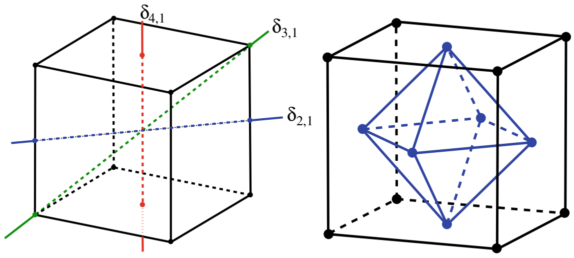

Fig. 3.5 Left: 3 of the 13 rotational axes that leave a cube unchanged; right: the centers of a cube's faces form a regular octahedron

(iii) three four-fold axes $\delta_{4,i}$ $(i = 1, 2, 3)$ passing through the centers of opposite faces.

The group has a total of 24 elements. Its sub-groups include T,D_4,D_3, and their respective sub-groups. The class structure of the group is $(r = 5)$,

$$O = \{E\} \cup \{3\delta_{4,i}, 3\delta_{4,i}^3\} \cup \{3\delta_{4,i}^2\} \cup \{6\delta_{2,i}\} \cup \{4\delta_{3,i}, 4\delta_{3,i}^2\} .$$

The group O is isomorphic (and even equivalent[4]) to the symmetry group of a regular octahedron. This can be seen in Fig. 3.5, where it becomes evident that the centers of the faces of a cube are the vertices of a regular octahedron.

3.2.5 *Icosahedron Group Y*

The final point group of the first kind is the *Icosahedron Group* Y, which comprises all rotations that leave a regular icosahedron unchanged. An icosahedron is a body with 20 equilateral triangles as faces, as shown in Fig. 3.6 (left). The 120 elements of Y consist of:

(i) 15 two-fold axes $\delta_{2,i}$ $(i = 1, \ldots, 15)$ through the centers of opposite edges.
(ii) 10 three-fold axes $\delta_{3,i}$ $(i = 1, \ldots 4)$ through opposite vertex corners and faces.
(iii) Three four-fold axes $\delta_{4,i}$ $(i = 1, 2, 3)$ through the centers of opposite faces.

The group Y is isomorphic to the symmetry group of a dodecahedron, as depicted in Fig. 3.6 (right). However, the icosahedron group does not occur in solids, as we will demonstrate in the next section, so we will not elaborate on it further here.

[4] See Footnote 2.

With (3.6) we have established the necessary criterion to determine possible rotational symmetries in solids. Later on, we will see that all of these rotational symmetries do indeed occur in some lattices. The point groups of the first kind that satisfy (3.6) are listed as follows:

$$C_1, C_2, C_3, C_4, D_2, C_6, D_3, D_4, D_6, T, O \ . \tag{3.7}$$

It was previously shown in Sect. 3.1 that any improper rotation can be expressed as a product of a proper rotation and the inversion. Since the inversion is always a symmetry of a Bravais lattice, the angles (3.6) are also the only possible ones that can occur in the rotational part of improper rotational symmetries in solids.

3.4 The Point Groups of the Second Kind

If G is an improper point group, then its sub-group G_0 consisting of proper rotations is a normal sub-group of G with index 2. This means that there exist two cosets, G_0 and L_0, where L_0 contains all the improper rotations.

Proof Demonstrating that G_0 and L_0 have equal numbers of elements would be sufficient to establish their index as $j = g/g_0 = 2$. Since E is always an element of G_0, the latter cannot be empty. Let $\tilde{O}$ be an element of L_0. Then, we have

$$\{\underbrace{\tilde{O}\cdot G_0}_{=L_0}, \underbrace{\tilde{O}\cdot L_0}_{=G_0}\} \overset{(2.4)}{=} G \ ,$$

because the elements $\tilde{O}\cdot G_0$ and $\tilde{O}\cdot L_0$ have determinants 1 and -1 respectively. This proves the above statement. $\sqrt{}$

It should be noted that the inversion itself may not be a member of L_0. For instance, in a tetrahedron, there are mirror planes in addition to the rotational axes, but the inversion is not a symmetry operation. In the following sections, we will examine improper point groups that either include or exclude the inversion.

3.4.1 Improper Point Groups Without the Inversion

As we will demonstrate now, improper point groups that do not include the inversion are isomorphic to one of the proper point groups already introduced in Sect. 3.2, making them mathematically identical. In Sect. 3.5, however, we will provide physical justifications why it is still meaningful to introduce these groups and to distinguish them from their proper counterparts.

Table 3.2 The 32 inequivalent point groups in solids

Order	Abstract point group	Point groups of the 1. kind	Point groups of the 2. kind with I	Point groups of the 2. kind without I
1	C_1	C_1 [1]		
2	C_2	C_2 [2]	C_i $[\bar{1}]$	C_s [illegible]
3	C_3	C_3 [3]		
4	C_4	C_4 [4]		S_4 $[\bar{4}]$
4	D_2	D_2 [222]	C_{2h} $\left[\frac{2}{m}\right]$	C_{2v} $\left[2\frac{2}{m}\frac{2}{m}\right]$
6	C_6	C_6 [6]	S_6 $[\bar{3}]$	C_{3h} $\bar{6}$
6	D_3	D_3 [32]		C_{3v} $\left[3\frac{2}{m}\right]$
8	D_4	D_4 [422]		C_{4v} $\left[4\frac{2}{m}\frac{2}{m}\right]$, D_{2d} $\left[\bar{4}2\frac{2}{m}\right]$
8	$C_4 \times C_2$		C_{4h} $\left[\frac{4}{m}\right]$	
8	$D_2 \times C_2$		D_{2h} $\left[\frac{2}{m}\frac{2}{m}\frac{2}{m}\right]$	
12	D_6	D_6 [622]	D_{3d} $\left[\bar{3}\frac{2}{m}\right]$	C_{6v} $\left[6\frac{2}{m}\frac{2}{m}\right]$, D_{3h} $\left[\bar{6}\frac{2}{m}2\right]$
12	T	T [23]		
12	$C_6 \times C_2$		C_{6h} $\left[\frac{6}{m}\right]$	
16	$D_4 \times C_2$		D_{4h} $\left[\frac{4}{m}\frac{2}{m}\frac{2}{m}\right]$	
24	O	O [432]		T_d $\left[\bar{4}3\frac{2}{m}\right]$
24	$D_6 \times C_2$		D_{6h} $\left[\frac{6}{m}\frac{2}{m}\frac{2}{m}\right]$	
24	$T \times C_2$		T_h $\left[\frac{2}{m}\bar{3}\right]$	
48	$O \times C_2$		O_h $\left[\frac{4}{m}\bar{3}\frac{2}{m}\right]$	

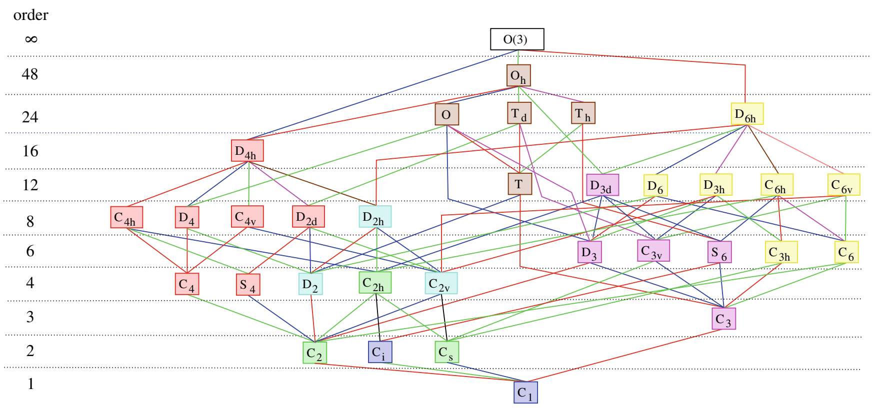

Fig. 3.9 The sub-group relationships of the 32 point groups in solids

Exercises

1. Verify the class division of the group D_3 claimed in Sect. 3.2 using the multiplication Table 2.5.
2. We consider the molecule shown in Fig. 3.13 which has a point group G with 8 elements.

   (a) List all the elements of G along with their inverses and construct the multiplication table. Determine the international notation of this group.
   (b) Find a normal sub-group H of G with 2 elements. Give the corresponding cosets and determine the group table of the factor group G/H.

   Hint: The point group G has three two-fold axes of rotation, two of which one may not see immediately. To construct the multiplication table, which can be quite time-consuming, it may again be helpful to write a computer program.
3. Consider a solid with (identical) atoms on a simple cubic lattice. Into this solid we bring another atom on

   (a) an edge,
   (b) a surface diagonal,
   (c) a space diagonal,

   of a cubic unit cell, see Fig. 3.12. Determine in all three cases the proper and the full point group at the site of the atom.

   Note: In all three cases one has to distinguish between the respective points in the middle and all other points. In your considerations, you should assume that the position of the other atoms remains unchanged, i.e. they simply generate a (constant) potential for the additional atom.
4. What point group does a body have that is infinitely extended in one spatial direction and has the shape of a

   (i) square,
   (ii) rectangle,

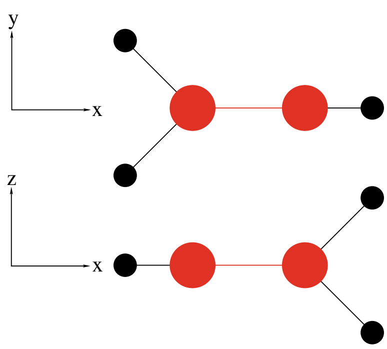

Fig. 3.12 Cubic unit cell and the three lines (in green and dashed) on which the additional atom is brought

The left-hand side of (4.10) is evidently an element of $\underline{V}^{\bar{d}}$. Consequently, for all i, $\tilde{D}_i \cdot \vec{s}_k$ must also be in $\underline{V}^{\bar{d}}$. Thus, either $\bar{d} = d$ or $\bar{d} = 0$, as otherwise there would exist a non-trivial subspace that is invariant under all $\tilde{D}_i$, which contradicts the irreducibility of $\tilde{D}_i$. We shall examine both possibilities:

(a) When $\bar{d} = d$, it follows that $d' \geq d$ since d' vectors $\vec{s}_k$ cannot span a d-dimensional vector space $\underline{V}^d$.
(b) If $\bar{d} = 0$ it must be $\tilde{S} = \tilde{0}$.

(ii) If we take the adjoint of (4.9) and follow the same arguments as in case (i), we obtain either $\bar{d} = d'$, which implies $d \geq d'$, or $\tilde{S} = \tilde{0}$. Here we have used the fact that, if $\bar{D}$ is an irreducible matrix group, then its adjoint group $\bar{D}^\dagger \equiv \tilde{D}_1^\dagger, \ldots, \tilde{D}_g^\dagger$ is also irreducible.

The results from i) and ii) combined mean that it is either $d = d' = \bar{d}$ (and $\tilde{S}$ is then non-singular) or $\tilde{S} = \tilde{0}$. $\surd$

4.1.2.2 Schur's Lemma, Part Two

Let $\bar{D}$ be an irreducible matrix group. If there is a square matrix $\tilde{S} \neq \tilde{0}$ which commutes with all $\tilde{D}_i \in \bar{D}$,

$$\tilde{D}_i \cdot \tilde{S} = \tilde{S} \cdot \tilde{D}_i \quad \forall i \ ,$$

then $\tilde{S}$ is a multiple of the identity matrix,

$$\tilde{S} = \lambda \cdot \tilde{1} \ . \tag{4.11}$$

Proof Let $\lambda \in \mathbb{C}$ be an eigenvalue of $\tilde{S}$. Then $\tilde{S}' \equiv \tilde{S} - \lambda \cdot \tilde{1}$ also commutes with all $\tilde{D}_i$. However, $\tilde{S}'$ is singular, and therefore it is $\tilde{S}' = \tilde{0}$ because of the first part of Schur's lemma, which proves (4.11). $\surd$

4.2 Representations

Representations of groups play a crucial role in establishing the relationship between group theory and its applications in physics. Let G be a group and $\bar{\Gamma}$ a matrix group. If there exists a homomorphic map $f : G \to \bar{\Gamma}$, then f is said to be a representation of G. By definition, a homomorphic map satisfies the following condition:

$$\tilde{\Gamma}(a \cdot b) = \tilde{\Gamma}(a) \cdot \tilde{\Gamma}(b) \qquad \forall\, a, b \in G \ . \tag{4.12}$$

For those new to this field, it can be confusing that the same term 'representation' is used for both the map f itself and the image of the map, which is the matrix group $\bar{\Gamma}$.

$$\tilde{\Gamma}^{(\mathrm{r})}(\delta_{2x}) = \begin{pmatrix} 0&1&0&0\\ 1&0&0&0\\ 0&0&0&1\\ 0&0&1&0 \end{pmatrix} \quad , \quad \tilde{\Gamma}^{(\mathrm{r})}(\delta_{2y}) = \begin{pmatrix} 0&0&1&0\\ 0&0&0&1\\ 1&0&0&0\\ 0&1&0&0 \end{pmatrix} \quad , \quad \tilde{\Gamma}^{(\mathrm{r})}(\delta_{2z}) = \begin{pmatrix} 0&0&0&1\\ 0&0&1&0\\ 0&1&0&0\\ 1&0&0&0 \end{pmatrix} \quad .$$

Proof (of the previous statement) We prove successively the representation property and the isomorphism

(i) To show that $\bar{\Gamma}^{(\mathrm{r})}$ is a representation, we multiply (4.17) from the left with another element a_k,

$$a_k \cdot (a_i \cdot a_j) \overset{(4.7)}{=} \sum_l \Gamma^{(\mathrm{r})}_{l,j}(a_i) \cdot a_k \cdot a_l \overset{(4.6)}{=} \sum_l \Gamma^{(\mathrm{r})}_{l,j}(a_i) \cdot \sum_m \Gamma^{(\mathrm{r})}_{m,l}(a_k) \cdot a_m$$
$$= \sum_m \left[\sum_l \Gamma^{(\mathrm{r})}_{l,j}(a_i) \cdot \Gamma^{(\mathrm{r})}_{l,j}(a_i) \right] \cdot a_m \ . \tag{4.18}$$

The brackets on the left side of this equation are, of course, meaningless because of the associative law and it is equal to

$$(a_k \cdot a_i) \cdot a_j \overset{(4.17)}{=} \sum_m \left[\Gamma^{(\mathrm{r})}_{m,j}(a_k \cdot a_i) \right] \cdot a_m \ . \tag{4.19}$$

A comparison of (4.18) and (4.19) then proves that

$$\tilde{\Gamma}^{(\mathrm{r})}(a_k \cdot a_i) = \tilde{\Gamma}^{(\mathrm{r})}(a_k) \cdot \tilde{\Gamma}^{(\mathrm{r})}(a_i) \ .$$

(ii) If G and $\bar{\Gamma}^{(\mathrm{r})}$ were not isomorphic there would be at least two elements $a_i \neq a_i'$ with $\tilde{\Gamma}^{(\mathrm{r})}(a_i) = \tilde{\Gamma}^{(\mathrm{r})}(a_j)$. But then, because of (4.17),

$$a_i \cdot a_j = a_i' \cdot a_j \quad \Rightarrow \quad a_i = a_i' \ ,$$

which leads to a contradiction.

Similar to Schur's lemma, we will need the regular representation only in the proofs in Chap. 5, but it will not play a role in the rest of the book.

Theorem 3 *The reduced form of the regular representation* $\bar{\Gamma}^{(\mathrm{r})}$ *of a group* G *contains each of the irreducible representations* $\bar{\Gamma}^{p}$ *of* G *exactly* d_p *times, where* d_p *is the dimension of the irreducible representation* $\bar{\Gamma}^{p}$.

Since the reduced representations have the same dimensions as the original representation (see (4.16)), the following equation results from Theorems 1 and 3

$$g = \sum_{p=1}^{r} d_p^2 \quad , \tag{4.20}$$

5.2.2 *Proof of Theorems 1–4*

We prove the Theorems 1–4 in 4 steps.

(i) We consider only unitary representations $\bar{\Gamma}^p$, which is possible because every representation is equivalent to a unitary one (see Sect. 4.1.1) and the corresponding character χ^p is invariant under similarity transformations. For each (not necessarily irreducible) representation $\bar{\Gamma}$, we define the r-dimensional character vector

$$\vec{v}^{\Gamma} \equiv \left(\sqrt{\frac{r_1}{g}}\chi_1^{\Gamma}, \ldots, \sqrt{\frac{r_r}{g}}\chi_r^{\Gamma}\right)^T \ . \tag{5.11}$$

If $\bar{\Gamma} = \bar{\Gamma}^p$ is irreducible, it holds for the associated character vector $\vec{v}^p$ that

$$\left(\vec{v}^p\right)^\dagger \cdot \vec{v}^q = \delta_{p,q} \ .$$

To prove this equation, we evaluate the left hand side,

$$\left(\vec{v}^p\right)^\dagger \cdot \vec{v}^q \overset{(5.11)}{=} \sum_i^r \frac{r_i}{g} \cdot \left(\chi_i^p\right)^* \cdot \chi_i^q = \frac{1}{g}\sum_a \left(\chi_i(a)\right)^* \cdot \chi_i(a) \ ,$$

where a are the elements of the group. With the definition (4.15) of the character we then find

$$\left(\vec{v}^p\right)^\dagger \cdot \vec{v}^q = \frac{1}{g}\sum_{i=1}^{d_p}\sum_{j=1}^{d_q} \Gamma_{i,i}^p(a^{-1}) \cdot \Gamma_{j,j}^p(a) \overset{(5.1)}{=} \delta_{p,q}\frac{1}{d}\sum_{i=1}^{d_p} = \delta_{p,q} \ . \checkmark \tag{5.12}$$

Equation (5.12) establishes the validity of (5.9). Conversely, it can be deduced that the maximum number of irreducible representations is r, based on the fact that an r-dimensional space can contain no more than r orthogonal vectors $\vec{v}^p$. In order to prove Theorem 1, it is necessary to demonstrate that there are also at least r irreducible representations, which will bring the total number to exactly r. This will be done in connection with point (iii). However, before that, we address Theorem 3.

(ii) Let

$$\bar{\Gamma}^{(\mathrm{r})} = \sum_p n_p^{(\mathrm{r})} \cdot \bar{\Gamma}^p \ ,$$

be the reduction of the regular representation. The same relation then applies to the corresponding character vectors

$$\vec{v}^{(\mathrm{r})} = \sum_p n_p^{(\mathrm{r})} \cdot \vec{v}^p \ , \tag{5.13}$$

Then we can deduce from Schur's lemma (part two)

$$\tilde{S}_j = \mu_j \cdot \tilde{1} \; .$$

Especially for the irreducible representations $\bar{\Gamma}^p$ with dimension d_p we find the matrices

$$\tilde{S}_j^p = \mu_j^p \cdot \tilde{1} \; . \tag{5.19}$$

The trace of the two sides of this equation and

$$\sum_{a \in \mathcal{C}_j} 1 = r_j \; ,$$

yields

$$\mu_j^p = \frac{r_i \chi_i^p}{d_p} \; . \tag{5.20}$$

On the other hand, because of the definition of (5.18), it is

$$\tilde{S}_i^p \cdot \tilde{S}_j^p = \sum_{\substack{a \in \mathcal{C}_i \\ b \in \mathcal{C}_j}} \tilde{S}^p(a \cdot b) \overset{(2.8)}{=} \sum_{k=1}^{r} f_{ijk} \cdot \tilde{S}_k \; ,$$

where f_{ijk} are the multiplication coefficients introduced in Sect. 2.3.3. With (5.19) and (5.20) we find

$$r_i \cdot r_j \cdot \chi_i^p \cdot \chi_j^p = d_p \sum_{k=1}^{r} c_{ijk} \cdot r_k \cdot \chi_k^p \; .$$

Next we carry out the sum over p on both sides and use (5.17),

$$r_i \cdot r_j \sum_p \chi_i^p \cdot \chi_j^p = c_{ij1} \cdot r_1 \cdot g \; .$$

Recall that $r_1 = 1$ and with (2.8) we obtain

$$\sum_p \chi_i^p \cdot \chi_j^p = \frac{g}{r_j} \delta_{i,\bar{j}} \overset{j \to \bar{j}}{\Longrightarrow} \sum_p \chi_i^p \cdot \chi_{\bar{j}}^p = \frac{g}{r_j} \delta_{i,j} \; , \tag{5.21}$$

where we have used that a class and its inverse have the same number of elements, $r_{\bar{j}} = r_j$. To finish this part of the proof, we have to evaluate $\chi_{\bar{i}}^p$ in (5.21). With $a \in \mathcal{C}_i$ and $a^{-1} \in \mathcal{C}_{\bar{j}}$ we show in Exercise 7 that

$$G_1 = \{a_1 \ldots, a_{g_1}\} ,$$
$$G_2 = \{b_1 \ldots, b_{g_2}\} ,$$

and

$$\bar{\Gamma}^1 = \{\tilde{\Gamma}^1(a_1), \ldots, \tilde{\Gamma}^1(a_{g_1})\} ,$$
$$\bar{\Gamma}^2 = \{\tilde{\Gamma}^2(b_1), \ldots, \tilde{\Gamma}^2(b_{g_2})\} ,$$

(not necessarily irreducible) representations of G_1 and G_2.

(a) Show that two elements $(a_i; b_j)$ and $(a_i'; b_j')$ of G are in a class (i.e. $(a_i; b_j) \sim (a_i'; b_j')$) if, and only if $a_i \sim a_i'$ in G_1 and $b_j \sim b_j'$ in G_2. What classes are there in $G = G_1 \times G_2$ and how many elements does each class have?
(b) Show that the product matrices

$$\Gamma^{1\otimes 2}_{(ij),(kl)}(a_n b_m) \equiv \Gamma^1_{i,k}(a_n) \cdot \Gamma^2_{j,l}(b_m)$$

are a representation of the group G (*product representations*).
(c) Show that $\bar{\Gamma}^{1\otimes 2}$ is irreducible if $\bar{\Gamma}^1$ and $\bar{\Gamma}^2$ are irreducible (use the result from Sect. 5.2.3).

2. Using the result from Exercise 1, determine the irreducible representations of

$$D_{3d} = D_3 \times (E, I) .$$

Use the fact that (E, I) is isomorphic to C_2 (see Table 6.1) and the irreducible representations of D_3 (see the example in Sect. 4.2).
3. It is evident that a group comprising of orthogonal matrices,

$$G = \{\tilde{D}_1, \ldots, \tilde{D}_g\} ,$$

forms a (real, faithful) three-dimensional representation of the corresponding (abstract) point group (as explained in Sect. 3.5). This representation, however, is typically reducible. Determine the irreducible components of these representations for the groups D_2 and D_3.
Hint: A helpful approach is to employ (5.23) in combination with the character tables 5.1.
4. Let G' be a sub-group of a group G and $\bar{\Gamma}^p$ one of the irreducible representations of G. Then $\bar{\Gamma}^p$ is obviously also a (in general reducible) representation of G', the so-called 'subduced representation' $\bar{\Gamma}^{(s)}$. Determine for the group $G = D_3$ and its sub-groups

(a) $G' = \{E, \delta_3, \delta_3^2\}$,
(b) $G' = \{E, \delta_{2,x}\}$,

$$\Gamma^A : \Psi_A(\vec{r}) = f(|\vec{r}|) \quad \text{or} \quad \Psi_A(\vec{r}) = z \cdot f(|\vec{r}|) \ , \qquad (6.3)$$
$$\Gamma^B : \Psi_B(\vec{r}) = x \cdot f(|\vec{r}|) \quad \text{or} \quad \Psi_B(\vec{r}) = y \cdot f(|\vec{r}|) \ ,$$

where $f(|\vec{r}|)$ is any rotationally symmetric function in the Hilbert space L^2. To check whether Ψ_A and Ψ_B are representation functions, one must apply the symmetry operators $\hat{U}_a$ to them,

$$\hat{U}_E \Psi_A(\vec{r}) = \Psi_A(\vec{r}) \ , \quad \hat{U}_E \Psi_B(\vec{r}) = \Psi_B(\vec{r}) \ ,$$
$$\hat{U}_{\delta_2} \Psi_A(\vec{r}) = \Psi_A(\vec{r}) \ , \quad \hat{U}_{\delta_2} \Psi_B(\vec{r}) = -\Psi_B(\vec{r}) \ . \surd$$

6.1.2 Representation Functions of Irreducible Representations

The d basis functions of a d-dimensional irreducible representation $\bar{\Gamma}^p$ form an orthogonal function system.

Proof We consider the scalar product of two basis functions $|\lambda\rangle$, $|\mu\rangle$,

$$\langle \lambda | \mu \rangle = \frac{1}{g} \sum_{a \in G} \langle \lambda | \hat{U}_a^\dagger \cdot \hat{U}_a | \mu \rangle \ ,$$

where we have used that

$$1 = \hat{U}_a^\dagger \cdot \hat{U}_a = \frac{1}{g} \sum_{a \in G} \hat{U}_a^\dagger \cdot \hat{U}_a \ .$$

With (6.1) we then find

$$\langle \lambda | \mu \rangle = \frac{1}{g} \sum_{\lambda', \mu'} \sum_{a \in G} \left(\Gamma^p_{\lambda', \lambda}(a) \right)^* \cdot \Gamma^p_{\mu', \mu}(a) \cdot \langle \lambda' | \mu' \rangle \overset{(5.2)}{=} \frac{1}{d} \delta_{\lambda, \mu} \sum_{\lambda'} \langle \lambda' | \mu' \rangle \sim \delta_{\lambda, \mu} \ . \ \surd$$

In the following, we assume that the representation functions are normalized. The representation functions of a d-dimensional representation $\bar{\Gamma}$ form a basis for a d-dimensional subspace $\underline{V}^d$ of the Hilbert space $\underline{H}$. This subspace is referred to as the representation space of $\bar{\Gamma}$. It is possible for a representation to have multiple representation spaces, which may be infinite in number. For instance, there exists an infinite set of states of the form (6.3), since there are infinitely many functions $f(|\vec{r}|)$ that can be chosen to be orthogonal. On the other hand, a representation space uniquely determines the corresponding representation (up to equivalence).

Therefore

$$D_{\lambda',\lambda}(a \cdot b) = \sum_{\lambda''} D_{\lambda',\lambda''}(a) \cdot D_{\lambda'',\lambda}(b) \ . \quad \surd$$

6.1.4 Irreducibility of Representation Spaces

If a representation space $\underline{V}^d$ of dimension d can be expressed as a direct sum of two representation spaces of smaller dimension, i.e.

$$\underline{V}^d = \underline{V}^{d_1} \oplus \underline{V}^{d_2} \quad (d_1 + d_2 = d) \ , \tag{6.5}$$

it is referred to as reducible.

Otherwise, it is called irreducible. The representation corresponding to $\underline{V}^d$ is reducible if and only if $\underline{V}^d$ itself is reducible.

Proof We have to give the proof in both directions:

(i) We assume that $\underline{V}^d$ is reducible and is spanned by the states $\{|\lambda\rangle\}$. Then we have to show that the representation $\bar{\Gamma}$ defined by the matrices $\tilde{\Gamma}(a)$ with the elements

$$\Gamma_{\lambda',\lambda}(a) \equiv \langle\lambda'|\hat{U}_a|\lambda\rangle \ ,$$

are reducible. Since $\underline{V}^d$ is reducible, there are bases $\{|\mu\rangle\}$ $(\mu = 1, \ldots, d_1)$ and $\{|\mu\rangle\}$ $(\mu = d_1 + 1, \ldots, d)$ that span representation spaces $\underline{V}^{d_1}$ and $\underline{V}^{d_2}$ with the property (6.5). The two bases are linked via some matrix $\tilde{S}$, i.e.

$$|\lambda\rangle = \sum_{\mu} S_{\mu,\lambda}|\mu\rangle \ . \tag{6.6}$$

The assumption that the bases are orthogonal does not limit the generality of the proof. Then, the matrix $\tilde{S}$ is unitary. With this and (6.4) we find $(\tilde{D} \to \tilde{\Gamma})$

$$\langle\lambda|\hat{U}_a|\lambda'\rangle = \Gamma_{\gamma,\gamma'}(a) \overset{(6.6)}{=} \sum_{\mu,\mu'} S^*_{\mu,\lambda} \cdot S_{\mu',\lambda'} \cdot \langle\mu|\hat{U}_a|\mu'\rangle \ .$$

In matrix form, this equation is given by $(\Gamma'_{\mu,\mu'}(a) \equiv \langle\mu|\hat{U}_a|\mu'\rangle)$

$$\tilde{S}^{-1} \cdot \tilde{\Gamma}'(a) \cdot \tilde{S} = \tilde{\Gamma}(a) \quad \Rightarrow \quad \tilde{\Gamma}'(a) = \tilde{S} \cdot \tilde{\Gamma}(a) \cdot \tilde{S}^{-1} \ .$$

Since $\bar{\Gamma}'$ is block diagonal, $\bar{\Gamma}$ is reducible. $\surd$

(ii) We assume that $\bar{\Gamma}$ is reducible and $\underline{V}$ is one of its representation spaces spanned by the vectors $\{|\lambda\rangle\}$. The proof that $\underline{V}$ is then reducible uses the same steps as under (i). Let $\tilde{S}$ be the (unitary) matrix that reduces $\bar{\Gamma}$. Then, one can easily show that in the base

$$|\bar{\lambda}\rangle^p \equiv \sum_{m=1}^{n_p} U_{1,(p,m,\lambda)}|p,m,\bar{\lambda}\rangle \ . \tag{6.13}$$

Note that, on the right-hand side of this equation, the index of $\tilde{U}$ is indeed λ, i.e. the value of λ in $|\lambda\rangle^p$ and not $\bar{\lambda}$ which is the label for the partner functions of $|\lambda\rangle^p$. The states $|\bar{\lambda}\rangle$ (of which $|\lambda\rangle^p$ is one for $\bar{\lambda} = \lambda$) indeed form a representation space, because

$$\hat{U}_a|\bar{\lambda}\rangle^p \overset{(6.13)}{=} \sum_{m=1}^{n_p} U_{1,(p,m,\lambda)} \cdot \hat{U}_a|p,m,\bar{\lambda}\rangle$$
$$\overset{(6.11)}{=} \sum_{\bar{\lambda}'} \Gamma^p_{\bar{\lambda}',\bar{\lambda}} \cdot U_{1,(p,m,\lambda)}|p,m,\bar{\lambda}'\rangle \overset{(6.13)}{=} \sum_{\bar{\lambda}'} \Gamma^p_{\bar{\lambda}',\bar{\lambda}}|\bar{\lambda}'\rangle^p \quad \checkmark \ .$$

Before we look at examples of the development theorem, we will first derive a practical way to determine the components in (6.7) in the following section. This is based on the projection operators introduced by Wigner [1].

6.2 Projection Operators

Let $\bar{\Gamma}^p$ be the d_p-dimensional (unitary) representations of a group G of unitary operators $\hat{U}_a$ $(p = 1, \dots, r)$. Then, for each p we define the d_p^2 operators

$$\hat{P}^p_{\lambda,\lambda'} \equiv \frac{d_p}{g} \sum_a \left(\Gamma^p_{\lambda,\lambda'}(a)\right)^* \cdot \hat{U}_a \ . \tag{6.14}$$

The following is true

(i) The d_p operators $\hat{P}^p_{\lambda,\lambda}$ are projection operators[3] and applied to an arbitrary state $|\Psi\rangle$ in (6.7), yield exactly the component $|\lambda\rangle^p$.
(ii) For fixed λ, the $d_p - 1$ operators applied to $|\Psi\rangle$ $(\mu \neq \lambda)$ yield the partner functions $|\mu\rangle^p$ of $|\lambda\rangle^p$.

Proof

(i) $\hat{P}^p_{\lambda,\lambda}$ is a projection operator, because

$$\left(\hat{P}^p_{\lambda,\lambda}\right)^\dagger \overset{(6.14)}{=} \frac{d_p}{g} \sum_a \underbrace{\Gamma^p_{\lambda,\lambda}(a)}_{=\left(\Gamma^p_{\lambda,\lambda}(a^{-1})\right)^*} \cdot \underbrace{\hat{U}_a^\dagger}_{=\hat{U}_{a^{-1}}} \overset{(a^{-1}\to a)}{=} \frac{d_p}{g} \sum_a \left(\Gamma^p_{\lambda,\lambda}(a)\right)^* \cdot \hat{U}_a = \hat{P}^p_{\lambda,\lambda} \ ,$$

[3] Recall that a projection operator $\hat{P}$ has the properties $\hat{P}^\dagger = \hat{P}$ and $\hat{P}^2 = \hat{P}$.

Proof Using (6.18) we find

$$\hat{H} = \hat{U}_a \cdot \hat{H} \cdot \hat{U}_a^\dagger \ ,$$

which we substitute into the matrix element (6.22),

$$H^{(p,\lambda)}_{m,m'} = \langle \varphi_{p,m,\lambda} | \hat{H} | \varphi_{p,m',\lambda} \rangle = \langle \varphi_{p,m,\lambda} | \hat{U}_a \cdot \hat{H} \cdot \hat{U}_a^\dagger | \varphi_{p,m',\lambda} \rangle \tag{6.24}$$
$$\stackrel{(6.1)/(6.21)}{=} \sum_{\lambda'} \Gamma_{\lambda',\lambda}(a) \left(\Gamma_{\lambda',\lambda}(a) \right)^* \langle \varphi_{p,m,\lambda'} | \hat{H} | \varphi_{p,m',\lambda'} \rangle \ .$$

Since the left-hand side does not depend on a, the same must be true for the right-hand side. We can now sum over a on both sides in (6.24), which then leads to

$$\langle \varphi_{p,m,\lambda} | \hat{H} | \varphi_{p,m',\lambda} \rangle = \frac{1}{d_p} \sum_{\lambda'} \langle \varphi_{p,m,\lambda'} | \hat{H} | \varphi_{p,m',\lambda'} \rangle \ .$$

where we used the orthogonality theorem (5.2). Since the right-hand side is independent of λ, the assertion follows. $\surd$

Example As an example, we consider a rectangular 'molecule' with one orbital per site on which a single quantum mechanical particle is located (see Fig. 6.2). The Hamiltonian contains a hopping t, t' to the nearest neighbors which in first quantization reads

$$\hat{H} = \sum_{i,j=1}^{4} t_{i,j} |i\rangle\langle j| \ ,$$

where the values of $t_{i,j}$ are specified in Fig. 6.2. In matrix form the Hamiltonian is given as

$$\tilde{H} = \begin{pmatrix} 0 & t' & 0 & t \\ t' & 0 & t & 0 \\ 0 & t & 0 & t' \\ t & 0 & t' & 0 \end{pmatrix} \ .$$

There are obviously 4 symmetry operations, besides the one-element a rotation δ_2 around the z-axis with angle π as well as the two mirror planes σ_1 ($x = 0$) and σ_2

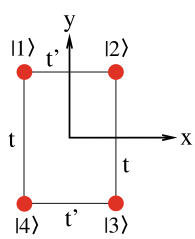

Fig. 6.2 A rectangular 'molecule' with one orbital per site

Table 6.2 Character table of the group C_{2v}

C_{2v}	E	δ_2	σ_1	σ_2
A_1	1	1	1	1
A_2	1	1	−1	−1
B_1	1	−1	1	−1
B_2	1	−1	−1	1

($y = 0$). Therefore, the symmetry group of the molecule is C_{2v} (see Chap. 3). It has 4 (of course one-dimensional) irreducible representations, which are shown in the character Table 6.2. To use (6.21), we need a basis of representation spaces. We can determine it with the projection operators (6.16). In this case, it is sufficient to take only one of the four states $|i\rangle$ and apply the 4 operators $\hat{P}^p$ to it,

$$\begin{aligned}
\hat{P}^{A_1}|1\rangle &\overset{6.2.1}{=} \frac{1}{4}\Big(\hat{U}_E|1\rangle + \hat{U}_{\delta_2}|1\rangle + \hat{U}_{\sigma_1}|1\rangle + \hat{U}_{\sigma_2}|1\rangle\Big) \\
&= \frac{1}{4}\left(|1\rangle + |4\rangle + |2\rangle + |3\rangle\right) \equiv \sqrt{4}|\Psi_{A_1}\rangle \ , \\
\hat{P}^{A_2}|1\rangle &= \frac{1}{4}\left(|1\rangle + |4\rangle - |2\rangle - |3\rangle\right) \equiv \sqrt{4}|\Psi_{A_2}\rangle \ , \\
\hat{P}^{B_1}|1\rangle &= \frac{1}{4}\left(|1\rangle - |4\rangle + |2\rangle - |3\rangle\right) \equiv \sqrt{4}|\Psi_{B_1}\rangle \ , \\
\hat{P}^{B_2}|1\rangle &= \frac{1}{4}\left(|1\rangle - |4\rangle - |2\rangle + |3\rangle\right) \equiv \sqrt{4}|\Psi_{B_2}\rangle \ .
\end{aligned}$$

where the factor $\sqrt{4}$ has been introduced to normalize the 4 states $|\Psi_p\rangle$. These 4 states are orthogonal and therefore form a base of the Hilbert space. Since they belong to different representations, $\hat{H}$ must be diagonal in this basis, i.e. the matrices (6.22) here are one-dimensional with respect to $m_p, m_{p'}$,

$$\begin{aligned}
\tilde{H}' &= \begin{pmatrix} \langle\Psi_{A_1}|\hat{H}|\Psi_{A_1}\rangle & 0 & 0 & 0 \\ 0 & \langle\Psi_{A_2}|\hat{H}|\Psi_{A_2}\rangle & 0 & 0 \\ 0 & 0 & \langle\Psi_{B_1}|\hat{H}|\Psi_{B_1}\rangle & 0 \\ 0 & 0 & 0 & \langle\Psi_{B_2}|\hat{H}|\Psi_{B_2}\rangle \end{pmatrix} \\
&= \begin{pmatrix} t+t' & 0 & 0 & 0 \\ 0 & t-t' & 0 & 0 \\ 0 & 0 & -t+t' & 0 \\ 0 & 0 & 0 & -t-t' \end{pmatrix} .
\end{aligned}$$

In this simple case, we have therefore succeeded in diagonalizing a Hamiltonian just by choosing a proper basis based on group theory.

Table 7.1 Character table of the group O_H

O_H			E	$6C_4$	$3C_4^2$	$8C_3$	$6C_2'$	I	$3\sigma_h$	$6\sigma_d$	$8S_6$	$6S_4$
$x^2+y^2+z^2=r^2$	xyz	A_{1g}	1	1	1	1	1	1	1	1	1	1
		A_{2g}	1	−1	1	1	−1	1	1	−1	1	−1
		A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1
		A_{2u}	1	−1	1	1	−1	−1	−1	1	−1	1
$(x^2-y^2, 3z^2-r^2)$		E_g	2	0	2	−1	0	2	2	0	−1	0
		E_u	2	0	2	−1	0	2	−2	0	1	0
		T_{1g}	3	1	−1	0	−1	3	−1	−1	0	1
(zx, yz, xy)	(x, y, z)	T_{2g}	3	−1	−1	0	1	3	−1	1	0	−1
	$(x(z^2-y^2), y(z^2-x^2), z(x^2-y^2))$	T_{1u}	3	1	−1	0	−1	−3	1	1	0	−1
		T_{2u}	3	−1	−1	0	1	−3	1	−1	0	1

the representation matrices from the representation functions using (6.8).[2] Let us examine this table in greater detail.

(i) We have only provided representation functions that are linear, quadratic, or cubic in terms of x, y, and z. Higher-order functions are required for other representations. As explained later in Chap. 8, the linear, quadratic or cubic functions are applicable to atoms with filled shells of s, p, d or f orbitals. Orders beyond three are usually not relevant in solid-state physics. For completeness, we also give the missing representation functions of orders $3-6$ in x, y, z:

$$A_{2u} : xyz\,, \tag{7.1}$$

$$\begin{aligned}
A_{2g} &: x^4(y^2-z^2)+y^4(z^2-x^2)+z^4(x^2-y^2)\,,\\
A_{1u} &: xyz\left[x^4(y^2-z^2)+y^4(z^2-x^2)+z^4(x^2-y^2)\right]\,,\\
E_u &: xyz\left[(x^2-y^2, 3z^2-r^2)\right]\,,\\
T_{1g} &: xy(x^2-y^2), xz(x^2-z^2), yz(y^2-z^2)\,.
\end{aligned} \tag{7.2}$$

(ii) A convention has been established for the naming of representations:

– One-dimensional representations are labeled as A or B. The difference between A and B denotes the positive or negative character of proper rotations around the main symmetry axis.
– Two- and three-dimensional representations are denoted by E and T, respectively.

[2] As an alternative, one can find all the representation matrices for the 32 point groups on https://www.cryst.ehu.es/. Unlike the customary practice in this book, we provide this specific webpage as it is, to the best of the author's knowledge, the only source that provides all the representation matrices not only for the point groups, but also for other groups.

Table 7.2 Character table of the group C_4

C_4			E	C_4	$C_4^2 = C_2$	C_4^3
$x^2 + y^2, z^2$	z	A	1	1	1	1
$x^2 - y^2, xy$		B	1	-1	1	-1
(zx, zy)	(x, y)	E	$\left\{\begin{matrix} 1 \\ 1 \end{matrix}\right.$	$\begin{matrix} \mathrm{i} \\ -\mathrm{i} \end{matrix}$	$\begin{matrix} -1 \\ -1 \end{matrix}$	$\left.\begin{matrix} -\mathrm{i} \\ \mathrm{i} \end{matrix}\right\}$

- If $I \in G$, the subscript g or u indicates whether the representation is symmetric or antisymmetric under inversion.[3]
- Representations such as A' and A'' differ in their symmetry or antisymmetry relative to the mirror plane perpendicular to the main symmetry axis.[2]

(iii) When dealing with groups that have complex-valued characters, it is necessary to analyze their character tables more closely. For instance, consider the group C_4, whose character table is presented in Table 7.2. This group is Abelian, and therefore its four irreducible representations are one-dimensional. However, in accordance with the literature, the character table shows two representations with complex characters that are denoted as two-dimensional. Here we explain why: the functions

$$p_{[x,y]} \equiv f(|\mathbf{r}|)[x, y] ,$$

define a two-dimensional representation space of C_4 with the representation matrices

$$\tilde{\Gamma}(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} , \quad \tilde{\Gamma}(C_4) = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} ,$$
$$\tilde{\Gamma}(C_2) = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} , \quad \tilde{\Gamma}(C_4^3) = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} .$$

These representation matrices, however, are reducible and can be diagonalized via the transformation

$$\Psi_+ \equiv p_x + \mathrm{i}p_y \quad , \quad \Psi_- \equiv p_x - \mathrm{i}p_y .$$

In this basis, the representation matrices are

$$\tilde{\Gamma}'(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} , \quad \tilde{\Gamma}'(C_4) = \begin{pmatrix} \mathrm{i} & 0 \\ 0 & \mathrm{i} \end{pmatrix} ,$$
$$\tilde{\Gamma}'(C_2) = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} , \quad \tilde{\Gamma}'(C_4^3) = \begin{pmatrix} -\mathrm{i} & 0 \\ 0 & \mathrm{i} \end{pmatrix} .$$

[3] In Exercise 5.2.3 of Chap. 5 we show that all representation functions must have one of the two properties.

8.3 Degenerate Perturbation Theory

In the first order of the perturbation theory, a degenerate representation space $\underline{V}^p$ (of a representation $\bar{\Gamma}^p$) of $\hat{H}_0$ is given as[4]

$$\underline{V}^p = \underline{\tilde{V}}^{p_1} \oplus \underline{\tilde{V}}^{p_2} \oplus \dots \, , \tag{8.3}$$

where the $\underline{\tilde{V}}^{p_i}$ must be irreducible representation spaces to the symmetry group of $\hat{H} = \hat{H}_0 + \hat{V}$. The reason is that in the first order only a basis change is made in $\underline{V}^p$. The representations $\underline{\tilde{V}}^{p_i}$ that are involved then result, as in Sect. 8.2, from the reduction of $\bar{\Gamma}^p$, i.e. with the help of the respective correlation tables.

Example To provide an example, we revisit the scenario of a particle in a cubic box discussed in Sect. 7.2. Specifically, we focus on the first three eigenspaces, which serve as proper representation spaces of an irreducible representation of O_h. We introduce the term $\hat{V} = \alpha\hat{z}^2$ to the system's Hamiltonian, leading to $G_0 = O_h$ and $G = D_4$. As the first eigenspace of $\hat{H}_0$ is non-degenerate, it cannot experience energetic splitting. Consequently, we examine the second and third eigenspaces:

(i) The eigenspace $\underline{V}^{[1,1,2]}$ belongs to the representation T_{1u}. According to the correlation Table 8.2 it is

$$T_{1u} \overset{O_h \to D_{4h}}{\rightarrow} A_{2u} \oplus E_u \, .$$

The states introduced in Sect. 7.2 are already bases of the spaces $\underline{V}^{A_{2u}}$ and $\underline{V}^{E_u}$, where

$$\begin{aligned} A_{2u} &: \Psi_{112} \quad (\sim z) \, , \\ E_u &: \{\Psi_{121}, \Psi_{211}\} \quad (\sim \{x, y\}) \, . \end{aligned}$$

(ii) Likewise, the eigenspace $\underline{V}^{[1,2,2]}$ belongs to the representation T_{1g} and the correlation table yields

$$T_{2g} \overset{O_h \to D_{4h}}{\rightarrow} B_{2g} \oplus E_g \, ,$$

where

$$\begin{aligned} B_{2g} &: \Psi_{221} \quad (\sim x \cdot y) \, , \\ E_g &: \{\Psi_{122}, \Psi_{212}\} \quad (\sim \{x \cdot y, y \cdot z\}) \, . \end{aligned}$$

It is crucial to understand the following fact: The splitting of G into irreducible representation spaces $\underline{\tilde{V}}^{p_i}$, which occurs at zeroth order, remains valid beyond the realm of perturbation theory. If this was not the case, there had to be a point where, as $\hat{V}$ steadily increases, a sudden transition into a fundamentally different

[4] The first order of degenerate perturbation theory with regard to the energy is also referred to as the zeroth order with regard to the eigenstates.

which also commute with $\hat{H}_0$, it follows, e.g.

$$\begin{aligned} \hat{L}_\pm \hat{H}_0 |n,l,m\rangle &= E_{n,l} \hat{L}_\pm |n,l,m\rangle \sim E_{n,l} |n,l,m\pm 1\rangle \\ = \hat{H}_0 \hat{L}_\pm |n,l,m\rangle &\sim \hat{H}_0 |n,l,m\pm 1\rangle = E_{n,l} |n,l,m\pm 1\rangle \ . \end{aligned}$$

Therefore, all states $|n,l,m\rangle$ $(m = -l, \ldots, l)$ have the same energy and there is an $(2l+1)$-fold degeneracy of the spectrum. In real space the eigenfunctions (in spherical coordinates) have the form

$$\Psi_{n,l,m}(r,\theta,\varphi) = R_{n,l}(r) Y_{l,m}(\theta,\varphi) \ ,$$

with the spherical harmonics

$$Y_{l,m}(\theta,\varphi) \sim P_l^m(\cos(\theta)) e^{\mathrm{i}m\varphi} \ ,$$

and the *associated Legendre polynomials* $P_l^m(\cos(\theta))$. The exact form of the functions $P_l^m(\cos(\theta))$ and $R_{n,l}(r)$ is irrelevant for our following considerations. The wave functions for the lowest values of l are

(i) $l = 0$, s-orbitals:

$$Y_{0,0} \sim \text{const} \ ,$$

(ii) $l = 1$, p-orbitals:

$$Y_{1,\pm 1} \sim \sin(\theta) e^{\pm \mathrm{i}\varphi}, \ \ Y_{1,0} \sim \cos(\theta) \ ,$$

(iii) $l = 2$, d-orbitals:

$$Y_{2,\pm 2} \sim \sin^2(\theta) e^{\pm 2\mathrm{i}\varphi}, \ \ Y_{2,\pm 1} \sim \sin(\theta)\cos(\theta) e^{\pm \mathrm{i}\varphi}, \ \ Y_{2,0} \sim (3\cos^2(\theta) - 1) \ ,$$

(iv) $l = 3$, f-orbitals:

$$\begin{aligned} &Y_{3,\pm 3} \sim \sin(\theta)^3 e^{\pm 3\mathrm{i}\varphi}, \ \ Y_{3,\pm 2} \sim \sin(\theta)^2 \cos(\theta) e^{\pm 2\mathrm{i}\varphi}, \\ &Y_{3,\pm 1} \sim \sin(\theta)(5\cos(\theta)^2 - 1) e^{\pm \mathrm{i}\varphi}, \ \ Y_{3,0} \sim (5\cos(\theta)^3 - 3\cos(\theta)) \ . \end{aligned}$$

Group-Theoretical Treatment of the Problem

The symmetry group of $\hat{H}_0$ is $O(3)$, which comprises of operators $\hat{U}_{\tilde{D}}$ with arbitrary orthogonal matrices $\tilde{D}$. Our objective is to find the representation matrices and, more importantly, the characters of this group (in order to use again (5.23)). To avoid dealing with infinite groups, we will take a pragmatic approach and make use of the results obtained in Sect. 8.4.1.

As $O(3)$ represents the maximum symmetry group of $\hat{H}_0$, the functions $Y_{l,m}(\theta, \varphi)$ ($m = -l, \ldots, l$) must form a representation space of dimension $(2l + 1)$ for $O(3)$, as stated by our postulate from Sect. 6.3.3. This enables us to determine some representation matrices and the corresponding characters.

(i) Let $\tilde{D}$ be a matrix that describes a rotation around the z-axis with the angle α. Then obviously

$$\hat{U}_{\tilde{D}} \cdot Y_{l,m}(\theta, \varphi) = e^{-\mathrm{i} \cdot m \cdot \alpha} \cdot Y_{l,m}(\theta, \varphi) \ .$$

The representation matrix of $\tilde{D}$ is therefore diagonal and given as

$$\tilde{\Gamma}^l(\alpha) = \begin{pmatrix} e^{-\mathrm{i}l\alpha} & & & 0 \\ & e^{-\mathrm{i}(l-1)\alpha} & & \\ & & \ddots & \\ 0 & & & e^{\mathrm{i}l\alpha} \end{pmatrix} .$$

Using the well-known geometric sum formula, we can calculate the character $\chi^l(\alpha)$ as:

$$\chi^l(\alpha) = \sum_{m=-l}^{l} e^{\mathrm{i} \cdot m \cdot \alpha} = \frac{\sin\left[\left(l + \frac{1}{2}\right)\alpha\right]}{\sin\left[\frac{\alpha}{2}\right]} \ . \tag{8.4}$$

It is worth noting that for other axes of rotation, the representation matrices are not diagonal, but the characters remain independent of the axis, as long as the rotation angle α is the same. Since we will only be using these characters in the following, we do not need to consider the representation matrices of other axes of rotation.

(ii) As one shows in all textbooks on quantum mechanics, the spherical harmonics behave under inversion $\tilde{I}$ as

$$\hat{U}_{\tilde{I}} \cdot Y_{l,m}(\theta, \varphi) = (-1)^l Y_{l,m}(\theta, \varphi) \ .$$

which means that

$$\chi^l(I) = (-1)^l l(l+1) \ .$$

(iii) For a rotational inversion $\tilde{S} \equiv \tilde{I} \cdot \tilde{D}$ one finds analogously

$$\bar{\chi}^l(\alpha) = (-1)^l \frac{\sin\left[\left(l + \frac{1}{2}\right)\alpha\right]}{\sin\left[\frac{\alpha}{2}\right]} \ . \tag{8.5}$$

In particular, in the special case of a reflection on a plane, we find $\bar{\chi}^l(\alpha = \pi) = 1$ (since $\sin\left[(l + 1/2)\,\pi\right] = (-1)^l$).

8.4.2 Splitting of Orbital Energies in Crystal Fields

We can use the character tables of our 32 point groups along with the characters of the group $O(3)$ (derived above) to evaluate the qualitative splitting of atomic orbitals using (5.23).[5] As an example, we consider the case of the group $G = O_h$.

By reducing the subduced representation of the first 4 atomic eigenspaces ($l \leq 2$), we obtain:

$$\Gamma^{(s)}_{l=0} = A_{\mathrm{g}} \,, \tag{8.6}$$

$$\Gamma^{(s)}_{l=1} = T_{1\mathrm{u}} \,,$$

$$\Gamma^{(s)}_{l=2} = E_{\mathrm{g}} + T_{2\mathrm{g}} \,,$$

$$\Gamma^{(s)}_{l=2} = A_{2\mathrm{u}} + T_{1\mathrm{u}} + T_{2\mathrm{u}} \,. \tag{8.7}$$

Real linear combinations of functions $Y_{l,m}(\theta,\varphi)$ and $Y_{l,-m}(\theta,\varphi)$ are called *axial* or *tesseral orbitals*,

$$A_{l,m} \equiv \frac{1}{\sqrt{2}}(Y_{l,m} + Y_{l,-m}) \quad (0 \leq m \leq l) \,,$$

$$A_{l,-m} \equiv \frac{1}{\sqrt{2}\mathrm{i}}(Y_{l,m} - Y_{l,-m}) \quad (0 < m \leq l) \,.$$

In the case of the s, p and d shells, these are also the orbitals that arise in a cubic environment. For these shells, they are therefore also denoted as *cubic orbitals*. Since all other point groups in solids are sub-groups of O_h, they are also a proper starting point to find the suitable orbitals of the other point groups. In the case of the s and p orbitals, there is no splitting and one finds the (probably well-known) real orbitals

$$\alpha_s(r,\theta,\varphi) = R_s(r)Y_{0,0}(\theta,\varphi),$$

$$\beta_x(r,\theta,\varphi) = \frac{1}{\sqrt{2}}R_p(r)\left[Y_{1,1}(\theta,\varphi) + Y_{1,-1}(\theta,\varphi)\right] \sim x \,,$$

$$\beta_y(r,\theta,\varphi) = \frac{1}{\sqrt{2}\mathrm{i}}R_p(r)\left[Y_{1,1}(\theta,\varphi) - Y_{1,-1}(\theta,\varphi)\right] \sim y \,,$$

$$\beta_z(r,\theta,\varphi) = R_p(r)Y_{1,0}(\theta,\varphi) \sim z \,.$$

For the 5 d-orbitals we obtain the triple degenerate $t_{2\mathrm{g}}$-orbitals, which can be written, for example, as follows

[5] A critical reader might object that we have proved (5.23) only for finite groups. In physics, however, we can always argue with the fact that our results agree with the experiment.

for all $a \in G$. The proof of $\bar{\Gamma}^{p\otimes p'}$ being a representation is simple,

$$\begin{aligned}\Gamma^{p\otimes p'}_{(ik),(jl)}(a\cdot b) &\overset{(9.6)}{=} \Gamma^{p}_{i,j}(a\cdot b)\cdot\Gamma^{p'}_{k,l}(a\cdot b)\\ &= \sum_{n,m}\Gamma^{p}_{i,n}(a)\cdot\Gamma^{p}_{n,j}(b)\cdot\Gamma^{p'}_{k,m}(a)\cdot\Gamma^{p'}_{m,l}(b)\\ &\overset{(9.6)}{=} \sum_{n,m}\Gamma^{p\otimes p'}_{(ik),(nm)}(a)\cdot\Gamma^{p\otimes p'}_{(nm),(jl)}(b)\ ,\end{aligned}$$

where, in the second step, we have used that $\bar{\Gamma}^{p}$, $\bar{\Gamma}^{p'}$ are representations.

Product representations can, of course, also be created with reducible representations. We then denote these as $\bar{\Gamma}\otimes\bar{\Gamma}'$. In this chapter, we will mainly consider such product representations.

Even for two irreducible representations, $\bar{\Gamma}^{p\otimes p'}$ is, in general, reducible. This already follows from the dimension, because if, for example, $\bar{\Gamma}^{p}$ has the maximum occurring dimension d_p of a group, then $\bar{\Gamma}^{p\otimes p}$ has the dimension d_p^2, so it must be reducible. Therefore, in general,

$$\bar{\Gamma}^{p\otimes p'} = \sum_{\tilde{p}} c(p,p'|\tilde{p})\cdot\bar{\Gamma}^{\tilde{p}}\ ,$$

with coefficients $c(p,p'|\tilde{p})\in\mathbb{N}_0$.

The determination of the coefficients $c(p,p'|\tilde{p})$ succeeds as usual with (5.23). For this we need the characters of the product representation, which can readily be calculated,

$$\chi^{p\otimes p'}(a) = \sum_{k,l}\Gamma^{p\otimes p}_{(kl),(kl)}(a) \overset{(9.6)}{=} \sum_{k,l}\Gamma^{p}_{k,k}(a)\cdot\Gamma^{p'}_{l,l}(a) = \chi^{p}(a)\cdot\chi^{p'}(a)\ . \tag{9.7}$$

With (5.23) we then find

$$c(p,p'|\tilde{p}) = \frac{1}{g}\sum_i r_i\cdot\chi_i^{p\otimes p'}\cdot\left(\chi_i^{\tilde{p}}\right)^* \overset{(9.7)}{=} \frac{1}{g}\sum_i r_i\cdot\chi_i^{p}\cdot\chi_i^{p'}\cdot\left(\chi_i^{\tilde{p}}\right)^*\ . \tag{9.8}$$

With this equation and with the help of the character tables, we are now in the position to find all the coefficients of interest.

Example As an example we consider the group D_3, and use its character Table 8.1 to find, for example, for the reduction of $\bar{\Gamma}^{E\otimes E}$:

Table 9.1 The multiplication table for the irreducible representations of the group D_3. Since the table is symmetrical (see (9.8)) we have not specified all elements

D_3	A_1	A_2	E
A_1	A_1	A_2	E
A_2		A_1	E
E			$A_1 + A_2 + E$

$$c(E, E|A_1) = \frac{1}{6}(\underbrace{1}_{=r_1} \cdot \underbrace{2 \cdot 2}_{=\chi_1^{E\otimes E}} \cdot \underbrace{1}_{=\chi_1^{A_1}} + 2 \cdot (-1) \cdot (-1) \cdot 1 + 3 \cdot 0 \cdot 0 \cdot 1) = 1 \ ,$$

$$c(E, E|A_2) = \frac{1}{6}(1 \cdot 2 \cdot 2 \cdot 1 + 2 \cdot (-1) \cdot (-1) \cdot 1 + 3 \cdot 0 \cdot 0 \cdot 1) = 1 \ ,$$

$$c(E, E|E) = \frac{1}{6}(1 \cdot 2 \cdot 2 \cdot 2 + 2 \cdot (-1) \cdot (-1) \cdot (-1) + 3 \cdot 0 \cdot 0 \cdot 0) = 1 \ .$$

Hence, we obtain

$$\bar{\Gamma}^{p\otimes p'} = \bar{\Gamma}^{A_1} + \bar{\Gamma}^{A_2} + \bar{\Gamma}^{E} \ .$$

The results of reducing product representations from irreducible representations are summed up in tables known as *multiplication tables*. An example of such a table for the group D_3 can be seen in Table 9.1. It is worth noting that the use of the same names for both these tables and the group multiplication tables is unlikely to cause confusion in most cases. Multiplication tables are readily available on numerous websites.

The multiple product representations are defined in the same way

$$\bar{\Gamma} \equiv \bar{\Gamma}_1 \otimes \bar{\Gamma}_2 \otimes \cdots \otimes \bar{\Gamma}_n \ ,$$

with the representation matrices

$$\Gamma_{I,L}(a) \equiv \Gamma_{(i_1,\ldots,i_n),(l_1,\ldots,l_n)}(a) \equiv \Gamma_{i_1,l_1}(a) \cdot \Gamma_{i_2,l_2}(a) \cdots \Gamma_{i_n,l_n}(a) \ , \tag{9.9}$$

where we have introduced the multiple indices

$$I \equiv (i_1, \ldots, i_n), \ L \equiv (l_1, \ldots, l_n) \ . \tag{9.10}$$

9.3 Independent Tensor Components

Our objective now is to identify all the interdependencies among the tensor components α_I and a set of independent components. Although in some specific cases, the components α_I can be selected independently, this is not generally the case. As we

Our objective now is to examine which of the tensor components $\beta_{(p,m_p,\lambda_p)}$ can have non-zero values without violating (9.11). To achieve this, we substitute (9.13) into (9.11),

$$\sum_{p,m_p,\lambda_p} S^*_{I,(p,m_p,\lambda_p)} \beta_{(p,m_p,\lambda_p)} = \sum_{L,p,m_p,\bar{\lambda}_p} \Gamma_{L,I}(a) \cdot S^*_{L,(p,m_p,\bar{\lambda}_p)} \cdot \beta_{(p,m_p,\bar{\lambda}_p)} \ .$$

We multiply this equation with $S_{I,(p',m_{p'},\lambda_{p'})}$ and sum over I. Then, with the unitarity of $\tilde{S}$ and (9.12), it follows

$$\beta_{(p,m_p,\lambda_p)} = \sum_{\bar{\lambda}_p} \Gamma^p_{\lambda_p,\lambda_{p'}}(a) \cdot \beta_{(p,m_p,\bar{\lambda}_p)} \ . \tag{9.14}$$

If we represent the components in a vector with respect to λ_p and $\bar{\lambda}_p$, i.e.

$$\vec{\beta}_{p,m_p} \equiv (\beta_{p,m_p,1}, \ldots, \beta_{p,m_p,d_p})^T \ ,$$

we see that (9.14) simply means that $\vec{\beta}_{p,m_p}$ is an eigenvector of every matrix $\tilde{\Gamma}^p(a)$ to the eigenvalue 1. We will now show that this implies that $\vec{\beta}_{p,m_p} = 0$ for all $p \neq 1$, where $p = 1$ corresponds to the trivial representation A_1, i.e. the one-dimensional representation for which $\Gamma^1(a) = 1$ for all a.

Proof

(i) If $d_p > 1$, the direction of $\vec{\beta}_{p,m_p} \neq \vec{0}$ would be a one-dimensional subspace that is invariant with respect to all $\tilde{\Gamma}^p(a)$. This leads to a contradiction with the statement that we formulated and proved at the beginning of Sect. 4.1.2.

(ii) If $d_p = 1$ and $\beta_{p,m_p} \neq 0$ then it follows

$$\Gamma^p(a) \cdot \beta_{p,m_p} = \beta_{p,m_p} \quad \forall a \ .$$

which proves the statement.

With these findings we can now summarize the main results:

(i) There are exactly n_1 independent tensor components β_{1,m_1}, i.e. as many as the number of occurrences of the representation $\bar{\Gamma}^1$ in the product representation (9.9).

(ii) The tensor α_I can then be written as

$$\alpha_I = \sum_{m_1=1}^{n_1} S^*_{I,(1,m_1)} \cdot \beta_{(1,m_1)} \ . \tag{9.15}$$

where $\beta_{(1,m_1)}$ are the independent tensor components.

As usual, finding the number n_1 is easy in practice because one can use the standard Equation (5.23) for this purpose. The determination of the coefficients $S^*_{I,(1,m_1)}$ in (9.15) is a bit more difficult, but at least possible with elementary methods of linear algebra. The reason is that in (9.12) we are only interested in the sector of the one representation, so we have to consider

$$\tilde{\mathcal{S}}^\dagger \cdot \tilde{\Gamma}(a) \cdot \tilde{\mathcal{S}} = \tilde{1}_{n_1 \times n_1} \ ,$$

instead of (9.12). Here

$$\tilde{\mathcal{S}} = (\vec{s}_1, \ldots, \vec{s}_{n_1}) \ , \tag{9.16}$$

is a rectangular matrix and the vectors $\vec{s}_{m_1}$ are exactly the coefficients $S^*_{I,(1,m_1)}$ in (9.15). When we multiply (9.16) with $\tilde{\mathcal{S}}$ from the left we obtain

$$\tilde{\Gamma}(a) \cdot \tilde{\mathcal{S}} = \tilde{\mathcal{S}} \ .$$

This implies that the vectors $\vec{s}_{m_1}$ are eigenvectors of all matrices $\tilde{\Gamma}(a)$ with an eigenvalue of 1. Although we cannot rule out the possibility that numerical mathematics may offer a better method, we provide a way to solve this problem numerically: First, we determine all eigenvectors of the matrices $\tilde{\Gamma}(a)$ that have an eigenvalue that is not equal to 1. Then, using the singular value decomposition,[3] we can find a basis $\vec{b}_i$ of the subspace spanned by these vectors. The vectors $\vec{s}_{m_1}$ that we need to find must be orthogonal to all $\vec{b}_i$. This leads to a homogeneous linear system of equations given by

$$(\vec{b}_1, \vec{b}_2, \ldots) \cdot \vec{s}_{m_1} = \vec{0} \ .$$

Once more, when it comes to numerically solving this problem, the singular value decomposition is likely the most effective tool.

Example As an example, we consider a polarizability tensor $\tilde{\alpha}^{(2)}$ of rank 2 which we can analyze analytically. This leads to the 9-dimensional representation matrices

$$\Gamma_{(i,j),(k,l)}(a) = D_{i,k}(a) \cdot D_{j,l}(a) \ . \tag{9.17}$$

With these, we obtain for the characters

$$\chi(a) = \underbrace{\sum_i D_{i,i}(a)}_{\equiv \bar{\chi}(a)} \cdot \sum_j D_{i,i}(a) = \bar{\chi}(a)^2 = \bar{\chi}_i^2$$

for all elements in a class $\mathcal{C}_i$. The number n_1 then becomes

[3] William H. Press et al. Numerical Recipes in C: the Art of Scientific Computing. Cambridge [Cambridgeshire]; New York: Cambridge University Press, 1992.

for the number of independent tensor components, i.e. there are no dependencies in the tensor $\tilde{\alpha}^{(2)}$ for this group and none of the matrix elements vanishes.

(iii) In Exercise 4, it is shown that for the group O_h one finds $n_1 = 1$. Thus,

$$\tilde{\alpha}^{(2)} = \alpha \cdot \tilde{1} ,$$

i.e. in a cubic solid the polarizability tensor is of the same form as in homogeneous matter like liquids or gases.

In closing this section, we briefly examine tensors containing axial components, such as the magnetic susceptibility tensor $\tilde{\chi}^{(2)}$, which describes the leading order relationship between a magnetic moment and an applied magnetic field, both of which are axial vectors, via the equation

$$\vec{M} = \tilde{\chi}^{(2)} \cdot \vec{B} .$$

Here, one can proceed in exactly the same way as in our previous considerations, since the matrices $\tilde{D}'(a)$, defined as (the meaning of G_0 and L_0 is explained in Sect. 3.4)

$$\tilde{D}'(a) \equiv \tilde{D}(a) \quad \text{for} \quad |\tilde{D}(a)| = 1 \text{ (i.e. } a \in G_0) ,$$
$$\tilde{D}'(a) \equiv -\tilde{D}(a) \quad \text{for} \quad |\tilde{D}(a)| = -1 \text{ (i.e. } a \in L_0) ,$$

are also a representation of the point group, because

(i) $a, b \in G_0$: it is obviously $\tilde{D}'(a \cdot b) = \tilde{D}'(a) \cdot \tilde{D}'(b)$ $\surd$

(ii) $a \in G_0, b \in L_0$:

$$\tilde{D}'(\underbrace{a \cdot b}_{\in L_0}) = -\tilde{D}(a \cdot b) = (-\tilde{D}(a)) \cdot \tilde{D}(b) = \tilde{D}'(a) \cdot \tilde{D}'(b) \quad \surd$$

(iii) $a, b \in L_0$:

$$\tilde{D}'(\underbrace{a \cdot b}_{\in G_0}) = \tilde{D}(a \cdot b) = (-\tilde{D}(a)) \cdot (-\tilde{D}(b)) = \tilde{D}'(a) \cdot \tilde{D}'(b) \quad \surd$$

The same then applies to product representations built with the matrices $\tilde{D}'(a)$ $\surd$.

An alternative basis consists of eigenstates of $\hat{\vec{J}}^2$, $\hat{J}_z$ and $\hat{\vec{J}}_i^2$ where

$$\hat{\vec{J}} \equiv \hat{\vec{J}}_1 + \hat{\vec{J}}_2 \ .$$

The eigenvalue equations of $\hat{\vec{J}}^2$ and $\hat{J}_z$ are

$$\hat{\vec{J}}^2 |j, m; j_1, j_2\rangle = j(j+1)|j, m\rangle \ , \quad j = |j_1 - j_2|, |j_1 - j_2| + 1, \ldots, j_1 + j_2 \ ,$$
$$\hat{J}_z |j, m; j_1, j_2\rangle = m|j, m; j_1, j_2\rangle \quad m = -j, \ldots, j \ .$$

Apparently, the two bases can be expressed by each other,

$$|j, m; j_1, j_2\rangle = \sum_{m_1, m_2} \left(\begin{array}{cc|c} j_1 & j_2 & j \\ m_1 & m_2 & m \end{array} \right) |j_1, m_1; j_2, m_2\rangle \ ,$$

where the coefficients in this equation are denoted as *Clebsch-Gordan coefficients*. How to calculate these coefficients is shown in most books on quantum mechanics. They play a crucial role in the Wigner-Eckart theorem, which we formulate next.

10.1.2 The Wigner-Eckart Theorem for Angular Momenta

Some readers may have already learned about the Wigner-Eckart theorem for angular momenta in their introductory lecture on quantum mechanics. We will briefly review this theorem before generalizing it for general symmetry groups.

Analogous to (9.26), we define a set of $2j + 1$ operators $\hat{T}_{j,m}$ $(m = -j, \ldots, j)$ that behave like

$$\tilde{U}_{\tilde{D}} \cdot \hat{T}_{j,m} \cdot \tilde{U}_{\tilde{D}}^\dagger = \sum_{m'=-j}^{j} R^j_{m,m'}(\tilde{D}) \cdot \hat{T}_{j,m'}$$

under rotations $\tilde{D} \in O(3)$ as *irreducible spherical tensor operators of rank k*. Here the rotation matrix $R^j_{m,m'}(\tilde{D})$ is given by the matrix elements

$$R^j_{m,m'}(\tilde{D}) \equiv \langle j, m|\tilde{U}_{\tilde{D}}^\dagger|j, m'\rangle$$

of the rotation operator $\tilde{U}_{\tilde{D}}^\dagger$ in the subspace j. For example, a tensor operator of rank $j = 1$ consists of three components which results from an arbitrary vector operator $\hat{\vec{V}}$, if we define

Appendix A
The Schoenflies and the International Notation

There are two established ways of naming point groups, the *Schoenflies* and the *international notation*. The Schoenflies notation is used more often if one is only interested in the point groups. In contrast, the international one is mainly to denote the rotational part of space groups. We will give a brief introduction to both notations in this appendix.

A.1 The Schoenflies Notation

In the Schoenflies notation, the proper point groups are named in the same way as they were introduced in Sect. 3.2. Most of the names of the improper point groups are derived from those of the proper ones by specifying which additional improper symmetry operations exist in the group. Historically, the notation of the groups argued with the existing mirror planes and did not use the inversion. We go a slightly different way here to motivate the notation:

(i) The groups C_i, C_{2h}, S_6, C_{4h}, D_{2h}, D_{3d}, C_{6h}, D_{4h}, D_{6h}, T_h, O_h:
These groups are constructed by adding the inversion I to the respective 11 proper point groups G_0 in (3.7), $G = G_0 \times (E, I)$. For the proper point groups $G_0 = \{C_1, C_6\}$ the notations C_i, S_6 are used instead of C_{1h}, C_{6h}. Remember that all these groups also contain some mirror planes, since these correspond to a product of a two-fold rotation and the inversion (see Sect. 3.1).

(ii) The groups C_s, C_{3h}, D_{3h}:
These groups are constructed by adding a mirror plane σ_h perpendicular to the main symmetry axis δ_n to the respective proper point groups C_1, C_3, D_3. In case of D_3 the two-fold axes, perpendicular to δ_n, must obviously lie in σ_h.

J. Bünemann, *Group Theory in Physics*, Undergraduate Lecture Notes in Physics,
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(iii) The groups C_{nv} $(n = 2, 3, 4, 6)$:
These groups are constructed by adding n mirror planes to C_n $(n = 2, 3, 4, 6)$ that all contain the axis of symmetry and have the same angle relative to each other.

(iv) The groups S_4, D_{2d}, T_d $(n = 2, 3, 4, 6)$:
These groups are constructed by replacing the two-fold symmetry axis in C_2, D_2, T by a four-fold *rotary inversion* axis $\sigma_4 \equiv I \cdot \delta_4$. Since $(\sigma_4)^2 = \delta_2$, the corresponding proper groups are subgroups in all three cases. Note that T_d is the symmetry group of a tetrahedron.

A.2 The International Notation

The international notation considers the three possible types of rotational symmetry axes:

(i) proper n-fold rotation axes δ_n are denoted as $n = 2, 3, 4, 6$.

(ii) n-fold rotary inversion axes $I \cdot \delta_n$ are denoted as $\bar{n}$ with $n = 1, 2, 3, 4, 6$. Then, an axis $\bar{n}$ contains the symmetry elements shown in Table A.1. In that table we use the common abbreviations

$$\sigma_2 \equiv \sigma \equiv I \cdot \delta_2 \ , \ \sigma_6 \equiv I \cdot \delta_3 \ , \ \sigma_4 \equiv I \cdot \delta_4 \ , \ \sigma_3 \equiv I \cdot \delta_6 \ .$$

Since a rotary inversion axes $\bar{2}$ is equivalent to a mirror plane, one often writes 'm' instead of '$\bar{2}$' .

(iii) If n is odd, $\bar{n}$ necessarily contains I, because

$$(I \cdot \delta_n)^n = \underbrace{I^n}_{I} \cdot \underbrace{\delta_n^n}_{E} = I$$

Therefore, the definition of the third kind of axes of rotation only makes sense for even n:

$$\frac{n}{m} \equiv \bar{n} \cup I$$

Table A.1 Elements of a rotary inversion axes $\bar{n}$

$\bar{n}$	Elements	Order $g(\bar{n})$
$\bar{1}$	$E\ I$	2
$\bar{2}$	$E\ \sigma$	2
$\bar{3}$	$E\ \sigma_6\ \delta_3^{-1}\ I\ \delta_3\ \sigma_6^{-1}$	6
$\bar{4}$	$E\ \sigma_4\ \delta_2\ \sigma_4^{-1}$	4
$\bar{6}$	$E\ \sigma_3\ \delta_3\ \sigma\ \delta_3^{-1}\ \delta_3^{-1}$	6

Appendix B
Solutions to the Exercises

Chapter 1

1. It is sufficient to show that

$$\langle \vec{r}|\hat{T}_{\tilde{D}^{-1}} \cdot \hat{T}_{\tilde{D}}|\vec{r}'\rangle = \delta(\vec{r} - \vec{r}') \quad , \tag{B.1}$$

for all basis states $|\vec{r}\rangle$, $|\vec{r}'\rangle$. When we insert a one-operator $\hat{1}$ built with these states, we find

$$\begin{aligned}\langle \vec{r}|\hat{T}_{\tilde{D}^{-1}} \cdot \hat{T}_{\tilde{D}}|\vec{r}'\rangle &= \int \mathrm{d}^3 r'' \langle \vec{r}|\hat{T}_{\tilde{D}^{-1}}|\vec{r}''\rangle\langle \vec{r}''|\hat{T}_{\tilde{D}}|\vec{r}'\rangle \\ &= \int \mathrm{d}^3 r'' \langle \tilde{D}^{-1} \cdot \vec{r}|\vec{r}''\rangle\langle \tilde{D} \cdot \vec{r}''|\vec{r}'\rangle \ .\end{aligned} \tag{B.2}$$

Since

$$\langle \tilde{D}^{-1} \cdot \vec{r}|\vec{r}''\rangle = \langle \vec{r}|\tilde{D} \cdot \vec{r}''\rangle = \delta(\vec{r} - \tilde{D} \cdot \vec{r}'')$$

and

$$\langle \tilde{D} \cdot \vec{r}''|\vec{r}'\rangle = \delta(\vec{r}' - \tilde{D} \cdot \vec{r}'')$$

Equation (B.1) follows from (B.2).

2. (a) With the definition of the momentum operator $\hat{\vec{p}} = -\frac{\mathrm{i}}{\hbar}\vec{\nabla}$, it follows

$$\hat{T}_{\vec{a}} \cdot \Psi(\vec{r}) = \sum_{j=1}^{\infty} \frac{1}{j!}(\vec{a} \cdot \vec{\nabla})^j \Psi(\vec{r})$$

which is just the Taylor-expansion of $\Psi(\vec{r} + \vec{a})$.

J. Bünemann, *Group Theory in Physics*, Undergraduate Lecture Notes in Physics,
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(b) In spherical coordinates it is $\hat{L}_z = \frac{\hbar}{\mathrm{i}} \frac{\partial}{\partial \varphi}$. Thus, we find

$$\hat{T}_\alpha \cdot \Psi(r, \theta, \varphi) = \sum_{j=1}^{\infty} \frac{1}{j!} \left(\frac{\partial}{\partial \varphi} \right)^j \Psi(r, \theta, \varphi) = \Psi(r, \theta, \varphi + \alpha) \ . \checkmark$$

Since the z-direction is not distinguished from all other, for any other direction $\vec{e}$ ($|\vec{e}| = 1$) of the rotation it must be

$$\hat{T}_{\alpha, \vec{e}} = \exp\left(\frac{\mathrm{i}}{\hbar} \alpha \left(\vec{e} \cdot \hat{\vec{L}} \right) \right) = \exp\left(\vec{\alpha} \cdot \hat{\vec{L}} \right) \equiv \hat{T}_{\vec{\alpha}}$$

with a vector $\vec{\alpha} \equiv \alpha \cdot \vec{e}$.

3. We follow the idea for a proof proposed in the exercise:

(i) Using well-known properties of determinants we can derive:

$$|\tilde{1} - \tilde{D}| = \underbrace{|\tilde{D}|}_{=1} |\tilde{1} - \tilde{D}| = |\tilde{D}^T| |\tilde{1} - \tilde{D}| = |\tilde{D}^T - \tilde{1}| = |\tilde{D} - \tilde{1}|$$
$$= -|\tilde{1} - \tilde{D}| \ .$$

Therefore, it is $|\tilde{1} - \tilde{D}| = 0$, which means that $\lambda = 1$ is an eigenvalue of $\tilde{D}$.

(ii) In a complex vector space, $\tilde{D}$ has 3 complex eigenvalues λ_i and there is a unitary matrix $\tilde{U}$ such that

$$\tilde{U} \cdot \tilde{D} \cdot \tilde{U}^\dagger = \tilde{D}^{\mathrm{d}} \equiv \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix} \ .$$

With

$$\tilde{D}^{\mathrm{d}} \cdot (\tilde{D}^{\mathrm{d}})^\dagger = \tilde{U} \cdot \tilde{D} \cdot \tilde{U}^\dagger \cdot \tilde{U} \cdot \tilde{D}^\dagger \cdot \tilde{U}^\dagger = \tilde{U} \cdot \tilde{D} \cdot \tilde{D}^\dagger \cdot \tilde{U}^\dagger = \tilde{U} \cdot \tilde{U}^\dagger = \tilde{1} \ ,$$

we can conclude that

$$\lambda_i^2 = 1 \quad \Rightarrow \quad \lambda_i = e^{\mathrm{i}\varphi_i} \ ,$$

with $\varphi_i \in \mathbb{R}$. Since one of these eigenvalues is 1 (e.g. $\varphi_3 = 0$) and $|\tilde{D}| = |\tilde{D}^{\mathrm{d}}| = 1$, it must be $\varphi_1 = -\varphi_2 \equiv \varphi$.

(iii) For $\varphi \neq 0$, the three eigenvectors $\vec{v}_i$ are orthogonal, because[1]

$$\vec{v}_i^\dagger \cdot \tilde{D} \cdot \vec{v}_j = e^{\mathrm{i}\varphi_i} \vec{v}_i^\dagger \cdot \vec{v}_j = e^{\mathrm{i}\varphi_j} \vec{v}_i^\dagger \cdot \vec{v}_j \quad \Rightarrow \quad \vec{v}_i^\dagger \cdot \vec{v}_j = \delta_{i,j} \ .$$

[1] Remember that $\hat{D}^T \vec{v}_i = e^{-\mathrm{i}\varphi} \vec{v}_i$.

Chapter 2

1. (a) Suppose that there are two elements $E_1 \neq E_2$ with $E_1 \cdot a = a$ and $E_2 \cdot a = a$ for all $a \in G$. Multiplying

$$E_1 \cdot a = a$$

from the right with a^{-1} yields $E_1 = E_2$. $\surd$

(b) The proof is the same as in (a) replacing E_i by a_i^{-1}.

(c) Let us assume that for every $a \in G$ there is a left inverse element a_L^{-1} with

$$a_\mathrm{L}^{-1} \cdot a = E \ .$$

If we multiply this equation from the left with a it follows

$$a \cdot a_\mathrm{L}^{-1} \cdot a = a \quad \Rightarrow \quad a \cdot a_\mathrm{L}^{-1} = E \quad \Rightarrow \quad a_\mathrm{R}^{-1} = a_\mathrm{L}^{-1} \ . \surd$$

2. With Table 2.5 we find for the class multiplications ($\mathcal{C}_1 \cdot \mathcal{C}_i = \mathcal{C}_i$ obviously holds)

$$\begin{aligned} \mathcal{C}_2 \cdot \mathcal{C}_3 &= \{\delta_3 \cdot \delta_{21}, \delta_3 \cdot \delta_{22}, \delta_3 \cdot \delta_{23}, \delta_3^2 \cdot \delta_{21}, \delta_3^2 \cdot \delta_{22}, \delta_3^2 \cdot \delta_{23}\} \\ &= \{\delta_{23}, \delta_{21}, \delta_{22}, \delta_{22}, \delta_{23}, \delta_{21}\} = 2\mathcal{C}_3 \ , \surd \\ \mathcal{C}_3 \cdot \mathcal{C}_3 &= \{\delta_{21} \cdot \delta_{21}, \delta_{21} \cdot \delta_{22}, \delta_{21} \cdot \delta_{23}, \delta_{22} \cdot \delta_{21}, \delta_{22} \cdot \delta_{22}, \delta_{22} \cdot \delta_{23}, \\ &\quad\ \delta_{23} \cdot \delta_{21}, \delta_{23} \cdot \delta_{22}, \delta_{23} \cdot \delta_{23}\} \\ &= \{E, \delta_3, \delta_3^2, \delta_3^2, E, \delta_3, \delta_3, \delta_3^2, E\} = 3\mathcal{C}_1 \cdot \mathcal{C}_2 \ . \surd \end{aligned}$$

3. If $f(a) = a^{-1}$ satisfies (2.15), we have

$$\underbrace{(a^{-1} \cdot b^{-1})^{-1}}_{=b \cdot a} = \underbrace{(a^{-1})^{-1} \cdot (b^{-1})^{-1}}_{a \cdot b} \ . \surd$$

4. (a) The elements of G are E, the three 4-fold rotations δ_4, δ_4^2, δ_4^3 around the symmetry axis of the molecule and the 4 mirror planes $\sigma_1, \ldots, \sigma_4$ shown in Fig. B.1. The inverse elements are

$$\begin{aligned} (\delta_4)^{-1} &= \delta_4^3 \ , \\ (\delta_4^2)^{-1} &= \delta_4^2 \ , \\ (\delta_4^3)^{-1} &= \delta_4 \ , \\ (\sigma_i)^{-1} &= \sigma_i \quad (i = 1, \ldots, 4) \ . \end{aligned}$$

As illustrated in the example of the group D_3 in Sect. 2.2.3, each group element corresponds to an arrangement of the vertices of the molecule (here A, B, C, D) after the group transformation. These are for the 8 group elements

(b) position 1:
proper point group: C_2,
improper point group: C_2+2 mirror planes = C_{2v},
position 2:
proper point group: D_4,
improper point group: $D_4 + I = D_{4h}$.

(c) position 1:
proper point group: C_3,
improper point group: C_3+3 mirror planes = C_{3v},
position 2:
proper point group: O,
improper point group: $O + I = O_h$.

4. (i) D_{4h},
   (ii) D_{2h},
   (iii) D_{3d},
   (iv) C_{2v}.
5. (i) In the case of the group D_2, one possible way is to start from the cuboid with which we illustrated this group in the Chap. 2, and to position an atom on each of the 8 vertices (see Fig. 2.1). There we had ignored consciously the improper symmetries of this body, since its actual point group is D_{2h}. We must now add atoms that preserve the proper symmetry transformations but eliminate the improper ones. Here, it is sufficient to break the inversion symmetry. This succeeds, for example, in the (artificial) molecule in Fig. B.4.
   (ii) The group D_{3h} contains a 6-fold rotation inversion axis, as well as three 2-fold axes of rotation and mirror planes. The inversion is no symmetry operation. This leads to a similar situation as in Fig. B.2, except that the two faces (left and right) must be chosen as regular hexagon (see the six (red) atoms in Fig. B.5).
6. The only symmetry that exists in any 2-dimensional system is the mirror plane. Together with the identity element, this leads to the group C_s.
7. It becomes D_{4h}.

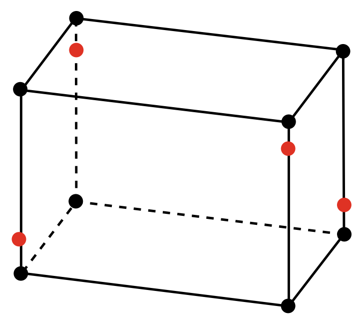

Fig. B.4 An artificial molecule with the symmetry group D_2

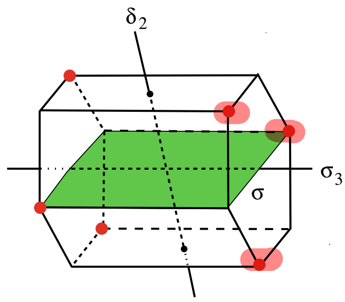

Fig. B.5 An artificial molecule with the symmetry group D_{3h}. Shown are the 6-fold rotation inversion axis (σ_3) and one of the three 2-fold rotation axes (σ_2) and one of the mirror planes σ

8. Given that two point groups are equivalent, there is, then, a matrix $\tilde{S}$ with

$$\tilde{S}^{-1} \cdot \tilde{D}_i \cdot \tilde{S} = \tilde{D}'_i \ ,$$

for all matrices $\tilde{D}_i$, $\tilde{D}'_i$ of the two groups. This equation then obviously also defines the isomorphism $\tilde{D}_i \leftrightarrow \tilde{D}'_i$, because
$\tilde{D}'_l = \tilde{D}'_i \cdot \tilde{D}'_j = (\tilde{S}^{-1} \cdot \tilde{D}_i \cdot \tilde{S}) \cdot (\tilde{S}^{-1} \cdot \tilde{D}_j \cdot \tilde{S}) = \tilde{S}^{-1} \cdot \tilde{D}_i \cdot \tilde{D}_j \cdot \tilde{S} = \tilde{S}^{-1} \cdot \tilde{D}_l \cdot \tilde{S}$.√

9. Suppose that $C_2 \times C_4$ is isomorphic to C_8. Then, there must be a generating element $(a; b) \in C_2 \times C_4$ with $a \in C_2$ and $b \in C_4$ and

$$(a; b)^l = E \ . \tag{B.3}$$

for (and only for) $l = 8$. a and b can be written as $a = a_g^m$, $b = b_g^n$ with generating elements a_g, b_g and some natural numbers m, n. Then, it follows

$$(a; b)^4 = (a_g^m; b_g^n)^4 = (a_g^{4m}; b_g^{4n}) = (E; E) = E$$

in contradiction to (B.3) , i.e. $C_2 \times C_4$ is not isomorphic to C_8.

Chapter 5

1. (a) If $a_i \sim a'_i$ and $b_j \sim b'_j$ there must be $a \in G_1$ and $b \in G_2$ such that

$$a_i = a^{-1} \cdot a'_i \cdot a \ \ \vee \ \ b_j = b^{-1} \cdot b'_j \cdot b \ \ \Rightarrow \ \ (a_i; b_j) = (a; b)^{-1} \cdot (a'_i; b'_j) \cdot (a; b)$$

and therefore $(a_i; b_j) \sim (a'_i; b'_j)$. Since the argument also works in the opposite direction, the assertion holds. Hence, for every pair of classes $\mathcal{C}_k \in G_1$, $\mathcal{C}_l \in G_2$ there exists a class $\mathcal{C}_{[k,l]} \in G_1 \times G_2$ that consists of all pairs (a_i, b_j) with $a_i \in \mathcal{C}_k$, $b_j \in \mathcal{C}_l$. The number of elements in $\mathcal{C}_{[k,l]}$ is $r_{[k,l]} = r_k \cdot r_l$.

Table B.5 Irreducible representations of the group D_{3d}. The matrices $\tilde{D}_i$ are defined in (2.16)

	E	δ_3	δ_3^2	δ_{21}	δ_{22}	δ_{23}	I	$(I\delta_3)$	$(I\delta_3^2)$	$(I\delta_{21})$	$I\delta_{22})$	$I\delta_{23})$
$\Gamma^{A\otimes A}$	1	1	1	1	1	1	1	1	1	1	1	1
$\Gamma^{A\otimes B}$	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1
$\Gamma^{A\otimes E}$	$\tilde{D}_1$	$\tilde{D}_2$	$\tilde{D}_3$	$\tilde{D}_4$	$\tilde{D}_5$	$\tilde{D}_6$	$\tilde{D}_1$	$\tilde{D}_2$	$\tilde{D}_3$	$\tilde{D}_4$	$\tilde{D}_5$	$\tilde{D}_6$
$\Gamma^{B\otimes A}$	1	1	1	-1	-1	-1	1	1	1	-1	-1	-1
$\Gamma^{B\otimes B}$	-1	-1	-1	1	1	1	-1	-1	-1	1	1	1
$\Gamma^{B\otimes E}$	$\tilde{D}_1$	$\tilde{D}_2$	$\tilde{D}_3$	$\tilde{D}_4$	$\tilde{D}_5$	$\tilde{D}_6$	$-\tilde{D}_1$	$-\tilde{D}_2$	$-\tilde{D}_3$	$-\tilde{D}_4$	$-\tilde{D}_5$	$-\tilde{D}_6$

For the group D_3 the relevant characters are

$$\chi(E) = 3, \chi(\delta_3) = \chi(\delta_3^2) = 0, \chi(\delta_{2,i}) = -1 \ .$$

Hence,

$$\begin{aligned} n_{A_1} &= \frac{1}{6}(1 \cdot 1 \cdot 3 + 2 \cdot 0 \cdot (-1) + 3 \cdot 1 \cdot (-1)) = 0 \ , \\ n_{A_2} &= \frac{1}{6}(3 + 0 + 3) = 1 \ , \\ n_E &= \frac{1}{6}(6 + 0 + 0) = 1 \ , \end{aligned}$$

i.e.

$$\Gamma = \Gamma^{A_2} \oplus \Gamma^E \ .$$

4. We use (5.23). In this case, all characters (χ_i^p and χ) are given in Tables 5.1 and 6.1.

(a) $G' = \{E, \delta_3, \delta_3^2\} \mathrel{\widehat{=}} C_3$

(i) $\bar{\Gamma}^{(s)} = A_1$:

$$\begin{aligned} n_A &= \frac{1}{3}(1 + 1 + 1) = 1 \ , \\ n_{E_1} &= \frac{1}{3}(1 + \underbrace{\omega + \omega^2}_{-1}) = 0 = n_{E_2} \ . \end{aligned}$$

Hence

$$A_1 \to A \ .$$

(ii) $\bar{\Gamma}^{(s)} = A_2$: same result as in (i),

$$A_2 \to A \ .$$

However, for some one-dimensional representation $\bar{\Gamma}^p$ it applies

$$\Gamma^p(c) = \Gamma^p(a) \cdot \Gamma^p(b) = \Gamma^p(b) \cdot \Gamma^p(a) = \Gamma^p(d)$$

i.e. the two different group elements c and d have the same character in each representation. This contradicts the orthogonality theorem (5.9) and therefore G must be Abelian. $\surd$

10. For both elements $a = I$ or $a = \sigma$ it applies $a^2 = E$, hence

$$\Gamma(a^2) = \Gamma(a)^2 = \Gamma(E) = 1 \ .$$

Thus it is $\Gamma(a) = \pm\tilde{1}$. $\surd$

11. In a non-Abelian group there are at least two group elements a, b for which

$$a \cdot b \neq b \cdot a$$

applies. This means that

$$a \cdot b \cdot a^{-1} \neq b$$

and there must therefore be an element

$$c \equiv a \cdot b \cdot a^{-1} \neq b$$

that is in the same class as b. Hence, there would be at least one class with more than one element. If there were only one-dimensional representations, however, all classes would have to consist of only one element according to (5.24) and Theorem 1 in Sect. 4.2. This contradicts our above finding and therefore there cannot be only one-dimensional representations. $\surd$

Chapter 6

1. To use (6.14), we need the effect of the rotations in C_3 on a vector $\vec{r}$. With (3.3) we find for δ_3 ($\varphi = \frac{2\pi}{3}$)

$$\begin{aligned} x &\to -\frac{x}{2} - \frac{\sqrt{3}}{2}y \ , \\ y &\to \frac{\sqrt{3}}{2}x - \frac{y}{2} \ , \\ z &\to z \ , \end{aligned}$$

and for δ_3^2 ($\varphi = \frac{4\pi}{3}$)

of C_{3v} using the operators $\hat{P}^{p}_{\lambda,\lambda}$,

$$\begin{aligned}\hat{P}^{A_1}_{1,1}|1\rangle &= \frac{1}{6}\left(\hat{T}_E|1\rangle + \hat{T}_{\delta_3}|1\rangle + \hat{T}_{\delta_3^2}|1\rangle + \hat{T}_{\sigma_1}|1\rangle + \hat{T}_{\sigma_2}|1\rangle + \hat{T}_{\sigma_3}|1\rangle\right)\\ &= \frac{1}{6}\left(|1\rangle + |2\rangle + |3\rangle + |2\rangle + |1\rangle + |3\rangle\right)\\ &= \frac{1}{3}\left(|1\rangle + |2\rangle + |3\rangle\right) \equiv \sqrt{3}|\Psi^{A_1}\rangle\end{aligned}$$

where the state $|\Psi^{A_1}\rangle$ is normalized. For the 3 other operators we find

$$\begin{aligned}\hat{P}^{A_2}_{1,1}|1\rangle &= \frac{1}{6}\left(\hat{T}_E|1\rangle + \hat{T}_{\delta_3}|1\rangle + \hat{T}_{\delta_3^2}|1\rangle - \hat{T}_{\sigma_1}|1\rangle - \hat{T}_{\sigma_2}|1\rangle - \hat{T}_{\sigma_3}|1\rangle\right) = 0\ ,\\ \hat{P}^{E}_{1,1}|1\rangle &= \frac{2}{6}\left(\hat{T}_E|1\rangle + \omega\hat{T}_{\delta_3}|1\rangle + \omega^2\hat{T}_{\delta_3^2}|1\rangle\right)\\ &= \frac{2}{6}\left(|1\rangle + \omega|2\rangle + \omega^2|3\rangle\right) \equiv \sqrt{3}|\Psi^{E}_{1}\rangle\ ,\\ \hat{P}^{E}_{2,2}|1\rangle &= \frac{2}{6}\left(|1\rangle + \omega^2|2\rangle + \omega|3\rangle\right) \equiv \sqrt{3}|\Psi^{E}_{2}\rangle\ .\end{aligned}$$

Because of our findings in Sect. 6.3.5, the Hamiltonian must be diagonal with respect to the three basis states $|\Psi^{A_1}\rangle$, $|\Psi^{E}_{1,1}\rangle$, $|\Psi^{E}_{2,2}\rangle$ with diagonal elements

$$\begin{aligned}\langle\Psi^{A_1}|\hat{H}|\Psi^{A_1}\rangle &= 2t\ ,\\ \langle\Psi^{E}_{1}|\hat{H}|\Psi^{E}_{1}\rangle &= \langle\Psi^{E}_{2}|\hat{H}|\Psi^{E}_{2}\rangle = -t\ .\end{aligned} \tag{B.4}$$

Note that (B.4) confirms our general finding (6.23).

(b) With the 3 states $|4\rangle$, $|5\rangle$, $|6\rangle$ we can define analogously

$$\begin{aligned}|\tilde{\Psi}^{A_1}\rangle &= \frac{1}{\sqrt{3}}\left(|4\rangle + |5\rangle + |6\rangle\right)\ ,\\ |\tilde{\Psi}^{E}_{1}\rangle &= \frac{1}{\sqrt{3}}\left(|4\rangle + \omega|5\rangle + \omega^2|6\rangle\right)\ ,\\ |\tilde{\Psi}^{E}_{2}\rangle &= \frac{1}{\sqrt{3}}\left(|4\rangle + \omega^2|5\rangle + \omega|6\rangle\right)\ .\end{aligned}$$

In the basis of the 6 states $|\Psi^{A_1}\rangle, \ldots, |\tilde{\Psi}^{E}_{2}\rangle$ the Hamiltonian is block-diagonal with 2×2 blocks of states $\{|\Psi^{A_1}\rangle, |\tilde{\Psi}^{A_1}\rangle\}$, $\{|\Psi^{E}_{i}\rangle, |\tilde{\Psi}^{E}_{i}\rangle\}$. The off-diagonal elements are

$$\langle\Psi^{A_1}|\hat{H}|\tilde{\Psi}^{A_1}\rangle = \langle\tilde{\Psi}^{E}_{i}|\hat{H}|\Psi^{E}_{i}\rangle = t'\ .$$

Thus, the Hamiltonian matrix has the form