4 rotation about the x-axis in this irreducible representation.

4.3. Consider the cubic group O_h. Find the basis functions for all the symmetric combinations of cubic forms (x, y, z) and give their irreducible representations for the point group O_h.

4.4. Consider the hypothetical molecule CH_4 (Fig. 4.4) where the four H atoms are at the corners of a square $(\pm a, 0, 0)$ and $(0, \pm a, 0)$ while the C atom is at $(0, 0, z)$, where $z < a$. What are the symmetry elements?

(a) Identify the appropriate character table.
(b) Using the basis functions in the character table, write down a set of (2×2) matrices which provide a representation for the two-dimensional irreducible representation of this group.
(c) Find the four linear combinations of the four H orbitals (assume identical s-functions at each H site) that transform as the irreducible representations of the group. What are their symmetry types?
(d) What are the basis functions that generate the irreducible representations.
(e) Check that xz forms a proper basis function for the two-dimensional representation of this point group and find its partner.
(f) What are the irreducible representations and partners of the following basis functions in the point group (assuming that the four hydrogens lie in the xy plane): (i) xyz, (ii) x^2y, (iii) x^2z, (iv) $x + \mathrm{i}y$.
(g) What additional symmetry operations result in the limit that all H atoms are coplanar with atom C? What is now the appropriate group and character table? (The stereograms in Figure 3.2 may be useful.)

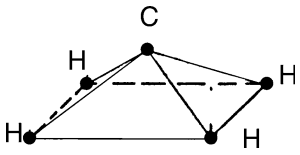

Fig. 4.4. Molecule CH_4

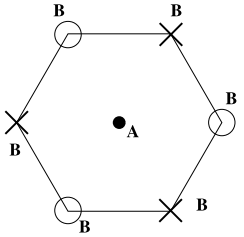

Fig. 4.5. Molecule AB_6

4.5. Consider a molecule AB_6 (Fig. 4.5) where the A atom lies in the central plane and three B atoms indicated by "◯" lie in a plane at a distance c above the central plane and the B atoms indicated by "✕" lie in a plane below the central plane at a distance $-c'$. When projected onto the central plane, all B atoms occupy the corners of a hexagon.

(a) Find the symmetry elements and classes.
(b) Construct the character table. To which point group (Chap. 3) does this molecule correspond? How many irreducible representations are there? How many are one-dimensional and how many are of higher dimensionality?
(c) Using the basis functions in the character table for this point group, find a set of matrices for each irreducible representation of the group.
(d) Find the linear combinations of the six s-orbitals of the B atoms that transform as the irreducible representations of the group.
(e) What additional symmetry operations result in the limit that all B atoms are coplanar with A? What is now the appropriate group and character table for this more symmetric molecule?
(f) Indicate which stereograms in Fig. 3.2 are appropriate for the case where the B atoms are not coplanar with A and the case where they are coplanar.

4.6. Consider the linear combinations of atomic orbitals on an equilateral triangle (Sect. 4.6).

(a) Generate the basis functions $|\Gamma_2 1\rangle$ and $|\Gamma_2 2\rangle$ for the linear combination of atomic orbitals for the Γ_2 irreducible representation obtained by using the projection operator acting on one of the atomic orbitals $\hat{P}_{11}^{(\Gamma_2)} a$ and $\hat{P}_{22}^{(\Gamma_2)} a$.
(b) Show that the resulting basis functions $|\Gamma_2 1\rangle$ and $|\Gamma_2 2\rangle$ lead to matrix representations that are not unitary.
(c) Show that the $|\Gamma_2 1\rangle$ and $|\Gamma_2 2\rangle$ thus obtained can be expressed in terms of the basis functions $|\Gamma_2 \alpha\rangle$ and $|\Gamma_2 \beta\rangle$ given in (4.47).

4.7. The aim of this problem is to give the reader experience in going from a group with higher symmetry to a group with lower symmetry and to give

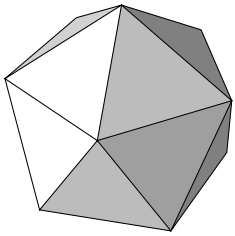

Fig. 4.6. Hypothetical XH_{12} molecule where the atom X is at the center of a regular dodecahedron

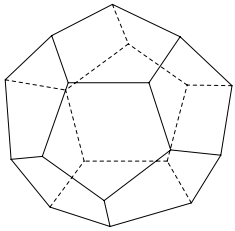

Fig. 4.7. Hypothetical XH_{12} molecule where the atom X is at the center of a regular truncated icosahedron

some experience in working with groups with icosahedral and fivefold symmetry. Consider the hypothetical XH_{12} molecule (see Fig. 4.6) which has I_h icosahedral symmetry, and the X atom is at the center. The lines connecting the X and H atoms are fivefold axes.

(a) Suppose that we stretch the XH_{12} molecule along one of the fivefold axes. What are the resulting symmetry elements of the stretched molecule?
(b) What is the appropriate point group for the stretched molecule?
(c) Consider the G_u and H_g irreducible representations of group I_h as a reducible representation of the lower symmetry group. Find the symmetries of the lower symmetry group that were contained in a fourfold energy level that transforms as G_u and in a fivefold level that transforms as H_g in the I_h group. Assuming the basis functions given in the character table for the I_h point group, give the corresponding basis functions for each of the levels in the multiplets for the stretched molecule.
(d) Suppose that the symmetry of the XH_{12} molecule is described in terms of hydrogen atoms placed at the center of each pentagon of a regular dodecahedron (see Fig. 4.7). A regular dodecahedron has 12 regular pentagonal faces, 20 vertices and 30 edges. What are the symmetry classes for the regular dodecahedron. Suppose that the XH_{12} molecule is stretched along one of its fivefold axes as in (a). What are the symmetry elements of the stretched XH_{12} molecule when viewed from the point of view of a distortion from dodecahedral symmetry?