Group Theory in Solid State Physics

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June 14, 2022

Contents

Chapter 1

Symmetries

1.1 Symmetries of bodies

It is often useful to imagine symmetries on the basis of extended bodies. A body is a set of spatial points, e.g. a sphere, which consists of all points $\vec{r}$ with the property $|\vec{r}| \leq R$. A symmetry transformation is then a mapping of the point set into itself. As we will see in the following, only linear transformations are relevant, i.e. affine transformations of the form

$$\vec{r} \to \vec{r}' = \tilde{D} \cdot \vec{r} + \vec{a}$$

with an orthogonal matrix $\tilde{D}$, i.e.,

$$\tilde{D} \cdot \tilde{D}^{\dagger} = \tilde{1}$$

and a constant vector $\vec{a}$. In infinitely extended crystals we must indeed consider affine symmetry transformations. In contrast, in finite bodies (corresponding to atoms or molecules in physics) only the orthogonal transformations are relevant, since every affine symmetry transformation is identical to an orthogonal transformation. For example, for a rectangle there is the orthogonal symmetry transformation of a 180° rotation around the red axis in Fig. 1.1. Equivalent to this, however, is the affine transformation shown in Fig 1.2 where a 180° rotation and a translation are combined.

As an example, we consider the symmetries of a tetrahedron, shown in Fig. 1.3. There are three obvious types of symmetry transformations:

i) 120° and 240° rotations around each axis through a corner and the opposite side's centre.

ii) 180° rotations around the centres of opposite edges.

iii) Reflections on any plane that contains two vertices and the midpoints of opposite edges.

Less obvious but also an orthogonal symmetry transformation are

iv) 90° and 270° rotations around the same axes as in ii) multiplied with an Inversion $\tilde{I} = -\tilde{1}$ at the origin (*rotary inversion axes*).

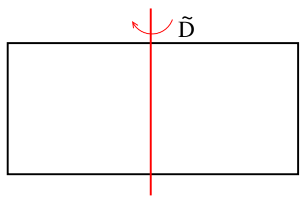

Figure 1.1: Orthogonal symmetry transformation of a rectangle.

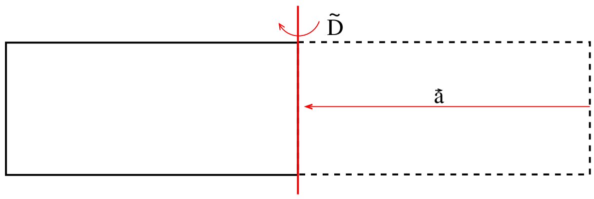

Figure 1.2: Affine symmetry transformation of a rectangle.

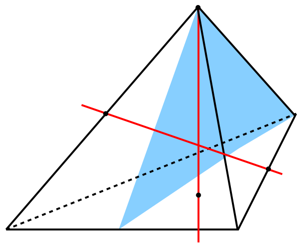

Figure 1.3: Symmetry transformations of a tetrahedron.

It is now important that the successive execution $S_1 \circ S_2$ of two symmetry transformations S_1 and S_2 is also such a symmetry transformation. This is the most important point which connects symmetries with the group theory, as we will see in the next chapter.

1.2 Symmetries in classical physics

A classical N-particle system is described by a Lagrangian

$$L(\{\vec{r}_l\},\{\dot{\vec{r}}_l\}) = \sum_i^N \frac{1}{2} m_i \dot{\vec{r}}_i^2 - V(\vec{r}_1,\ldots,\vec{r}_N)\ .$$

A spatial symmetry transformation is then a transformation $\{\vec{r}_l\} \to \{\vec{r}_l'\}$ that leaves the form of L invariant, i.e.,

$$L(\{\vec{r}_l(\{\vec{r}_l'\})\},\{\dot{\vec{r}}_l(\{\vec{r}_l'\},\{\dot{\vec{r}}_l'\})\}) = L(\{\vec{r}_l'\},\{\dot{\vec{r}}_l'\})\ .$$

Because of the terms $\sim \dot{\vec{r}}_i^2$, no non-linear transformations are possible here, but only the affine transformations introduced in section 1.1. Time-dependent symmetry transformations, e.g. Galilei transformations, are not relevant in solid-state physics and will not be considered in this script. The symmetry of a body K can easily be transferred to physical systems, for example by introducing a single-particle potential of the form

$$V(\vec{r}) = \begin{cases} V_0 \neq 0 & \text{if } \ \vec{r} \in K \\ 0 & \text{if } \ \vec{r} \notin K \end{cases}\ .$$

1.3 Symmetries in quantum mechanics

We only consider single-particle systems here. These are described by wave functions

$$\Psi(\vec{r}) = \langle \vec{r} | \psi \rangle$$

with the spatial basis $|\vec{r}\rangle$ and a Hamiltonian

$$\hat{H} = \frac{\hat{\vec{p}}^2}{2m} + V(\hat{\vec{r}})\ . \tag{1.1}$$

An affine spatial transformation corresponds to a transformation in the Hilbert space (of the square-integrable functions) $|\psi_1\rangle \to |\psi_2\rangle$, defined by

$$\Psi_1(\vec{r}\,') = \Psi_1(\tilde{D}\vec{r} + \vec{a}) \equiv \Psi_2(\vec{r}) \ .$$

The corresponding operator $\hat{T}_{\tilde{D}}$ (for the sake of simplicity, we set $\vec{a} = \vec{0}$ in the following) is then defined by

$$\langle \vec{r}|\hat{T}_{\tilde{D}}|\psi\rangle \stackrel{!}{=} \langle \tilde{D}\vec{r}|\psi\rangle = \psi(\tilde{D}\vec{r}) \quad \forall|\psi\rangle \ .$$

$\hat{T}_{\tilde{D}}$ is unitary, because

$$\begin{aligned}\langle\psi|\hat{T}^\dagger_{\tilde{D}}\hat{T}_{\tilde{D}}|\psi\rangle &= \int \mathrm{d}^3r \langle\psi|\hat{T}^\dagger_{\tilde{D}}|\vec{r}\rangle\langle\vec{r}|\hat{T}_{\tilde{D}}|\psi\rangle \\ &= \int \mathrm{d}^3r |\psi(\tilde{D}\vec{r})|^2 = 1 \ .\end{aligned}$$

Since this equation is valid for all $|\psi\rangle$, it follows that

$$\hat{T}^\dagger_{\tilde{D}}\hat{T}_{\tilde{D}} = 1 \ ,$$

where obviously

$$\hat{T}^\dagger_{\tilde{D}} = \hat{T}^{-1}_{\tilde{D}} = \hat{T}_{\tilde{D}^{-1}} \ .$$

Before we come to the central theorem of this section, let us look at how the operators $\hat{T}_{\tilde{D}}$ act on the momentum space basis $|\vec{p}\rangle$:

$$\begin{aligned}\langle\vec{p}|\hat{T}_{\tilde{D}}|\psi\rangle &= \int \mathrm{d}^3r \ \underbrace{\langle\vec{p}|\vec{r}\rangle}_{=\frac{1}{\sqrt{V}}e^{-\mathrm{i}\vec{p}\cdot\vec{r}}} \ \underbrace{\langle\vec{r}|\hat{T}_{\tilde{D}}|\psi\rangle}_{=\langle\tilde{D}\vec{r}|\psi\rangle} \\ &\stackrel{(\vec{r}\,'\equiv\tilde{D}\vec{r})}{=} \int \mathrm{d}^3r' \frac{1}{\sqrt{V}} e^{-\mathrm{i}\vec{p}\cdot(\tilde{D}^{-1}\vec{r}\,')}\langle\vec{r}\,'|\psi\rangle\end{aligned}$$

Since $\vec{p}\cdot(\tilde{D}^{-1}\vec{r}\,') = (\tilde{D}\vec{p})\cdot\vec{r}\,'$ we finally obtain

$$\langle\vec{p}|\hat{T}_{\tilde{D}}|\psi\rangle = \int \mathrm{d}^3r' \langle\tilde{D}\vec{p}|\vec{r}\,'\rangle\langle\vec{r}\,'|\psi\rangle = \langle\tilde{D}\vec{p}|\psi\rangle \ .$$

The essential connection to group theory is now provided by the following theorem: if $V(\vec{r})$ is invariant under the transformation $\tilde{D}$, then

$$[\hat{H}, \hat{T}_{\tilde{D}}] = 0 \ .$$

Proof:

We consider the two parts in the Hamiltonian (1.1) separately, first the kinetic energy:

$$\begin{aligned}\left[\frac{\hat{\vec{p}}^2}{2m}, \hat{T}_{\tilde{D}}\right] = 0 \qquad \Leftrightarrow \ \left\langle \vec{p}_1 \left| \frac{\hat{\vec{p}}^2}{2m}\hat{T}_{\tilde{D}} - \hat{T}_{\tilde{D}}\frac{\hat{\vec{p}}^2}{2m} \right| \vec{p}_2 \right\rangle &= 0 \quad \forall \vec{p}_1, \vec{p}_2 \\ = \left(\frac{\vec{p}_1^{\,2}}{2m} - \frac{\vec{p}_2^{\,2}}{2m}\right) \underbrace{\langle\vec{p}_1|\hat{T}_{\tilde{D}}|\vec{p}_2\rangle}_{=\langle\tilde{D}\cdot\vec{p}_1|\vec{p}_2\rangle=\delta(\tilde{D}\cdot\vec{p}_1-\vec{p}_2)} & \\ = \left(\frac{\vec{p}_1^{\,2}}{2m} - \frac{(\tilde{D}\cdot\vec{p}_1)^2}{2m}\right) &= 0 \ .\end{aligned}$$

The proof for the potential energy follows completely analogous with the only difference that one multiplies the commutator from left and right with spatial eigenstates $|\vec{r}_1\rangle$ and $|\vec{r}_2\rangle$.

We can now formulate more generally and beyond the one-particle Hamiltonian (1.1): In quantum mechanics, every unitary operator which commutes with $\hat{H}$ describes a symmetry transformation of the system. As in classical mechanics, the following also applies here: if $\hat{T}_1$, $\hat{T}_2$ are symmetry transformations, so is $\hat{T}_1 \cdot \hat{T}_2$, because $\hat{T}_1 \cdot \hat{T}_2$ is obviously also unitary and it is

$$[\hat{H}, \hat{T}_1 \cdot \hat{T}_2] = 0 \; .$$

This leads again to the connection with the group theory in the following chapters.

Chapter 2

Groups: Definitions and Properties

2.1 Definition of Groups

A *group* G is a set of elements, $a, b, c, \ldots$ (or $a_1, a_2, \ldots$), having the following properties:

(1) A relationship called *multiplication* is defined between the elements of the group, which assigns to every ordered pair of elements a, b an element $c = a \cdot b$ of the group. c is called the *product* of a and b.

(2) The multiplication satisfies the *associative law*

$$(a \cdot b) \cdot c = a \cdot (b \cdot c) \ .$$

(3) The group contains the *identity element*, that is, an element E such that

$$a \cdot E = E \cdot a = a$$

for every element a of the group.

(4) The group contains, for every element a, the corresponding *inverse element* a^{-1} with the defining property

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

In our group definition, we have already restricted ourselves by assuming that the group elements can be counted. Of course there are also groups that are uncountable, for example the group $O(3)$, which consists of the set of all orthogonal matrices. A group G is said to be *finite* if it contains a finite number of elements. The number g of elements is called the *order* of G. In solid-state physics, all groups concerned are finite or can be made finite by introducing periodic boundary conditions. A finite group is specified by its *multiplication table* or *group table*, which lists the product of every pair. For example, the only group with order $g = 2$ has the multiplication table shown in table 2.1(left). The first column (line) of a group table shows the first (second) factor a (b), and the corresponding product $c = a \cdot b$ is shown in the table.

The statement that there exists only one group for $g = 2$ actually requires an additional definition: two groups G and G' are considered as identical when they are *isomorphic* ($G \widehat{=} G'$), i.e., when there is a bijective mapping

$$f : G \leftrightarrow G'$$

such that

$$f(a \cdot b) = f(a) \cdot f(b) \tag{2.1}$$

for all $a, b \in G$. If there was another group of order $g = 2$ it would have a different multiplication table, e.g., the one in table 2.1 (right). This table, however, is not consistent with the assumed order of the group, since, if we multiply $a \cdot a = a$ with a^{-1} it follows $a = E$. This means that the set would have only one and not two elements ($g = 1$).

A group G is said to be *Abelian* if the multiplication satisfies the commutative law

$$a \cdot b = b \cdot a \qquad \forall a, b \in G \,.$$

The smallest integer number n with

$$a^n \equiv \underbrace{a \cdot a \cdot \ldots a}_{\text{n elements}} = E$$

is called the *order of the element*. In finite groups, an order can be assigned to every element.
Proof: We define the series of group elements

$$b_1, b_2, \ldots, b_i \ldots \equiv a, a^2, \ldots, a^i \ldots \quad .$$

In a finite group, it must be $b_i = b_j$ for some $j > i$. Then we can conclude[1]

$$a^i = a^j|_{\cdot(a^{-1})^i} \Rightarrow \ a^i \cdot (a^{-1})^i = a^j \cdot (a^{-1})^i \Rightarrow E = a^{j-i} \ . \ \blacksquare \tag{2.2}$$

A group G is said to be *cyclic* if there is a *generating element* $a \in G$ such that a^i takes the value of every element of the group when i takes all integer numbers $i \leq g$. The order of the generating element of a cyclic group is equal to the order of that group. For every order g, there exists exactly one cyclic group of that order. Any cyclic group is Abelian.[2]

For any given order g there is a finite number $N(g)$ of groups and a finite number $N_a(g)$ of Abelian groups. Table 2.2 shows these numbers for various values of g. For every order, there is at least one Abelian group, namely the cyclic group of that order. The minimum order for which there exists more than one group is $g = 4$. The non-Abelian group of smallest order has g=6. We will discuss these three groups in the following section.

2.2 Examples

As examples, we consider the groups D_2, C_4 (both $g = 4$) and D_3 ($g = 6$).

2.2.1 The group D_2

The group D_2 (also denoted as the *dihedral group*) is a group of order $g = 4$.[3]. We imagine the groups to take the form of certain spatial transformations (rotations and reflections). The dihedral group can then be regarded as the set of all rotations in space (ignoring the reflection symmetries) which map a cuboid with edges of unequal length onto itself, see Fig. 2.1. These

[1] The bar in (2.2) means that both sides of the quation are multiplied with $(a^{-1})^i$ from the right.
[2] Both these statements can be readily shown as an excercise.
[3] The notations for point groups, such as D_2, are introduced systematically in Chapter 3.

	E	a
E	E	a
a	a	E

	E	a
E	E	a
a	E	a

Table 2.1: Left: multiplication table of the only group with order $g = 2$; Right: A $g = 2$ multiplication table which violates the group axioms.

g	1	2	3	4	5	6	7	8	10	12	24	48
$N(g)$	1	1	1	2	1	2	1	5	2	5	15	32
$N_a(g)$	1	1	1	2	1	1	1	3	1	2	3	5

Table 2.2: Number of groups $N(g)$ and Abelian groups $N_a(g)$ for various values of the group order g.

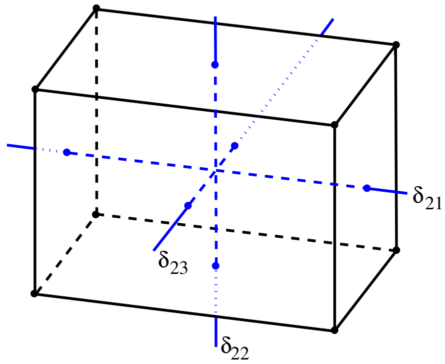

Figure 2.1: Symmetry group D_2: Cuboid with edges of unequal length.

are evidently, apart from the identity transformation, the three rotations through π about the axes δ_{2i} $(i = 1, 2, 3)$. Since repetition of a rotation through π about a coordinate axis gives the identity transformation, these axes are said to be *twofold rotational axes* or *twofold axes of symmetry*.[4] Elements corresponding to rotations will be denoted by δ throughout this manuscript, with one subscript denoting the order of the element and the other counting the axis of rotation.

We can now easily set up the multiplication table for D_2, see Table 2.3. The group D_2 is obviously Abelian because the multiplication table is symmetrical. Every element is its own inverse. Hence, the main diagonal contains only unit elements. The group is not cyclical because no element δ_{2i} is a multiple of another.

	E	δ_{21}	δ_{22}	δ_{23}
E	E	δ_{21}	δ_{22}	δ_{23}
δ_{21}	δ_{21}	E	δ_{23}	δ_{22}
δ_{22}	δ_{22}	δ_{23}	E	δ_{21}
δ_{23}	δ_{23}	δ_{22}	δ_{21}	E

Table 2.3: Multiplication table of the dihedral group D_2.

2.2.2 The cyclic group C_4

The only other group of order 4 is the cyclic group C_4. Its elements. can be regarded as corresponding to all the rotations which leave unchanged a right square pyramid, see Fig. 2.2. These are clearly all the powers of the rotation δ_4 about the fourfold axis of the pyramid. The multiplication table for C_4 is as shown in Table 2.4. The group C_4, being cyclic, is neccessarily Abelian. Note that

$$\delta_4^{-1} = \delta_4^3 \ , \quad \left(\delta_4^3\right)^{-1} = \delta_4 \ .$$

[4]In general, a *n-fold rotation* has a rotation angle of $\varphi_n = 2\pi/n$.

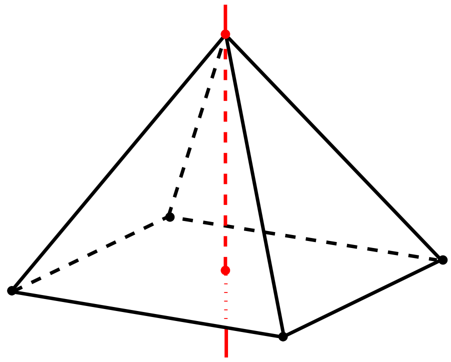

Figure 2.2: Symmetry group C_4: right square pyramid.

	E	δ_4	δ_4^2	δ_4^3
E	E	δ_4	δ_4^2	δ_4^3
δ_4	δ_4	δ_4^2	δ_4^3	E
δ_4^2	δ_4^2	δ_4^3	E	δ_4
δ_4^3	δ_4^3	E	δ_4	δ_4^2

Table 2.4: Multiplication table of the cyclic group C_4.

2.2.3 The group D_3

The simplest non-Abelian group D_3 is of order 6. It can be thought of as being represented by the set of all rotations that leave a prism with the base of an equilateral triangle invariant. These are rotations about a threefold axis perpendicular to the triangles, and rotations about three twofold axes through the centers of opposing edges and sides. The elements of the group D_3 are therefore E, δ_{21}, δ_{22}, δ_{23}, δ_3, δ_3^2, see Fig. 2.3. Setting up the multiplication table is not as straighforward as in the previous examples. We consider the rotation axes as motionless and need to find out at which position the three vertices $A, \ldots F$ are positioned after two rotations have been carried out. As an example, we want to show that $\delta_{21} \cdot \delta_3 = \delta_{22}$. To this end, we consider

$$\begin{pmatrix} A \\ B \\ C \\ D \\ E \\ F \end{pmatrix} \xrightarrow{\delta_3} \begin{pmatrix} C \\ A \\ B \\ F \\ D \\ E \end{pmatrix} \xrightarrow{\delta_{21}} \begin{pmatrix} F \\ E \\ D \\ C \\ B \\ A \end{pmatrix}$$

The same rotation is given by δ_{22}, i.e.,

$$\begin{pmatrix} A \\ B \\ C \\ D \\ E \\ F \end{pmatrix} \xrightarrow{\delta_{22}} \begin{pmatrix} F \\ E \\ D \\ C \\ B \\ A \end{pmatrix} .$$

Note that the direction of the rotations can be chosen arbitrarily. This choice influences the multiplication table, but leads here only to an irrelevant rearrangement of the group elements. Our choice leads to the group table is shown in Table 2.5.

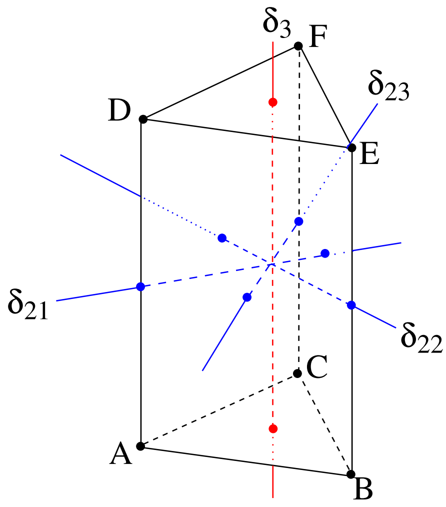

Figure 2.3: Symmetry group D_3: leaves a prism with the base of an equilateral triangle invariant.

$$\begin{array}{lcl} \text{order } 1 & : & E \\ \text{order } 2 & : & \delta_{21}\ ,\ \delta_{22}\ ,\ \delta_{23}\ , \\ \text{order } 3 & : & \delta_3\ ,\ \delta_3^2\ . \end{array}$$

	E	δ_3	δ_3^2	δ_{21}	δ_{22}	δ_{23}
E	E	δ_3	δ_3^2	δ_{21}	δ_{22}	δ_{23}
δ_3	δ_3	δ_3^2	E	δ_{23}	δ_{21}	δ_{22}
δ_3^2	δ_3^2	E	δ_3	δ_{22}	δ_{23}	δ_{21}
δ_{21}	δ_{21}	δ_{22}	δ_{23}	E	δ_3	δ_3^2
δ_{22}	δ_{22}	δ_{23}	δ_{21}	δ_3^2	E	δ_3
δ_{23}	δ_{23}	δ_{21}	δ_{22}	δ_3	δ_3^2	E

Table 2.5: Multiplication table of the group D_3.

2.3 Classes of conjugate elements

2.3.1 The rearrangement theorem

A simple, but very usefull statement is the *rearrangement theorem*. It states that, for all finite groups $G = \{a_1, \ldots, a_g\}$ and any element $a \in G$, we have

$$G' \equiv a \cdot G \equiv \{a \cdot a_1, \ldots, a \cdot a_g\} = G\ . \tag{2.3}$$

Here the last equation means that the sets on both sides are the same, i.e., disregarding the order of the elements. In other words, the multiplication of all elements of a group with one of its elements merely rearranges the group. As a consequence, in each line (and each column) of a multiplication table all group elements appear, as it has been the case in our three examples in section 2.2.

Proof: Let us assume that not all of the elements of G were contained in G'. In that case, at least two of the elements of G' (e.g., $a \cdot a_i$ and $a \cdot a_j$) had to be the same. Then, however, we find $a \cdot a_i = a \cdot a_j \Rightarrow a_i = a_j$ which contradicts the definition of G'.$\blacksquare$

2.3.2 Definition and Properties of Classes

Two elements $a, b \in G$ are said to be *conjugate* ($a \sim b$) if and only if there exists an element $c \in G$ such that $a = c^{-1} \cdot b \cdot c$. This defines mathematically an *equivalence relationship* because it is reflexive ($a \sim a$), symmetric ($a \sim b \Leftrightarrow b \sim a$), and transitive ($a \sim b \wedge a \sim c \Rightarrow b \sim c$). The symmetry is obvious. That $a \sim a$ follows with $c = E$. If $a \sim b \wedge a \sim c$ there are group elements x, y such that

$$a = x^{-1} \cdot b \cdot x = y^{-1} \cdot c \cdot y \ .$$

Multiplying the right equation from left(right) with $x(x^{-1})$ yields

$$b = (\underbrace{x \cdot y^{-1}}_{=z^{-1} \in G}) \cdot c \cdot (\underbrace{y \cdot x^{-1}}_{\equiv z \in G})$$

which means that $b \sim c$. The conjugacy relationship defines a division of G into *classes of conjugate elements* (or simply *classes*); the number r of classes in G is called the *class number*.

For example, the group D_3 contains $r = 3$ classes C_i,[5]

$$D_3 = \sum_{i=1}^{3} C_i = C_1 \cup C_3 \cup C_3 \ ,$$

with

$$C_1 = \{E\} \ , \ C_2 = \{\delta_3, \delta_3^2\} \ , \ C_3 = \{\delta_{21}, \delta_{22}, \delta_{23}\} \ .$$

Let us now consider some further properties of classes of conjugate elements. In Abelian groups, every element is a class by itself because

$$b = c^{-1} \cdot a \cdot c \Rightarrow b = a \cdot c^{-1} \cdot c = a \ .$$

The number of classes is then equal to the order of the group, $r = g$. The identity element is always a class by itself because

$$E = c^{-1} \cdot a \cdot c|_{c \cdot (\ldots) \cdot c^{-1}} \Rightarrow E = a \ .$$

Elements in the same class have the same order (as defines in section 2.1). For, if a and $b = c^{-1} \cdot a \cdot c$ are conjugate elements and if the order of a is n, then

$$E = a^n = (c \cdot b \cdot c^{-1})^n = \underbrace{(c \cdot b \cdot c^{-1})(c \cdot b \cdot c^{-1}) \ldots (c \cdot b \cdot c^{-1})}_{\text{n elements}} = c \cdot b^n \cdot c^{-1}|_{c^{-1} \cdot (\ldots) \cdot c} \Rightarrow b = E \ .$$

Thus a class includes only rotations about axes of the same order. The converse is not valid. Two elements having the same order may well belong to different classes. For example, the elements δ_{2x} and δ_{2y} of the group D_2 are both of order 2 but belong to different classes since they are elements of an Abelian group.

The inverse class $C_{\bar{i}}$ of C_i consists (by definition) of the inverse elements of C_i. Obviously this is a class, because if with $a, b \in C_i$ and $c \in G$, $a = c^{-1} \cdot b \cdot c$ then it also holds

$$a^{-1} = \left(c^{-1} \cdot b \cdot c\right)^{-1} = c^{-1} \cdot b^{-1} \cdot c \cdot \ \surd$$

[5]Here, and throughout this work, sums are often taken in the sense used in set theory, i.e. it is

$$\sum_l \equiv \cup_l$$

.

It can happen that $C_{\bar{j}} = C_j$, as it is the case in all classes of the group D_3.

We can formulate a rearrangement theorem for classes: Let $C = \{b_1, \ldots, b_m\}$ be a class in G and $a \in G$. Then it is

$$\{a^{-1} \cdot b_1 \cdot a, \ldots, a^{-1} b_m a\} = C \ . \tag{2.4}$$

Proof: Since $d_i \equiv a^{-1} \cdot b_i \cdot a \sim b_i$ it is $d_i \in C$. The rearrangement theorem, however, tells us that all elements on the right-hand side of (2.4) are different, which proves equation (2.4). ■

2.3.3 Class Multiplication

If $C_1, \ldots, C_r$ are the classes of a group G with $r_1, \ldots, r_r$ elements. Then, a product $C_i \cdot C_j$ of two classes $C_i = \{a_1, \ldots, a_{r_i}\}$ and $C_j = \{b_1, \ldots, b_{r_j}\}$ is defined as[6]

$$\begin{aligned} C_i \cdot C_j &= \sum_{\gamma,\beta} a_\gamma \cdot b_\beta \\ &= \{a_1 \cdot b_1, \ldots, a_1 \cdot b_m, a_2 \cdot b_1, \ldots a_{r_i} \cdot b_{r_j}\} \ . \end{aligned}$$

The product is a set of $r_i \cdot r_j$ elements, which may not all be distinct. Then the following theorem holds: The set $C_i \cdot C_j$ consists of entire classes of G and we may write[5]

$$C_i \cdot C_j = \sum_{k=1}^{r} f_{ijk} C_k \ . \tag{2.5}$$

The *class multiplication coefficients* f_{ijk} are positive integers or zero.

Proof: We must show that, if a occurs n times in $C_i \cdot C_j$, then the entire class C_k containing a also occurs n times in $C_i \cdot C_j$. If a occurs n times in $K_i K_j$, there must be n different pairs $a_\lambda^{(i)} \in C_i$, $a_\lambda^{(j)} \in C_j$ with

$$a_\lambda^{(i)} a_\lambda^{(j)} = a \ \ (\lambda = 1, \ldots, n).$$

Now, if K_k is generated from a by the elements b_l $(l = 1, \ldots, r_k)$ so that

$$C_k = \sum_{l=1}^{r_k} b_l^{-1} a b_l \ ,$$

then the elements

$$b_l^{-1} \cdot a \cdot b_l = b_l^{-1} \cdot a_\lambda^{(i)} \cdot b_l = b_l^{-1} \cdot a_\lambda^{(i)} \cdot a_\lambda^{(j)} \cdot b_l = \underbrace{b_l^{-1} \cdot a_\lambda^{(i)} \cdot b_l}_{\in C_i} \underbrace{b_l^{-1} \cdot a_\lambda^{(j)} \cdot b_l}_{\in C_j} \ \ (\lambda = 1, \ldots, n)$$

form the class C_k n times and are contained in $C_i \cdot C_j$. ■

In a later chapter we need an expression for f_{ij1} where $C_1 \equiv \{E\}$. Obviously $f_{ij1} \neq 0$ only if $j = \bar{i}$, i.e., if C_j is the inverse class of C_i. The class C_1 then appears in $C_i \cdot C_{\bar{i}}$ exactly r_i times, namely whenever an element from C_i is multiplied with its inverse in $C_{\bar{i}}$. Mathematically this means[7]

$$c_{ij1} = r_i \delta_{i,\bar{j}} = r_{\bar{i}} \delta_{i,\bar{j}} \tag{2.6}$$

[6]We introduce the class multiplication only because it will be needed in a proof in section 5.2.2. Apart from that it is of no importance in this book. The reader may therefore skip this section.

[7]Here we use the standard Kronecker symbol

$$\delta_{i,j} = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{if } i \neq j \end{cases}$$

As an example, we consider the group D_3. The multiplication of the class $C_2 = C_{\bar{2}}$ with itself yields

$$\begin{aligned} C_2 \cdot C_2 &= \{\delta_3 \cdot \delta_3, \delta_3 \cdot \delta_3^2, \delta_3^2 \cdot \delta_3, \delta_3^2 \cdot \delta_2^3\} \\ &= \{\delta_3^2, E, E, \delta_3\} = C_2 + 2C_1 \ . \end{aligned} \tag{2.7}$$

In the same way, one finds

$$C_1 \cdot C_i = C_i \ , \ C_2 \cdot C_3 = 2C_3 \ , \ C_3 \cdot C_3 = 3C_1 + 3C_2 \ . \tag{2.8}$$

2.3.4 Subgroups and Cosets

A subset G' of a group G is called a *subgroup of G* if its elements themselves satisfy the group axioms. This means in particular that $E \in G'$ and if $a, b \in G'$ then also $a \cdot b \in G'$. According to this definition, trivial subgroups of G are always $\{E\}$ and G itselve. In D_3,

$$\{E, \delta_3, \delta_3^2\} \quad \text{and} \quad \{E, \delta_{2i}\} \ \ (i = 1, 2, 3)$$

are subgroups. On the other hand, however, $G' = \{E, \delta_{21}, \delta_{22}, \delta_{23}\}$ is not a subgroup since, for example, $\delta_{21} \cdot \delta_{22} = \delta_3 \notin G'$.

Let G' be a subgroup of G of order g' and $a \in G$. Then the set

$$L_a \equiv \{a \cdot a_1, \ldots a \cdot a_{g'}, \} = a \cdot G'$$

with also g' elements is called a *left coset of* G'. Two left cosets L_a and L_b (with $a \neq b$) are either identical or have no element in common.

Proof: Let L_a and L_b be given with $a \neq b$. Suppose, contrary to the assertion, that there are elements $c_1, c_2 \in G$, for which

$$c_1 \in L_a, L_b \ , \tag{2.9}$$

$$c_2 \in L_a \ \text{ and } \ c_2 \notin L_b \ . \tag{2.10}$$

Then, because of (2.9), elements $d_1, d_2 \in G'$ exist with

$$c_1 = a \cdot d_1 \ , \tag{2.11}$$

$$c_1 = b \cdot d_2 \ . \tag{2.12}$$

This results in

$$a = c_1 \cdot d_1^{-1} \overset{(2.11)}{=} b \cdot d_2 \cdot d_1^{-1} \ . \tag{2.13}$$

Analogously, because of (2.10), there is a group element $d_1' \in G'$ with

$$c_2 = a \cdot d_1' \overset{(2.13)}{=} b \cdot \underbrace{d_2 \cdot d_1^{-1} \cdot d_1'}_{\in G'} \ .$$

Thus $c_2 \in L_b$ in contradiction to the assumption in (2.10). ■

We can summarize as follows: Each subgroup G' of induces a unique partition of G into disjoint left cosets of the same size. Since this decomposition is always possible, g' (the order of G') must always divide g. Therefore if g is prime, a group cannot have non-trivial subgroups. The number of different left cosets $j = g/g'$ is called the *index* j of the subgroup G' relative to G.

In a completely analogous way, one can also make a division into right cosets R_a. Really relevant is only the case where right and left cosets are identical. We will discuss this situation in the following:

2.3.5 Normal subgroups

A subgroup H of G is said to be *normal* or *invariant subgroup* if and only if its right cosets are identical with its left cosets.

In Abelian groups, every subgroup is clearly a normal subgroup. Every subgroup of index 2 is also a normal subgroup, since there are only two left cosets and two right cosets, one of it being the subgroup itself ($\mathcal{L}_E = \mathcal{R}_E = G'$).

For example, one of the subgroups of $G = D_3$ is $G' = \{E, \delta_{21}\}$. Its three left and right cosets are

$$\begin{array}{l|l} \mathcal{L}_E = G' & \mathcal{R}_E = G' \\ \mathcal{L}_{\delta_3} = \mathcal{L}_{\delta_{23}} = \{\delta_3, \delta_{23}\} & \mathcal{R}_{\delta_3} = \mathcal{R}_{\delta_{22}} = \{\delta_3, \delta_{22}\} \\ \mathcal{L}_{\delta_3^2} = \mathcal{L}_{\delta_{22}} = \{\delta_3^2, \delta_{22}\} & \mathcal{R}_{\delta_3^2} = \mathcal{R}_{\delta_{23}} = \{\delta_3^2, \delta_{23}\} \end{array} .$$

Evidently, left and right cosets are different and G' is therefore not a normal subgroup. In contrast, the subgroup $H = \{E, \delta_3, \delta_3^2\}$ of D_3 has to be normal because it has an index $j = 2$. Its cosets are

$$\begin{aligned} \mathcal{L}_E &= \mathcal{R}_E = H \ , \\ \mathcal{L}_{\delta_{21}} &= \mathcal{R}_{\delta_{21}} = \{\delta_{21}, \delta_{22}, \delta_{23}\} \ . \end{aligned}$$

We can formulate a usefull criterion on whether or not a subgroup is normal: H is a normal subgroup of G if and only if H consists of entire classes of G; that is, if an element of G belongs to H, then the entire class of that element must belong to H.

Proof: If

$$H = \{b_1, \ldots, b_m\}$$

consists of entire classes of G and $a \in G$, we find that

$$\mathcal{R}_a = \{b_1 \cdot a, \ldots, b_m \cdot a\} = a \cdot \{a^{-1} \cdot b_1 \cdot a, \ldots, a^{-1} \cdot b_m \cdot a\} \overset{(2.4)}{=} \mathcal{L}_a$$

and H is a normal subgroup. Conversely, if $\mathcal{R}_a = \mathcal{L}_a\ \forall a$, then $H \cdot a = a \cdot H$ which leads to

$$H = a \cdot H \cdot a^{-1} \ .$$

Since this equation is valid for all a, every class element appears on the right side (for some a) or none. So the same must be true for the left side, which proves the statement. ■

2.3.6 Factor Groups

If H is a normal subgroup of G, the cosets $\mathcal{L}_a$ are themselves a group, called the *factor group* G/H, when we define the group algebra as

$$\mathcal{L}_a \cdot \mathcal{L}_a = \mathcal{L}_{a \cdot b} \ , \tag{2.14}$$

$$E = \mathcal{L}_E \ , \tag{2.15}$$

$$\mathcal{L}_a^{-1} = \mathcal{L}_{a^{-1}} \ . \tag{2.16}$$

The group properties obviously hold, e.g. the associative law

$$\mathcal{L}_a \cdot (\mathcal{L}_b \cdot \mathcal{L}_c) = \mathcal{L}_a \cdot (\mathcal{L}_{b \cdot c} = \mathcal{L}_{a \cdot b \cdot c} = \mathcal{L}_{a \cdot b} \cdot \mathcal{L}_c = (\mathcal{L}_a \cdot \mathcal{L}_b) \cdot \mathcal{L}_c \ \surd$$

The elements of $\mathcal{L}_{a \cdot b}$ are all products $a_i \cdot b_j$ of elements $a_i \in \mathcal{L}_a$, $b_j \in \mathcal{L}_b$. Of course, since $\mathcal{L}_{a \cdot b}$ also has g' elements, each of the $(g')^2$ products $a_i \cdot b_j$ appears in $\mathcal{L}_{a \cdot b}$ only once.

Proof: With $a_i \in \mathcal{L}_a$ and $b_j \in \mathcal{L}_b$ we first have to show that $a_i \cdot b_j \in \mathcal{L}_{a\cdot b}$. There exist $h_1, h_2 \in H$ with $a_i = h_1 \cdot a, b_i = b \cdot h_2$. From this it follows

$$a_i \cdot b_j = h_1 \cdot a \cdot b \cdot h_2 \ .$$

Since $a{\cdot}b{\cdot}h_2 \in \mathcal{L}_{a\cdot b}$ and $\mathcal{R}_{a\cdot b} = \mathcal{L}_{a\cdot b}$ there must be another element $h_2' \in H$ with $a{\cdot}b{\cdot}h_2 = h_2'{\cdot}a{\cdot}b$. With this we obtain

$$a_i \cdot b_j = \underbrace{h_1 \cdot h_2'}_{\in H} \cdot a \cdot b \quad \Rightarrow a_i \cdot b_j \in \mathcal{L}_{a\cdot b}$$

Conversely, let $c \in \mathcal{L}_{a\cdot b}$ be given. Then there exists an $h \in H$ with

$$c = a \cdot \underbrace{b \cdot h}_{\equiv b'} \ ,$$

where $a \in \mathcal{L}_a$ and $b' \in \mathcal{L}_b$, i.e., every element of $\mathcal{L}_{a\cdot b}$ can be written as a product of elements of $\mathcal{L}_a$ and $\mathcal{L}_b$. ■

As an example we consider again the group D_3. The only non-trivial normal subgroup here is $H = \{E, \delta_3, \delta_3^2\}$. The factor group G/H then has the two elements $\mathcal{L}_E$ and $\mathcal{L}_{\delta_{21}}$ and is isomorph to C_2.

2.4 Direct Products

For two groups

$$G_1 \equiv \{a_1, a_2, \dots a_{g_1}\}, G_2 \equiv \{b_1, b_2, \dots b_{g_2}\}$$

of orders g_1,g_2 one can define the *direct product*

$$G \equiv G_1 \times G_2$$

with the $g = g_1 \cdot g_2$ elements

$$c_1 \equiv (a_1; b_1), c_2 \equiv (a_1; b_2), \dots, c_{g_2} \equiv (a_1; b_{g_2}), c_{g_2+1} \equiv (a_2; b_1), \dots, c_g \equiv (a_{g_1}; b_{g_2}) \ .$$

With the definition

$$(a_i; b_j) \cdot (a_k; b_l) \equiv (a_i \cdot a_k; b_j \cdot b_l)$$

of the multiplication in G, the group axioms in Sec. 2 are met where

$$c_E \equiv (a_E; b_E) \quad , \quad (a_i; b_j)^{-1} = (a_i^{-1}; b_j^{-1}) \ .$$

In some cases a group G can be written as a direct product of two of its subgroups, for example the group

$$D_2 = \{E, \delta_{2x}\}\{E, \delta_{2y}\} \times \{E, \delta_{2x}\}\{E, \delta_{2y}\} = \{E, \delta_{2x}, \delta_{2y}\, \underbrace{\delta_{2x}\delta_{2y}}_{\delta_{2z}}\} \ .$$

Chapter 3

Point Groups

3.1 Definition of Point Groups

Our definition starts from the *orthogonal group* $O(3)$ of all three-dimensional orthogonal matrices $\tilde{O}$,

$$\tilde{O}^T \cdot \tilde{O} = \tilde{O} \cdot \tilde{O}^T = \tilde{1} \; . \tag{3.1}$$

The group multiplication here is the ordinary matrix multiplication and

$$E = \tilde{1} \; , \; \tilde{O}^{-1} = \tilde{O}^T \; .$$

We define *point groups* as all <u>finite</u> subgroups of $O(3)$. Note that $O(3)$ has also infinite subgroups, e.g., the set of all orthogonal matrices which describe a rotation about a fixed axis (isomorph to $O(2)$). One distinguishes *point groups of the first kind* (or *proper point groups*) $G_{(1)}$ which satisfy[1]

$$|\tilde{O}| = 1 \;\; \forall \tilde{O} \in G_{(1)}$$

from *point groups of the second kind* (or *improper point groups*) $G_{(2)}$ where

$$|\tilde{O}| = -1$$

for at least one $\tilde{O} \in G_{(2)}$. One calls elements with $|\tilde{O}| = 1(-1)$ proper (improper) rotations. Improper rotations $\tilde{O}$ can always be written as a product of a proper rotation $\tilde{O}' \in G_{(1)}$ and the inversion matrix

$$\tilde{I} = -\tilde{1}$$

because the matrix $\tilde{O}' \equiv \tilde{I} \cdot \tilde{O}$ has a determinant $|\tilde{O}'| = 1$ and it is $\tilde{O} = \tilde{I} \cdot \tilde{O}'$. For example, the mirror plane $z = 0$, represented by the matrix

$$\tilde{O} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

is equivalent to a rotation through π about the z-axis,

$$\tilde{O}' = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

followed by the inversion. The same holfs, of course, for any mirror plane.

[1] Recall that orthogonal matrices $\tilde{O}$ can only have determinants $|\tilde{O}| \pm 1$ which follows from equation (**??**

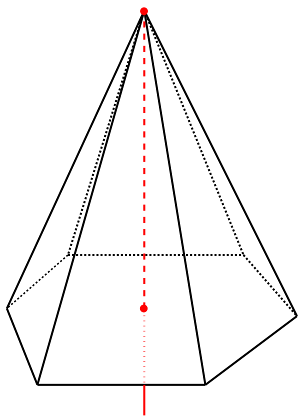

Figure 3.1: Example for a body which is left unchanged by the elements of a group C_n (here, $n = 6$).

With our definition so far, the point group of a body or a physical system depends obviously on the choice of the origin of the coordinate system. We always chose the origin which has the largest symmetry group and assume that such an origin exists in a in an unequivocal way. A proof of this assumption is not necessary, since we will slightly re-define the term ‘point group’ in chapter 12 and with that new definition the point group of a solid will be indepedent of the origin.

3.2 The Point Groups of the First Kind

There are five types of point groups of the first kind which we shall introduce in the following:

The Groups C_n

The cyclic group C_n $(n = 2, 3, \ldots)$ contains all n-fold rotations δ_n^m $(m = 0, 1, \ldots, n-1)$ about a certain axis. Its elements can be regared as all rotations which leave unchanged a pyramid above a regular polygon with n vertices, see Fig. 3.1. The group $C_1 = \{E\}$ of order $g = 1$ is also considered as a member of this family. Note that point groups C_n and C'_n which only have different rotation axes are isomorphic.[2]

The subgroups of C_n are the groups C_l with l being a factor of n. As an Abelian group all elements of C_n are their own classes.

Here and in the following we use bodies that are easy to imagine but actually have a higher symmetry, namely mirror planes which we ignore for the definition of the proper point groups. But of course there are in all these cases more complicated bodies that actually have such a point group symmetry. For example, the body illustrated in Fig 3.2 has the point group C_2 and no further symmetries.

The Groups D_n

The *dihedral groups* D_n $(n = 2, 3, \ldots)$ expand the groups C_n by adding n two-fold rotation axes perpendicular to the main rotation axis. Its elements can be regared as all rotations which leave unchanged a prism above a regular polygon with n vertices, see Figs. 3.3. As we have seen already in the case of the group D_3, the groups D_n are non-Abelian. As figures 3.3

[2] In fact, the groups are not only isomorphic but also *equivalent*. Two point groups G and G' are said to be equivalent if there is a non-singular matrix $\tilde{S}$ (i.e. $|\tilde{S}| \neq 0$) such that for some proper arrangement of the elements it is $\tilde{O}_i = \tilde{S}\tilde{O}'_i(\tilde{S})^i$, $\forall \tilde{O}_i \in G$ (*equivalence transformation*). The term equivalence is dicussed in more detail in Section 4.1.

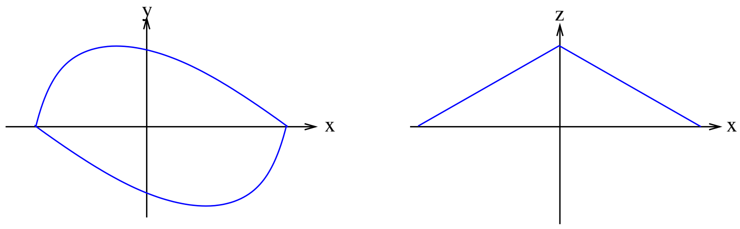

Figure 3.2: A body with C_2 symmetry

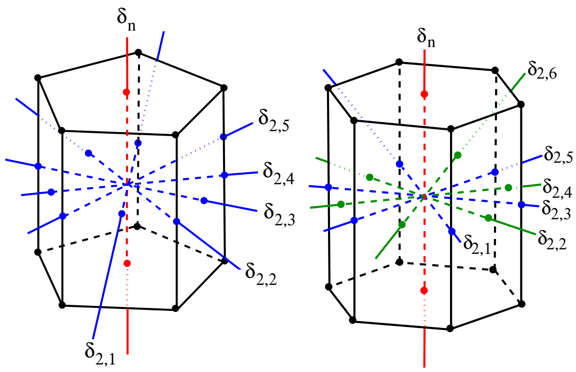

Figure 3.3: Examples for bodies which are left unchanged by the elements of a group D_n (here, $n = 5$ left, and $n = 6$ right); red: the n-fold symmetry axis, blue and green: the two-fold symmetry axes.

show, the situation is qualitatively different for odd and even values of n. For even n the two-fold symmetry axes connect two opposite faces or two opposite edges of the prism, whereas in the odd cases faces and edges are connected. The difference between even and odd n is also reflected in the class- und subgroup structure:

even n:

The subgroups of D_n are D_l and C_l with l being a factor of n. With $m \equiv n/2 \in \mathbb{N}$ we find that the group D_n consists of the following $r = m + 3$ classes

$$D_{2m} = \{E\} \cup \underbrace{\{\delta_n^m\}}_{180°} \cup \underbrace{\{\delta_n^{m'}, (\delta_n^{m'})^{-1}\}}_{1 \le m' < m} \cup \{\delta_{2,1}, \delta_{2,3}, \dots\} \cup \{\delta_{2,2}, \delta_{2,4}, \dots\} \, .$$

odd n:

The subgroups of D_n are the same as for even n plus C_2 because this group is not included in the subgroups of the main rotation axis. With $m \equiv (n-1)/2 \in \mathbb{N}$ we find the following $r = m + 2$ classes

$$D_{2m+1} = \{E\} \cup \underbrace{\{\delta_n^{m'}, (\delta_n^{m'})^{-1}\}}_{1 \le m' \le m} \cup \{\delta_{2,1}, \delta_{2,2}, \dots\}\} \, .$$

The Tetrahedral Group T

The *tetrahedral group* T consists of all rotations which leave unchanged a regular tetrahedron. These are (see Fig. 3.5)

i) three two-fold axes $\delta_{2,i}$ $(i = 1, 2, 3)$ through the centers of opposite edges,

ii) four three-fold axes $\delta_{3,i}$ $(i = 1, \dots 4)$ through the vertex corners and the opposite faces.

The group has three subgroups, D_2, C_3, and C_2 and consists of $r = 4$ classes,

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

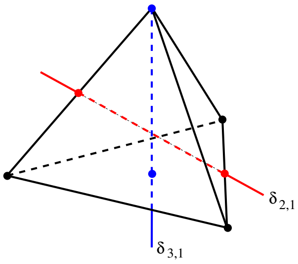

Figure 3.4: 2 of the 7 rotational axes that leave a regular tetrahedron unchanged.

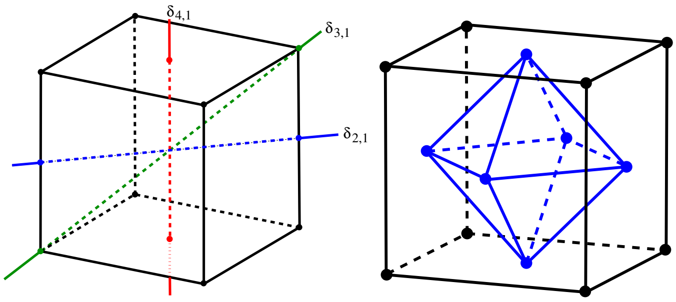

Figure 3.5: left: 3 of the 13 rotational axes that leave a cube unchanged; right:the centers of a cube's faces form a regular octahedron.

The Cubic Group O

The *cubic group* O consists of all rotations which leave unchanged a cube. These are (see Fig. 3.5)

i) six two-fold axes $\delta_{2,i}$ $(i = 1, \ldots, 6)$ through the centers of opposite edges

ii) four three-fold axes $\delta_{3,i}$ $(i = 1, \ldots 4)$ through the opposite vertex corners and the opposite faces

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

The subgroups of O are T, D_4, D_3 and the respective subgroups of these three groups. The class structure 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[2]) to the symmetry group of a regular octahedron. This becomes clear in Fig. 3.5 where we see that the centers of a cube's faces are the vertices of a regular octahedron.

Icosahedron Group Y

The last point group of the first kind is the *Icosahedron Group* Y which consists of all rotations that leave unchanged a regular Icosahedron. A Icosahedron is a body which has 20 equilateral triangles as faces, see Fig. 3.6, left. The elements of Y are

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 the opposite vertex corners and the opposite 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, see Fig. 3.6, right. Since the icosahedron group does not occur in solids, as we will show in the next section, we do not discuss it in more detail here.

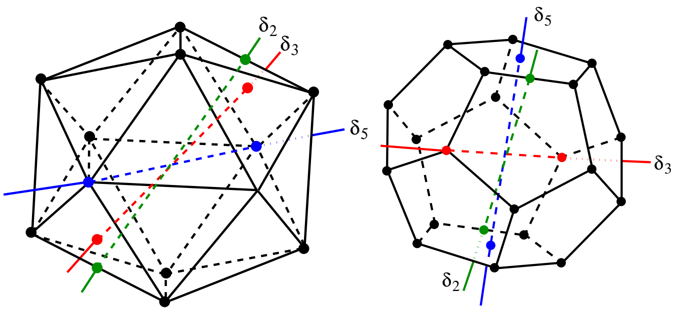

Figure 3.6: left: icosaedron; right: dodecahedron

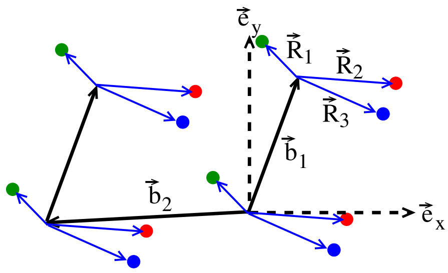

Figure 3.7: Example of a Bravais lattice in 2 dimensions. The Bravais lattice is defined by the vectors $\vec{b}_i$. The vectors $\vec{R}_i$ define a basis at each Bravais lattice site.

3.3 Point Groups in solids

Before we discuss the point groups of the 2nd kind, we want to prove an important theorem: In crystalline solids n-fold rotations can be symmetry transformations only if $n = 2, 3, 4,$ or 5.
Proof: A crystal is described by a Bravais lattice, defined by the basis vectors $\vec{b}_i$, and a basis belonging to each lattice point. A two-dimensional example is shown in Fig. 3.7. A rotation matrix $\tilde{O}$ that leaves a crystal lattice invariant will necessarily also leave the underlying Bravais lattice invariant. The points in a Bravais lattice are given by

$$\vec{B}(n_1, n_2, n_3) = \sum_{i=1}^{3} n_i \vec{b}_i \tag{3.2}$$

where $n_i \in \mathbb{Z}$. By a proper choice of the Euclidean basis vectors $\vec{e}_i$ a rotation can always be represented by a matrix of the form

$$\tilde{O} = \begin{pmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} .$$

Let $\tilde{U}$ be the matrix that connects the two basis sets, i.e.,

$$\vec{b}_i = \sum_j U_{j,i} \vec{e}_j \ .$$

Then the matrix representation $\tilde{O}'$ of the rotation in the basis $\vec{b}_i$,

$$\tilde{O} \cdot \vec{b}_i = \sum_j O'_{j,i} \vec{b}_j$$

is given by[3]

$$\tilde{O}' = \tilde{U}^{-1} \cdot \tilde{O} \cdot \tilde{U} \ . \tag{3.3}$$

[3]This equation is shown in every text book on linear algebra.

If $\tilde{O}$ is a symmetry transformation then $\tilde{O}$, applied to a Bravais lattice vector (3.2), must yield another such vector,

$$\tilde{O} \cdot \vec{B} = \sum_i n_i \tilde{O} \cdot \vec{b}_i = \sum_{i,j} n_i O'_{j,i} \vec{b}_j \stackrel{!}{=} \sum_j n'_j \vec{b}_j \ .$$

The resulting equation

$$\sum_i O'_{j,i} n_i = n'_j \in \mathbb{Z}$$

must be fullfilled for all values of n_i which is only possible if $O'_{j,i} \in \mathbb{Z}$, $\forall i, j$. Then the trace of the matrix (3.3) must be integer too,

$$\mathrm{tr}(\tilde{O}') = \mathrm{tr}(\tilde{U}^{-1} \cdot \tilde{O} \cdot \tilde{U}) = \mathrm{tr}(\tilde{O}) = 2\cos\alpha + 1 \equiv T(\alpha) \in \mathbb{Z}$$

where we have used the invariance of the trace under cyclic permutations. The function $T(\alpha)$ is integer only for the following angles

$$\alpha/\pi = \frac{1}{2}, \frac{1}{3}, \frac{1}{4}, \frac{1}{6}, \tag{3.4}$$

and of course in the trivial case of no rotation, $\alpha = 0$.

With the considerations in this section, we have derived the necessary criterion (3.4) for the rotational symmetries that are possible in solids. As we shall see later, all of these rotational symmetries do actually occur in some Bravais lattices. The point groups of the first kind which comply with (3.4) are

$$C_1, C_2, C_3, C_4, D_2, C_6, D_3, D_4, D_6, T, O \ . \tag{3.5}$$

As discussed above, every improper rotation can be written as a product of a proper rotation with the inversion. Since the inversion is always a symmetry of a Bravais lattice, the angles (3.4) are also the only ones that can be realised in the rotational part of improper rotational symmetrys in solids.

3.4 The Point Groups of the Second Kind

Let G be an improper point group. Then the subgroup G_0 of the proper rotations is a normal subgroup of the group with index 2, i.e. there are two cosets G_0 and L_0, where L_0 contains all improper rotations.

Proof: Obviously we only have to show that G_0 and L_0 have the same number of elements, since in this case the index is $j = g/g_0 = 2$. Since $E \in G_0$, G_0 cannot be empty. Let $\tilde{O}$ be in L_0. Then we find

$$\{\underbrace{\tilde{O} \cdot G_0}_{=L_0}, \underbrace{\tilde{O} \cdot L_0}_{=G_0}\} \stackrel{(2.3)}{=} G \ ,$$

since the elements $\tilde{O} \cdot G_0$ ($\tilde{O} \cdot L_0$) have a determinant 1 (-1) which proves the statement.■

Note that the inversion is not necessarily an element of L_0. For example, in a tetrahedron there are mirror planes in addition to the axes of rotation, although the inversion is obviously not a symmetry transformation. A mirror plane is an improper rotation, see section 3.1. In the following we look one after the other at the improper point groups that contain and do not contain the inversion.

3.4.1 Improper point groups that do not contain the inversion

As we shall show in the following, the improper point groups that do not contain the inversion are isomorphic to one of the proper point groups already introduced. So from a purely mathematical point of view, these groups could be ignored. However, in section we will find physical reasons why it still makes sense to introduce these groups as well.
Proof:
We decompose the group (as above),

$$G = \{G_0, L_0\}$$

and define

$$L'_0 \equiv \tilde{I} \cdot L_0 \ . \tag{3.6}$$

Then we do the proof in the following three steps:

i) L'_0 is (obviously) a set of proper rotations, of which none is in G_0. With $\tilde{O} \in L'_0$ it is $\tilde{I} \cdot \tilde{O} \in G$ (since $\tilde{I}^2 = \tilde{1}$). If $\tilde{O}$ was also in G_0 (and therefore also in G), then also

$$\tilde{I} \cdot \tilde{O} \cdot \tilde{O}^{-1} = \tilde{I} \in G \ ,$$

contrary to the assumption.

ii) The elements of L'_0 are all point group operations of a lattice, because every $\tilde{O} \in L_0$ leaves, by assumption, some Bravais lattice invariant and thus also $\tilde{I} \cdot \tilde{O} \in L'_0$ (because $\tilde{I}$ is a symmetry of all Bravais lattices). Therefore, the elements of L'_0 all comply with (3.4).

iii) Finally, the proper point group $G' \equiv \{G_0, L'_0\}$ is isomorphic to G which follows from the simple bijective mapping $f : G \leftrightarrow G'$:

$$a \in G_0 \quad \rightarrow f(a) = a \in G' \tag{3.7}$$
$$a \in L_0 \quad \rightarrow f(a) = I \cdot a \in G' \tag{3.8}$$

This mapping fulfills condition (2.1) because $\tilde{I}$ commutes with all point group elements.■

We consider a pyramid over a rectangle as an example. The proper point group of this body is $G_0 = C_2 = \{E, \delta_{2z}\}$ with the symmetry axis $\vec{e}_z$. In addition, there are two more

G_0	G	elements of L_0
C_1	C_s	ρ
C_2	S_4	σ_4, σ_4^3
C_2	C_{2v}	2ρ
C_3	C_{3h}	$\sigma_3, \sigma_3^3, \sigma_3^5$
C_3	C_{3v}	3ρ
C_4	C_{4v}	4ρ
D_2	D_{2d}	$\sigma_4, \sigma_4^3, 2\rho$
C_6	C_{6v}	6ρ
D_3	D_{3h}	$\sigma_3, \sigma_3^3, \sigma_3^5, 3\rho$
T	T_d	$6\rho,\ 3\sigma_4,\ 3\sigma_4^3$

Table 3.1: The improper point groups $G = \{G_0, Ł_0\}$ in solids that do not contain the inversion. The symbols used in this table are introduced in Appendix A.2 where we discuss the international notation.

improper symmetry transformations, the mirror planes σ_x $(x = 0)$ and σ_y $(y = 0)$. These form the coset of G_0: $L_0 = \{\sigma_x, \sigma_y\}$. Together they are the group

$$C_{2v} \equiv \{E, \delta_{2z}, \sigma_x, \sigma_y\}$$

Based on the above considerations, we know that C_{2v} must be isomorphic to a proper point group. We also found a to construct it. According to equation (3.6) we only have to multiply $\tilde{I}$ with L_0,

$$L_0' = \{\tilde{I}\sigma_x, \tilde{I}\sigma_y\} = \{\delta_{2,y}, \delta_{2,x}\}$$

where $\delta_{2,x}$, $\delta_{2,y}$ are two-fold rotations about the $x-$ and $y-$axis. Together with $G_0 = C_2$, we obtain the the proper point group D_2. In the same way, starting from the point groups of the first type, we can derive the corresponding point groups of the second type by adding certain improper symmetries. Table (12.1) shows the proper point groups G_0 of order g and the corresponding improper point groups $G = \{G_0, L_0\}$ of order $2g$ with G_0 as a normal subgroup.

3.4.2 Improper point groups that do contain the inversion

Improper point groups that do contain the inversion have the general form

$$G = G_0 \times (\tilde{1}, \tilde{I}) = \{G_0, \tilde{I} \cdot G_0\}$$

where G_0 is one of the 11 proper point groups. Four of these improper point groups are again isomorphic to one of the proper ones, namely

$$C_1 \times (\tilde{1}, \tilde{I}) \widehat{=} C_2 \ , \ C_2 \times (\tilde{1}, \tilde{I}) \widehat{=} D_2 \ , \ C_3 \times (\tilde{1}, \tilde{I}) \widehat{=} C_6 \ , \ D_3 \times (\tilde{1}, \tilde{I}) \widehat{=} D_6 \ .$$

Therefore we can now formulate provisionally: In solids exactly 18 different (abstract) point groups can be realised.

3.5 The 32 point groups in solids

In our statement that there are 18 different point groups, 'different' means 'not isomorphic'. Two point groups which are identical in the abstract sense, are not necessarily equivalent.[2]. For example, consider the two examples from section ,

$$C_{2v} = \left\{ \tilde{E}, \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \right\} \tag{3.9}$$

$$D_2 = \left\{ \tilde{E}, \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \right\} \tag{3.10}$$

These two sets of matrices cannot be converted into one another by an *equivalence transformation.* This can already be seen from the fact that the traces of these matrices are different and the trace is invariant under an equivalence transformation.

There are in total 32 *inequivalent* point groups in solids. They are listed in Table 3.2. All groups in a row are isomorphic to the same abstract point group given in the first column. The international notation is introduced in Appendix A.2.

The subgroup tree in Figure 3.5 makes it easy to find out which subgroups a group has.

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
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 $\left[\frac{4}{m}\bar{3}\frac{2}{m}\right]$	

Table 3.2: The 32 point groups in solids

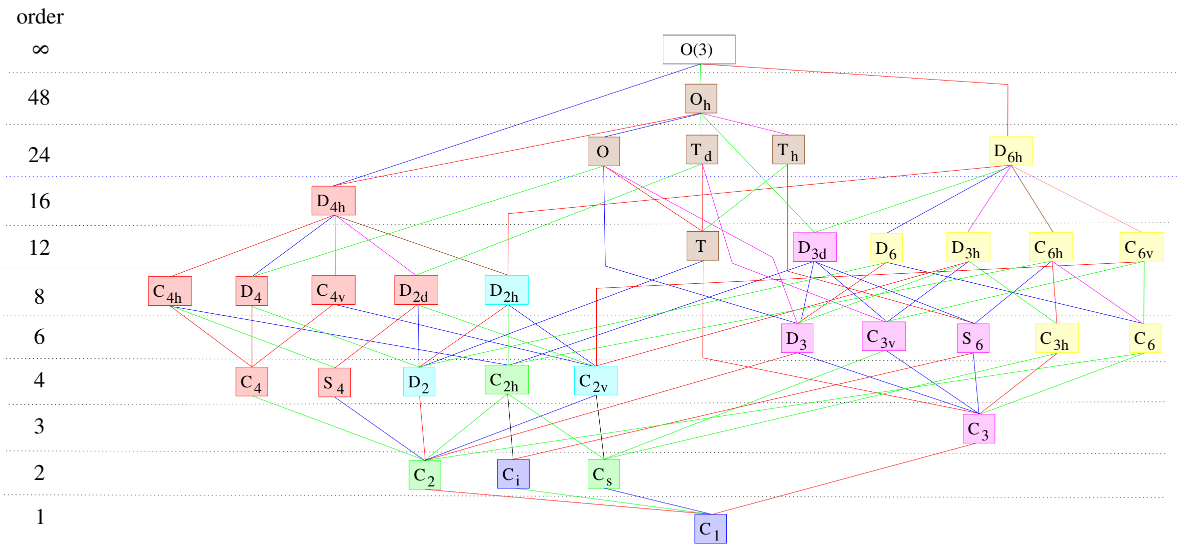

Figure 3.8: The subgroup relationships of the 32 point groups in solids .

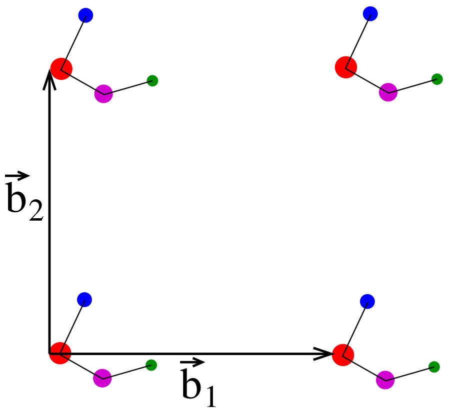

Figure 3.9: An artificial molecule on a square lattice

#	crystal system	point group	possible point groups
1.	triclinic	C_i	C_1
2.	moniclinic	C_{2h}	C_2, C_s
3.	orthorhombic	D_{2h}	C_{2v}, D_2
4.	rhombohedral	D_{3d}	C_3, S_6, D_3, C_{3v}
5.	tetragonal	D_{4h}	$C_4, S_4, C_{4h}, D_4, C_{4v}, D_{2d}$
6.	hexagonal	D_{6h}	$C_6, C_{3h}, C_{6h}, D_6, C_{6v}, D_{3h}$
7.	cubic	O_h	T, T_h, T_d, O, O_h

Table 3.3: The 7 crystal systems, the corresponding point group, possible point groups when there is a basis of more than one atom per Btavais lattice site

3.6 The seven chrystal systems

Finally, we want to turn to the question which of the 32 point groups can be realised in a Bravais lattice. Obviously, these cannot be all 32, since, for example, the inversion must always be included in such a point group. In fact, there are 7 point groups that can be realised in a Bravais lattices. These are called *crystal systems* and listed in Table 3.3. The table also shows which point groups can be realised when there is a basis with more than one atom per Bravais lattice site. In the figure 3.1 of the subgroup structure all point groups which cristallice in the same Bravais lattice are highlighted with the same color. The question why, for example, a basis with a C_1 symmetry cannot exist in a cubic lattice cannot be answered mathematically but only physically. For example, in figure 3.9 one can see that a molecule with the point group C_1 can, in principle, be located on a square lattice. So, mathematically, such a situation cannot be excluded. Physically, however, it is clear that this would not happen in real systems, since the interaction of the molecules would distort the square lattice. Therefore the fourth column in table 3.3 is an experimental finding and not a group theoretical statement.

The reader may remember that in the introductory lectures on solid state physics, one usually introduces 14 different Bravais lattices. For example, primitive (p), body-centered(bcc), and face-centered(fcc) cubic lattices are distinguished, see Fig. 3.10. The point group, however, is in all three cases O_h. To distinguish these three lattices from each another in group-theoretical terms one needs to considers space groups which include not only rotational symmetries but also translations symmetry. We will do that in chapter 12.

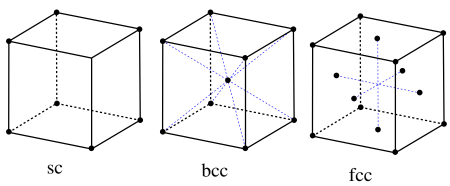

Figure 3.10: Primitive, body-centered, and face-centered cubic lattices

Chapter 4

Representations and Characters

4.1 Matrix Groups

A *matrix group* of order g and dimension d is a set of g quadratic (generally complex) matrices of dimension d,

$$\bar{D} \equiv \{\tilde{D}_1, \ldots, \tilde{D}_g\} \ ,$$

that satisfy the group axioms where the group multiplication is the ordinary matrix multpli- cation. Apparently all matrices of a matrix group must be non-singular ($|\tilde{D}_i| \neq 0$), since the inverse matrix has to exist and is also an element of the group. The matrix $\tilde{1}$ of dimension d must also be in the group. For example, the $g = 6$ matrices

$$\begin{aligned} \tilde{D}_1 &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \ , \ \tilde{D}_2 = \begin{pmatrix} \omega & 0 \\ 0 & \omega^2 \end{pmatrix} \ , \ \tilde{D}_3 = \begin{pmatrix} \omega^2 & 0 \\ 0 & \omega \end{pmatrix} \\ \tilde{D}_4 &= \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \ , \ \tilde{D}_5 = \begin{pmatrix} 0 & \omega \\ \omega^2 & 0 \end{pmatrix} \ , \ \tilde{D}_6 = \begin{pmatrix} 0 & \omega^2 \\ \omega & 0 \end{pmatrix} \end{aligned} \tag{4.1}$$

with $\omega \equiv \exp{(2\pi \mathrm{i}/3)}$ are a group, as can be easily checked. The group is not Abelian because, for example,

$$\tilde{D}_4 \cdot \tilde{D}_2 = \tilde{D}_6 \neq \tilde{D}_2 \cdot \tilde{D}_4 = \tilde{D}_5 \ .$$

Since there is only one non-Abelian group for $g = 3$, see table 2.2, the matrix group 4.1 must be isomorphic to D_3.

4.1.1 Equivalent and Irreducible Matrix Groups

Two matrix groups $\bar{D}, \bar{D}'$ of the same order and dimension are called *equivalent* ($\bar{D} \sim \bar{D}'$) if there is a non-singular matrix $\tilde{S}$ ($|\tilde{S}| \neq 0$) such that

$$\tilde{D}'_i = \tilde{S}^{-1} \cdot \tilde{D}_i \cdot \tilde{S} \ \ \forall i \qquad \text{or in short:} \qquad \bar{D}' = \bar{S}^{-1} \cdot \bar{D}' \cdot \bar{S} \ .$$

The matrix $\tilde{S}$ must be the **same** for all $\tilde{D}_i$. For $g = 1$ this definition corresponds to the equivalence of matrices in linear algebra.

We will need the following mathematical theorem frequently in this manuscript: Every (finite) matrix group is equivalent to a unitary one, i.e., a matrix group that consists only of unitary matrices.

Proof:

Let $\bar{D} = \{\tilde{D}_1, \ldots, \tilde{D}_g\}$ be a matrix group of dimension d. Then we define the matrix

$$\tilde{H} \equiv \sum_{i=1}^{g} \tilde{D}_i \cdot \tilde{D}_i^\dagger \ . \tag{4.2}$$

which is Hermitian and positive definite. The hermiticity is obvious and with an arbitrary vector $\vec{v} \in \mathbb{R}^d$ we find

$$\vec{v}^\dagger \cdot \tilde{H} \cdot \vec{v} = \sum_{i=1}^{g} \underbrace{\vec{v}^\dagger \cdot \tilde{D}_i}_{(\tilde{D}_i^\dagger \cdot \vec{v})^\dagger} \cdot \tilde{D}_i^\dagger \cdot \vec{v} = \sum_{i=1}^{g} \underbrace{|\tilde{D}_i^\dagger \cdot \vec{v}|^2}_{\geq 0} \geq 0$$

which proves the positive definiteness. Let $\tilde{H}$ be diagonalized by the unitary matrix $\tilde{U}$,

$$\tilde{U}^\dagger \cdot \tilde{H} \cdot \tilde{U} = \tilde{A} \equiv \begin{pmatrix} a_1 & & 0 \\ & \ddots & \\ 0 & & a_d \end{pmatrix} . \tag{4.3}$$

Because of the positive definiteness of $\tilde{H}$ we have $a_i \geq 0$. The following matrix is therefore well defined

$$\sqrt{\tilde{A}} \equiv \begin{pmatrix} \sqrt{a_1} & & 0 \\ & \ddots & \\ 0 & & \sqrt{a_d} \end{pmatrix}$$

and can be used to also define the transformation matrix $\tilde{S} \equiv \tilde{U} \cdot \sqrt{\tilde{A}}$ for which holds

$$\tilde{S} \cdot \tilde{S}^\dagger = \tilde{U} \cdot \tilde{A} \cdot \tilde{U}^\dagger \overset{(4.3)}{=} \tilde{H} . \tag{4.4}$$

As the last step we have to show that the transformed matrices

$$\tilde{D}_i' \equiv \tilde{S}^{-1} \cdot \tilde{D} \cdot \tilde{S} \tag{4.5}$$

are unitary:

$$\begin{aligned}
\tilde{D}_i' \cdot \left(\tilde{D}_i'\right)^\dagger &\overset{(4.5)}{=} \tilde{S}^{-1} \cdot \tilde{D}_i \cdot \tilde{S} \cdot \left(\tilde{S}^{-1} \cdot \tilde{D}_i \cdot \tilde{S}\right)^\dagger \\
&= \tilde{S}^{-1} \cdot \tilde{D}_i \cdot \tilde{S} \cdot \tilde{S}^\dagger \cdot \tilde{D}_i^\dagger \cdot \underbrace{\left(\tilde{S}^{-1}\right)^\dagger}_{\left(\tilde{S}^\dagger\right)^{-1}} \\
&\overset{(4.4)}{=} \tilde{S}^{-1} \cdot \tilde{D}_i \cdot \tilde{H} \cdot \tilde{D}_i^\dagger \cdot \left(\tilde{S}^\dagger\right)^{-1} \\
&\overset{(4.2)}{=} \sum_j \tilde{S}^{-1} \cdot \tilde{D}_i \cdot \tilde{D}_j \cdot (\tilde{D}_i \cdot \tilde{D}_j)^\dagger \cdot \left(\tilde{S}^\dagger\right)^{-1} .
\end{aligned}$$

Up to this point, we have not used yet the fact that the matrices $\tilde{D}_i$ form a group. With the rearrangement theorem (2.3), we can replace the sum over $\tilde{D}_i\tilde{D}_j$ by a sum over $\tilde{D}_j$ to obtain

$$\begin{aligned}
\tilde{D}_i' \cdot \left(\tilde{D}_i'\right)^\dagger &= \sum_j \tilde{S}^{-1} \cdot \tilde{D}_j \cdot (\tilde{D}_j)^\dagger \cdot \left(\tilde{S}^\dagger\right)^{-1} \\
&\overset{(4.2)}{=} \tilde{S}^{-1} \cdot \tilde{H} \cdot \left(\tilde{S}^\dagger\right)^{-1} \overset{(4.4)}{=} \tilde{1} \qquad \blacksquare
\end{aligned}$$

Let $\bar{D}$ and $\bar{D}'$ be matrix groups of the (same) order g and with the (possibly different) dimensions d and d'. Then the direct sum' $\bar{D} \oplus \bar{D}'$ of the matrix groups is defined as

$$\bar{D} \oplus \bar{D}' \equiv \{\tilde{D}_1 \oplus \tilde{D}_1', \ldots, \tilde{D}_g \oplus \tilde{D}_g'\}$$

with the $(d+d')$-dimensional matrices

$$\tilde{D}_i \oplus \tilde{D}'_i \equiv \begin{pmatrix} \tilde{D}_i & \tilde{0} \\ \tilde{0} & \tilde{D}'_i \end{pmatrix} .$$

Such matrices are called *block diagonal*.

A matrix group $\bar{D}$ is called *reducible* if it is equivalent to a direct sum of two matrix groups $\bar{D}^{(1)}, \bar{D}^{(2)}$ of smaller dimensions. This means that there is a matrix $\tilde{S}$ such that

$$\tilde{S}^{-1} \cdot \bar{D} \cdot \tilde{S} = \{\tilde{S}^{-1} \cdot \tilde{D}_1 \cdot \tilde{S}, \ldots, \tilde{S}^{-1} \cdot \tilde{D}_g \cdot \tilde{S}\} = \bar{D}^{(1)} \oplus \bar{D}^{(2)}$$

Otherwise $\bar{D}$ is called *irreducible*.

The following rule applies: If the matrix groups $\bar{D}$ and $\bar{D}'$ are equivalent, i.e., there is a matrix $\tilde{S}$ with

$$\bar{D}' = \tilde{S}^{-1} \cdot \bar{D} \cdot \tilde{S} , \tag{4.6}$$

then either both are reducible or both are irreducible.

Proof:

Assume that $\bar{D}$ is irreducible and $\tilde{P}^{-1} \cdot \bar{D} \cdot \tilde{P}$ is block diagonal (i.e. $\bar{D}'$ is reducible). Then we find with (4.6) that

$$\underbrace{\tilde{P}^{-1} \cdot \tilde{S}^{-1}}_{\equiv \tilde{R}^{-1}} \cdot \bar{D} \cdot \underbrace{\tilde{P} \cdot \tilde{S}}_{\equiv \tilde{R}}$$

is also block diagonal, contrary to the assumption.■

4.1.2 Schur's lemma

To prove Schur's lemma (see below), we will need the following fact: Let $\bar{D}$ be a matrix group of dimension d. Then, obviously, every $\tilde{D}_i \in \bar{B}$ is a linear map in the vector space $\underline{V}^d \equiv \mathbb{C}^d$. If $\tilde{D}$ is now irreducible, then there is no non-trivial subspace $\underline{V}^{d'}$ of $\underline{V}^d$ that is invariant to all $\tilde{D}_i$.[1] Invariance here means

$$\vec{v} \in \underline{V}^{d'} \implies \tilde{D}_i \cdot \vec{v} \in \underline{V}^{d'} .$$

Proof:

i) Let

$$\bar{D}' = \hat{S}^{-1} \cdot \bar{D} \cdot \hat{S} \tag{4.7}$$

be a unitary matrix group equivalent to $\bar{D}$ (which we know exists). If $\bar{D}'$ has an invariant subspace $\underline{V}^{d'}$, so does $\bar{D}$ (and vice versa), namely

$$\underline{U}^{d'} \equiv \hat{S} \cdot \underline{V}^{d'} . \tag{4.8}$$

The two sub spaces $\underline{V}^{d'}$, $\underline{U}^{d'}$ have the same dimension since $|\hat{S}| \neq 0$. That $\underline{U}^{d'}$ is an invariant subspace of $\bar{D}$ follows from

$$\tilde{D}_i \cdot \underline{U}^{d'} \stackrel{(4.8)}{=} \tilde{D}_i \cdot \tilde{S} \cdot \underline{V}^{d'} \stackrel{(4.7)}{=} \hat{S} \cdot \tilde{D}'_i \cdot \tilde{S}^{-1}\tilde{S} \cdot \underline{V}^{d'} = \tilde{S} \cdot \underbrace{\tilde{D}'_i \cdot \underline{V}^{d'}}_{\in \underline{V}^{d'}} \checkmark$$

With this result we can assume in the following second step of the proof that $\bar{D}$ is a unitary matrix group.

[1] *non-trivial* means $d' \neq 0$ and $d' \neq d$)

ii Let $\underline{V}^{d'}$ be a non-trivial subspace of $\bar{D}$ which is spanned by the orthonormal basis $\vec{b}_1, \ldots, \vec{b}_{d'}$, while the space orthogonal to $\underline{V}^{d'}$ is spanned by $\vec{c}_{d'+1}, \ldots, \vec{b}_d$. If we represent the matrices $\tilde{D}_i$ in this basis, we find the matrix element

$$\vec{c}_l^{\dagger} \cdot \underbrace{\tilde{D}_i \cdot \vec{b}_{l'}}_{\equiv \vec{b} \in \underline{V}^{d'}} = \vec{c}_l^{\dagger} \cdot \vec{b} = 0 \quad (\forall l, l')$$

In the last step we have used that $\vec{c}_l^{\dagger} \vec{b}$ is the inner product in a complex vector space and $\vec{c}_l$ is orthogonal to all $\vec{b}_{l'}$ and therefore also to $\vec{b}$. To determine the opposite matrix elements $\vec{b}_l^{\dagger} \cdot \tilde{D}_i \cdot \vec{c}_{l'}$ we first transpose it (the transpose of a number is invariant),

$$\vec{b}_l^{\dagger} \cdot \tilde{D}_i \cdot \vec{c}_{l'} = \vec{c}_{l'}^{\mathrm{T}} \cdot \tilde{D}_i^{\mathrm{T}} \cdot \left(\vec{b}_l^{\dagger}\right)^{\mathrm{T}} = (\vec{c}_{l'}^{\dagger} \cdot \tilde{D}_i^{\dagger} \cdot \vec{b}_l)^* \tag{4.9}$$

Now we use the unitarity of $\tilde{D}_i$

$$\vec{c}_{l'}^{\dagger} \cdot \tilde{D}_i^{\dagger} \cdot \vec{b}_l = \vec{c}_{l'}^{\dagger} \cdot \underbrace{\tilde{D}_i^{-1} \cdot \vec{b}_l}_{\equiv \vec{b} \in \underline{V}^{d'}} = \vec{c}_l^{\dagger} \cdot \vec{b} = 0 \quad (\forall l, l')$$

which proves that (4.9) vanishes. With this result we have shown that after a basis transformation into the basis $\vec{b}_1, \ldots, \vec{b}_{d'}, \vec{c}_{d'+1}, \ldots, \vec{b}_d$, every matrix is block diagonal (i.e. $\bar{D}$ is reducible) in contradiction to the assumption. ■

Schur's Lemma, part one

Let $\bar{D}$ and $\bar{D}'$ be irreducible matrix groups of the same order g and with dimensions d and d'. If there is a $(d \times d')$-dimensional matrix $\tilde{S}$ such that

$$\tilde{S} \cdot \tilde{D}_i' = \tilde{D}_i \cdot \tilde{S} \quad \forall i \; , \tag{4.10}$$

then it is either

i) $\tilde{S} = \tilde{0}$, or

ii) $\tilde{S}$ is square and non-singular, i.e., $\bar{D}$ and $\bar{D}'$ are equivalent.

Proof:

i) Let $\vec{s}_k$ be the d' columns of $\tilde{S}$ and $\underline{V}^{\bar{d}}$ $(\bar{d} \leq d)$ the space spanned by all $\vec{s}_k$. In the first step we want to show that either $\bar{d} = d$ or $\bar{d} = 0$. Equation (4.10), expressed by the vectors $\vec{s}_k$, has the following form

$$\sum_{k'} (\tilde{D}_i')_{k',k} \vec{s}_{k'} = \tilde{D}_i \cdot \vec{s}_k \qquad (\forall k = 1, \ldots, d') \; . \tag{4.11}$$

The left side of equation (4.11) is obviously an element of $\underline{V}^{\bar{d}}$. Therefore, $\tilde{D}_i \cdot \vec{s}_k$ must also be in $\underline{V}^{\bar{d}}$ $(\forall i\ )$. So it is either $\bar{d} = d$ or $d = 0$, because otherwise there would be a non-trivial subspace that is invariant to all $\tilde{D}_i$, in contradiction to the irreducibility of $\tilde{D}_i$. We consider the two cases:

a) If $\bar{d} = d$ then $d' \geq d$, because $d' < d$ vectors $\vec{k}_k$ can not span a d-dimensional vector space $\underline{V}^d$.

b) If $\bar{d} = 0$ it must be $\tilde{S} = \tilde{0}$.

ii) When we adjugate equation (4.10) and go through the same arguments as in ii) we find that it is either $\bar{d} = d'$ and therefore $d \geq d'$ or $\tilde{S} = \tilde{0}$. Here it is used that a matrix group $\bar{D}^\dagger \equiv \{\tilde{D}_1^\dagger, \ldots, \tilde{D}_g^\dagger\}$ is obviously also irreducible if $\bar{D}$ is.

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

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 $\tilde{D}_i$,

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

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

$$\tilde{S} = \lambda \tilde{1} \ . \tag{4.12}$$

Proof:
Let $\lambda \in \mathbb{C}$ be an eigenvalue of $\tilde{S}$. Then $\tilde{S} \equiv \tilde{S} - \lambda\tilde{1}$ also commutes with all $\tilde{D}_i$. But $\tilde{S}'$ is singular and therefore $\tilde{S}' = \tilde{0}$ because of the first part of Schur's lemma, which proves (4.12.)■

4.2 Representations

Let G be a group and $\bar{\Gamma}$ a matrix group. If a homomorphic map $f : G \to \bar{\Gamma}$ exists, f is called a *representation of G*. A *homomorphic* map satisfies

$$\tilde{\Gamma}(a \cdot b) = \tilde{\Gamma}(a) \cdot \tilde{\Gamma}(b) \quad \forall\, a, b \in G \ . \tag{4.13}$$

The same term representation is usually used for both the map f and the image of this map, i.e. the matrix group $\bar{\Gamma}$. The following are some further definitions and remarks:

i) A representation is not necessarily bijective, i.e. two elements $a \neq b \in G$ can be assigned the same matrix. For example,

$$\tilde{\Gamma}(a) = \tilde{1} \quad \forall\, a \in G$$

is always a (trivial) representation (with matrices $\tilde{1}$ of arbitrary dimension).

ii) If f is bijective, the representation $\bar{\Gamma}$ is isomorphic to G and is then called *faithful.*

iii) The following applies to all representations

$$\tilde{\Gamma}(E) = \tilde{1} \quad , \quad \tilde{\Gamma}(a^{-1}) = (\tilde{\Gamma}(a))^{-1} \ .$$

iv) The terms 'equivalence ',' reducibility', etc. are transferred directly from matrix groups to representations.

v) One-dimensional representations are always unitary, i.e., of the form

$$\Gamma(a) = e^{\mathrm{i}\varphi(a)} \quad , \quad \varphi(a) \in \mathbb{R} \ ,$$

because for every $a \in G$ there is an n with $a^n = E$. Then (4.13) leads to $\Gamma(a)^n = 1$ which proves the statement.

vi) Two one-dimensional representations $\bar{\Gamma}$, $\bar{\Gamma}'$ ($\Gamma(a) \in \mathbb{C}$) are inequivalent if and only if they are unequal, because with equivalence we find

$$\Gamma(a) = s^{-1}\Gamma'(a)s \overset{s\in\mathbb{C}}{=} \Gamma(a) \qquad \forall a \in G\ .$$

vii) A cyclic group of order g with the generating element a obviously has the g irreducible representations

$$\Gamma_l(a) = \exp\left(\frac{2\pi \mathrm{i}}{g}\cdot l\right) \quad , \quad \Gamma_l(a^m) = \exp\left(\frac{2\pi \mathrm{i}}{g}\cdot l\cdot m\right) \qquad (l = 1, \ldots, g)$$

We will show later that every Abelian group of order g has exactly g inequivalent irreducible representations, as it is the case here.

As an example, we consider the group D_3 (see Sections 2.2.3 and 3.1),

$$D_3 = \underbrace{\{E\}}_{\equiv C_1} \cup \underbrace{\{\delta_3, \delta_3^2\}}_{\equiv C_2} \cup \underbrace{\{\delta_{21}, \delta_{22}, \delta_{23}, \}}_{\equiv C_3}$$

It has the following three inequivalent, irreducible representations[2]

i) dimension $d = 1$, representation $\bar{\Gamma}^A$: $\Gamma(a) = 1$, $\forall a \in D_3$

ii) dimension $d = 1$, representation $\bar{\Gamma}^B$: $\Gamma(C_1) = 1$, $\Gamma(C_2) = 1$, $\Gamma(C_3) = -1$

ii) dimension $d = 2$, representation $\bar{\Gamma}^E$:

$$\begin{array}{lcl} C_1 & : & \tilde{\Gamma}(E) = \tilde{1} \\ C_2 & : & \tilde{\Gamma}(\delta_3) = \tilde{D}_3\ ,\ \tilde{\Gamma}(\delta_3^2) = \tilde{D}_2\ , \\ C_3 & : & \tilde{\Gamma}(\delta_{21}) = \tilde{D}_3\ ,\ \tilde{\Gamma}(\delta_{22}) = \tilde{D}_5\ ,\ \tilde{\Gamma}(\delta_{23}) = \tilde{D}_6 \end{array}$$

with the matrices $\tilde{D}_i$ introduced in (4.1). The representation $\bar{\Gamma}^E$ is therefore faithful.

In the following we will formulate three theorems that one can best prove collectively. The prove will be given in chapter 5.

Theorem 1: The number of representations in a group is equal to the number of its classes.[1]

The *character* $\chi(a)$ of a group element a in a representation (not necessarily irreducible) $\bar{\Gamma}$ is defined as

$$\chi(a) \equiv \mathrm{Tr}(\tilde{\Gamma}(a))\ . \tag{4.14}$$

The set of all characters is called the *character of the representation*. Equivalent representations obviously have the same character. All elements $a \in G$ that belong to the same class have the same character in a (not necessarily irreducible) representation.
Proof:
Let a, a' be in the same class, i.e. there is b with $b^{-1}\cdot a\cdot b = a'$. Then it is

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

[2] As we shall see in Chapter 6, the inequivalent irredecible representations of a symmetry group are of crucial importance in physical applications and will therefore be the subject of much of this book. For this reason, in the following, we will normally mean the inequivalent irredecible representations when we use the term ‘representations of a group’.

The invariance of the trace under cyclic permutations then proves the statement.■

Based on this statement and Theorem 1, each group is assigned a unique (square) so-called character table. For example, one gets the character table with the representation matrices of D_3 (with $\omega + \omega^2 = -1$), shown in table 4.1. In the first column the characters of the class $C_1 = \{E\}$ are usually given, so that the dimension of the representation is shown here. We will discuss the character tables of the 32 point groups in solids in Chapter 7.
The *reduction of a reducible representation* $\bar{\Gamma}$ means finding a matrix $\tilde{S}$ such that

$$\tilde{S}^{-1} \cdot \bar{\Gamma} \cdot \tilde{S} = \underbrace{\bar{\Gamma}^1 \oplus \ldots \bar{\Gamma}^1}_{n_1 \text{ times}} \oplus \underbrace{\bar{\Gamma}^2 \oplus \ldots \bar{\Gamma}^2}_{n_2 \text{ times}} \ldots \oplus \underbrace{\bar{\Gamma}^r \oplus \ldots \bar{\Gamma}^r}_{n_r \text{ times}} \tag{4.15}$$

where the $\bar{\Gamma}_p$ are the irreducible representations of a group and occur n_p times. We will use

$$\bar{\Gamma} = \sum_{p=1}^{r} n_p \bar{\Gamma}_p \,. \tag{4.16}$$

as an abbreviation for equation (4.15) throughout this book.

Theorem 2: The reduction of a reducible representation is unambiguous except for the sequence and equivalence transformations of the representations $\bar{\Gamma}_p$.

Let $G = \{a_1, \ldots, a_g\}$ be a group. Then for every $a_i \in G$ is

$$a_i \cdot a_j = \sum_l \Gamma^{(\mathrm{r})}_{l,j}(a_i) a_l \tag{4.17}$$

where the matrix elements $\Gamma^{(\mathrm{r})}_{l,j}(a_i)$ for a fixed j, i are non-zero ($= 1$) for exactly one value of l. The matrices $\tilde{\Gamma}(a_i)$ form the (faithful) so-called *regular representation* $\bar{\Gamma}^{(\mathrm{r})}$ of G. For example, the regular representation matrixes of D_2 are (compare the multiplication table 2.3) $\tilde{\Gamma}^{(\mathrm{r})}(E) = \tilde{1}$ and

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

Proof:

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

$$\begin{aligned} a_k \cdot (a_i \cdot a_j) &\overset{(4.17)}{=} \sum_l \Gamma^{(\mathrm{r})}_{l,j}(a_i) a_k \cdot a_l \overset{(4.17)}{=} \sum_l \Gamma^{(\mathrm{r})}_{l,j}(a_i) \sum_m \Gamma^{(\mathrm{r})}_{m,l}(a_k) a_m \\ &= \sum_m \Big[\sum_l \Gamma^{(\mathrm{r})}_{l,j}(a_i) \Gamma^{(\mathrm{r})}_{l,j}(a_i) \Big] a_m \end{aligned} \tag{4.18}$$

D_3	C_1	C_2	C_3
A	1	1	1
B	1	1	-1
E	2	-1	1

Table 4.1: Character table of the group D_3

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

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

A comparison of (4.18) and (4.19) 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.

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 equation (4.15)), the following equation follows from theorems 1 and 3

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

where r ist the number of classes of G. For our 32 point groups in solids, this equation, together with the information about the number of classes, determins the dimensions almost all representations uniquely. This can be seen in Table 4.2 where the solutions of equation (4.20) are shown for all relevant values of g. Ambiguity would only arise here if there were two solutions for the same g and r. This is not the case for the class numbers found in our 32 point groups with the exception of the groups D_{6h} and O_h.

Equation (4.20) has also a consequence for the irreducible representations of abelian groups. Since for these $r = g$, it follows,

$$d_p = 1 \quad \forall p = 1, \ldots, g,$$

i.e., Abelian groups have only one-dimensional representations.

order	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9	d_{10}	groups
1	1										C_1
2	1	1									C_2, C_i, C_s
3	1	1	1								C_3
4	1	1	1	1							C_4, S_4,D_2, C_{2h}, C_{2v}
6	1	1	2								D_3 , C_{3v}
6	1	1	1	1	1	1					C_6, S_6, C_{3h}
8	2	2									
8	1	1	1	1	2						D_4 , C_{4v}, D_{2d}
8	1	1	1	1	1	1	1	1			C_{4h}, D_{2h}
12	1	1	1	3							T
12	1	1	1	1	2	2					D_6, D_{3d}, C_{6v} ,D_{3h}
12	1	1	1	1	1	1	1	1	2		C_{6h}
12	1	1	1	1	1	1	1	1	1	1	
16	1	1	1	2	3						
16	1	1	1	1	2	2	2				
16	1	1	1	1	1	1	1	3			
16	1	1	1	1	1	1	1	1	2	2	D_{4h}
24	1	1	2	3	3						O , T_d
24	1	1	1	1	2	4					
24	1	1	1	2	2	2	3				
24	1	1	1	1	1	1	3	3			T_h
24	1	1	1	1	1	1	1	1	4		
24	1	1	1	1	2	2	2	2	2		D_{6h}
24	1	1	1	1	1	1	1	2	2	3	
24	1	1	1	1	1	1	1	1	2	2	
48	1	1	1	1	1	1	1	3	4	4	
48	1	1	1	1	1	1	2	2	3	5	
48	1	1	1	1	2	2	3	3	3	3	O_h
48	1	1	1	2	2	2	2	2	3	4	

Table 4.2: Solutions of equation (4.20) for all relevant values of g and class numbers r=1,. . . ,10. For $g = 48$ we only show the solutions with the class number $r = 10$ of the group O_h.

Chapter 5

Orthogonality Theorems

5.1 The Fundamental Theorem in the Theory of Representations

Let $\bar{\Gamma}^p$ and $\bar{\Gamma}^{p'}$ be the inequivalent irreducible representations of a group G of order g. Then the *fundamental theorem in the theory of representations* is given as

$$\sum_{a\in G} \Gamma^p_{i,j}(a)\Gamma^{p'}_{k,l}(a^{-1}) = \frac{g}{d}\delta_{i,l}\delta_{j,k}\delta_{p,p'} \ . \tag{5.1}$$

Here d, d' are the dimensions of $\bar{\Gamma}^p$, $\bar{\Gamma}^{p'}$. The seeming asymmetry of the right side with respect to d, d' is resolved by the fact that the right side is non-zero only if $p = p'$ and therefore $d = d'$. Note that the theorem does not make any statements if $\bar{\Gamma}^p$ and $\bar{\Gamma}^{p'}$ are equivalent or one of the representations (or both) are reducible. If one chooses $\bar{\Gamma}^p$ and $\bar{\Gamma}^{p'}$ as unitary, then

$$\Gamma_{k,l}(a^{-1}) = \left[\tilde{\Gamma}(a)^{-1}\right]_{k,l} = \left[\tilde{\Gamma}(a)^{\dagger}\right]_{k,l} = \Gamma_{l,k}(a)^*$$

and one obtains the alternative form

$$\sum_{a\in G} \Gamma^p_{i,j}(a)\left(\Gamma^{p'}_{l,k}(a)\right)^* = \frac{g}{d}\delta_{i,l}\delta_{j,k}\delta_{p,p'} \tag{5.2}$$

for the theorem.
Proof:
Let $\tilde{Z}$ be an arbitrary $d \times d'$-matrix with which we define the matrix

$$\tilde{P} \equiv \sum_{a\in G} \tilde{\Gamma}^p(a)\cdot \tilde{Z}\cdot \tilde{\Gamma}^{p'}(a)^{-1} = \sum_{a\in G} \tilde{\Gamma}^p(a)\cdot \tilde{Z}\cdot \tilde{\Gamma}^{p'}\left(a^{-1}\right) \ . \tag{5.3}$$

The following applies to this matrix,

$$\tilde{P}\cdot\tilde{\Gamma}^{p'}(b) = \tilde{\Gamma}^p(b)\cdot\tilde{P} \qquad (\forall b\in G) \tag{5.4}$$

because

$$\begin{aligned}
\tilde{P}\cdot\tilde{\Gamma}^{p'}(b) &\overset{(5.3)}{=} \sum_{a\in G}\tilde{\Gamma}^p(a)\cdot\tilde{Z}\cdot\tilde{\Gamma}^{p'}(a)^{-1}\tilde{\Gamma}^{p'}(b) \\
&= \tilde{\Gamma}^p(b)\cdot\sum_{a\in G}\left[\tilde{\Gamma}^p(b)^{-1}\cdot\tilde{\Gamma}^p(a)\right]\cdot\tilde{Z}\cdot\left[\tilde{\Gamma}^{p'}(b)^{-1}\cdot\tilde{\Gamma}^{p'}(a)\right]^{-1} \\
&= \tilde{\Gamma}^p(b)\cdot\sum_{a\in G}\tilde{\Gamma}^p(b^{-1}\cdot a)\cdot\tilde{Z}\cdot\tilde{\Gamma}^{p'}(b^{-1}\cdot a)^{-1} \\
&\overset{(2.4)}{=} \tilde{\Gamma}^p(b)\cdot\tilde{P} \ .
\end{aligned}$$

Equation (5.4) holds for any $\tilde{Z}$. We choose the matrix elements as

$$Z_{m,n} \equiv \delta_{m,j}\delta_{n,k} \tag{5.5}$$

with fixed values of j, k, i.e., the matrix $\tilde{Z}$ has only one non-vanishing matrix element $Z_{i,j} = 1$. With (5.4) and Schur's lemma we can conclude

i) If $\bar{\Gamma}^p$ and $\bar{\Gamma}^{p'}$ are irreducible and inequivalent it must be $\tilde{P} = \tilde{0}$ due to the first part of Schur's lemma. This leads to

$$0 = P_{i,l} \overset{(5.3)}{=} \sum_{a\in G}\sum_{m,n} \Gamma^p_{i,m}(a) Z_{m,n} \Gamma^{p'}_{n,l}\left(a^{-1}\right) \overset{(5.5)}{=} \sum_{a\in G} \Gamma^p_{i,j}(a)\Gamma^{p'}_{k,l}\left(a^{-1}\right) \ . \tag{5.6}$$

ii) If $p = p'$ and $\bar{\Gamma}^p$ is irreducible equation (5.4) and the second part of Schur's lemma demand that

$$\tilde{P} = \lambda \tilde{1} \ . \tag{5.7}$$

With the trace of both sides of this equation we find

$$\underbrace{\mathrm{Tr}(\tilde{P})}_{=g\,\underbrace{\mathrm{Tr}(\tilde{Z})}_{=\delta_{j,k}}} = \lambda \underbrace{\mathrm{Tr}(\tilde{1})}_{=d} \quad \Rightarrow \quad \lambda = \frac{g}{d}\delta_{j,k} \ .$$

The result for λ, inserted in equation (5.7) gives

$$P_{i,l} = \frac{g}{d}\delta_{j,k}\delta_{i,l} \overset{(5.3)/(5.5)}{=} \sum_{a\in G}\sum_{a\in G} \Gamma^p_{i,j}(a)\Gamma^p_{k,l}\left(a^{-1}\right) \ . \tag{5.8}$$

Equations (5.6) and (5.8) combined prove the fundamental theorem in the theory of representations. ■

5.2 Consequences

5.2.1 Theorem 4: Orthogonality of the characters

Let $\bar{\Gamma}^p$ be the representations of a group G of order g and χ^p_i its characters. Due to theorem 1, which we will prove in section 5.2.2, it is $i, p = 1, \ldots, r$, where r is the number of classes of G, as always. Under these conditions,

$$g\delta_{p,q} = \sum_{i=1}^{r} r_i \left(\chi^p_i\right)^* \chi^q_i \tag{5.9}$$

$$\frac{g}{r_i}\delta_{i,j} = \sum_{p=1}^{r} \left(\chi^p_i\right)^* \chi^p_j \tag{5.10}$$

where r_i is the number of elements in the i-th class.

5.2.2 Proof of Theorems 1-4:

i) We consider only unitary representations $\bar{\Gamma}^p$ which is possible because every representation is equivalent to a unitary one, see Sec. 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

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

Proof:

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

where a are the elements of the group. With the definition (4.14) of the character we then find

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

On the one hand, (5.12) proves equation (5.9). On the other hand it follows: There are at most r irreducible representations, because in an r-dimensional space there are at most r orthogonal vectors $\vec{v}^p$. To prove Theorem 1 it remains to be shown that there are also at least r irreducible representations since there are then precisely r such representations. We will do this under point iii).

ii) Let

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

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

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

Here we have used (4.15) and the fact that

$$\mathrm{Tr}(\tilde{S}^{-1} \cdot \tilde{\Gamma}^{(\mathrm{r})}(a) \cdot \tilde{S}) = \mathrm{Tr}(\tilde{\Gamma}^{(\mathrm{r})}(a)) = \sum_p n_p^{(\mathrm{r})} \mathrm{Tr}(\tilde{\Gamma}^p(a)) \ .$$

Multiplying equation (5.13) with $(\vec{v}^q)^\dagger$ from the left then gives

$$(\vec{v}^q)^\dagger \cdot \vec{v}^{(\mathrm{r})} = \sum_p n_p^{(\mathrm{r})} \, (\vec{v}^q)^\dagger \cdot \vec{v}^p \overset{(5.12)}{\Rightarrow} n_p^{(\mathrm{r})} = (\vec{v}^p)^\dagger \cdot \vec{v}^{(\mathrm{r})} \ . \tag{5.14}$$

Because of the definition of the regular representation it is

$$\vec{v}^{(\mathrm{r})} = (\sqrt{g}, 0, \ldots, 0)^T \ . \tag{5.15}$$

whereby we have chosen the class of the one-element as the first component. Recall that the character of E always gives the dimension of the representation $\chi^{(\mathrm{r})}(E) = g$ and

$r_1 = r_E = 1$. For the same reason, $\chi_1^p = \chi^p(E) = d_p$ which together with equation (5.14) gives

$$n_p^{(\mathrm{r})} = d_p \ . \tag{5.16}$$

This proves Theorem 3. The components of the vector equation (5.13) are then given as

$$\sqrt{g}\delta_{i,1} = \frac{\sqrt{r_i}}{\sqrt{g}} \sum_p d_p \cdot \chi_i^p \ ,$$

where we have used (5.15) and (5.16). Since the left side of this equation is zero for $i \neq 1$ and $r_1 = 1$, we can cancel $\sqrt{r_i}$ on the right side. With that we find

$$\sum_p d_p \cdot \chi_i^p = g\delta_{i,1} \ . \tag{5.17}$$

an auxiliary equation that we will need in the following part of the proof.

iii) For each class C_j we define, with respect to a representation $\bar{\Gamma}$ of dimension d, the matrix

$$\tilde{S}_j \equiv \sum_{a \in C_j} \tilde{\Gamma}(a) \ . \tag{5.18}$$

This matrix commutates with every matrix $\tilde{\Gamma}(b)$, because it is

$$\tilde{\Gamma}(b)^{-1}\tilde{S}_j\tilde{\Gamma}(b) \stackrel{(5.18)}{=} \sum_{a \in C_j} \tilde{\Gamma}(b^{-1} \cdot a \cdot b) \stackrel{(2.4)}{=} \tilde{S}_j \ .$$

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

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

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

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

The trace of the two sides of this equation and

$$\sum_{a \in C_j} 1 = r_j$$

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)

$$\tilde{S}_i^p \cdot \tilde{S}_j^p = \sum_{\substack{a \in C_i \\ a \in C_j}} \tilde{S}^p(a \cdot b) \stackrel{(2.5)}{=} \sum_{k=1}^{r} c_{ijk} \tilde{S}_k$$

where c_{ijk} are the multiplication coefficients introduced in Sec. 2.3.3. With Eqs. (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 equation (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 (2.6) 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 $a \in C_i$ and $a^{-1} \in C_{\bar{j}}$ we find ($\tilde{\Gamma}(a)^{-1} = \tilde{\Gamma}(a)^\dagger$)

$$\chi_{\bar{j}}^p = \mathrm{Tr}\left[\tilde{\Gamma}\left(a^{-1}\right)\right] = \mathrm{Tr}\left[\tilde{\Gamma}\left(a\right)^\dagger\right] = \sum_l \Gamma_{l,l}(a)^* = \left(\chi_j^p\right)^* \ .$$

This leads to

$$\sum_p \chi_i^p \cdot \left(\chi_j^p\right)^* = \frac{g}{r_j}\delta_{i,j} \ ,$$

which proves (5.10). With this equation we have now also shown that in the matrix of character vectors $(\vec{v}^1, \ldots, \vec{v}^r)$ not only all columns but also all rows are orthogonal. This means that the rows must be at least r-dimensional, i.e., there are at least r different character vectors. Since we have already shown in i) that there are at most r different character vectors, we now know that there are exactly r such vectors. This proves Theorem 1.

iv) Finally we have to prove Theorem 2, i.e. the uniqueness of the reduction of a representation. Let $\bar{\Gamma}$ be an arbitrary representation of a group G of order g with a reduced form

$$\bar{\Gamma} = \sum_{p=1}^r n_p \cdot \bar{\Gamma}^p \ .$$

Again, this equation translates into a corresponding equation for the characters

$$\chi_i = \sum_{p=1}^r n_p \cdot \chi_i^p \ , \tag{5.22}$$

where (as always) χ_i, χ_i^p are the characters of the class i. We multiply (5.22) with $r_i\,(\chi_i^p)^*$, sum over i, and use equation (5.9),

$$n_p = \frac{1}{g}\sum_{i=1}^r r_i \chi_i \left(\chi_i^p\right)^* \ . \tag{5.23}$$

Since the right side of (5.23) is uniquely defined, the same applies to the left side, i.e. n_p, proving Theorem 2. Equation (5.23) will be of great practical importance at various points in this book, since it can be used to easily determine if and how often an irreducible representation occurs in the reduction of a reducible representation.

5.2.3 Unique criterion for the irreducibility of a representation

The representation $\bar{\Gamma}$ of a group G is irreducible exactly if

$$\sum_{i=1} r_i |\chi_i|^2 = g \tag{5.24}$$

holds for its characters. Otherwise the left side is $> g$. Alternatively, we can write equation (5.24) as a sum over all group elements

$$\sum_{a \in G} |\chi(a)|^2 = g \; . \tag{5.25}$$

Proof:
Let

$$\bar{\Gamma} = \sum_p n_p \cdot \bar{\Gamma}^p \tag{5.26}$$

again be the reduction of $\bar{\Gamma}$. Then it follows with (5.9)

$$\sum_{i=1} r_i \chi_i^* \cdot \chi_i \overset{(5.26)}{=} \sum_{i=1} r_i \sum_{p,q} n_p \cdot n_q \, (\chi_i^p)^* \cdot \chi_i^q \overset{(5.9)}{=} g \sum_p n_p^2$$

If $\bar{\Gamma}$ is irreducible, only one n_p in (5.26) is non-zero and equal to 1. In all other cases, the sum over n_p^2 is greater then one. This proves the criterion.

As an example, we can now verify that the representations of the group D_3 introduced in Section (4.2) are indeed irreducible. With table 4.1 we find for the left side of (5.24)

$$\begin{aligned} A &: \quad 1 + 2 + 3 = 6 (= g) \surd \; , \\ B &: \quad 1 + 2 + 3 = 6 \surd \; , \\ E &: \quad 1 \cdot 2^2 + 2 \cdot (-1)^2 = 6 \surd \; . \end{aligned}$$

Chapter 6

Quantum mechanics and group theory

6.1 Representation spaces

6.1.1 Definition of representation spaces

Let G with elements $a \in G$ be a group isomorphic to the group of unitary operators $\hat{U}_a$ of a Hilbert space $\underline{H}$, i.e.

$$\hat{U}_a \cdot \hat{U}_b = \hat{U}_{a \cdot b} \quad \forall a, b \in G \; .$$

Furthermore, let $\bar{\Gamma}$ be a d-dimensional representation of G. Then a set $\{|\lambda\rangle\}$ of elements from $\underline{H}$ is called *basic functions of the representation* $\bar{\Gamma}$ or *representation functions* if

$$\hat{U}_a |\lambda\rangle = \sum_{\mu=1}^{d} \Gamma_{\mu\lambda} |\mu\rangle \qquad (\forall \lambda \;\text{ and }\; \forall a \in G) \; . \tag{6.1}$$

Obviously, if $\{|\lambda\rangle_1\}$ and $\{|\lambda\rangle_2\}$ are basis functions of the same representation $\bar{\Gamma}$, then

$$|\lambda\rangle = \alpha|\lambda\rangle_1 + \beta|\lambda\rangle_2, \qquad (\lambda = 1, \ldots, d)$$

is also such a function $\forall \alpha, \beta \in \mathbb{C}$. One then says, $|\lambda\rangle$ *belongs to the λ-th row of the representation* $\bar{\Gamma}$.

As an example we consider C_2, the proper point symmetry group of a pyramid over a rectangle, see Figure 2. It has two (one-dimensional) representations shown in Table 6.1.

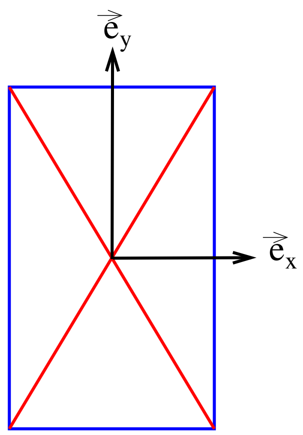

Figure 6.1: A body which is left unchanged by a group C_2 and the coordinate system of the representation functions.

Due to the one-dimensionality of the representations, the characters here are identical to the representation matrices

$$\Gamma^A_{1,1}(E) = 1 \ , \ \Gamma^A_{1,1}(\delta_2) = 1 \ , \ \Gamma^B_{1,1}(E) = 1 \ , \ \Gamma^B_{1,1}(\delta_2) = -1 \ .$$

that describe the transformation behaviour of representation functions. Examples for representation functions in the Hilbert space L^2 are

$$\begin{aligned} A &: \ \Psi_A(\vec{r}) = f(|\vec{r}|) \ \text{ or } \ \Psi_A(\vec{r}) = z \cdot f(|\vec{r}|) \\ B &: \ \Psi_B(\vec{r}) = x \cdot f(|\vec{r}|) \ \text{ or } \ \Psi_B(\vec{r}) = y \cdot f(|\vec{r}|) \end{aligned}$$

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,

$$\begin{aligned} \hat{U}_E \Psi_A(\vec{r}) = \Psi_A(\vec{r}) \ \ , \ \ \hat{U}_E \Psi_B(\vec{r}) = \Psi_B(\vec{r}) \ \ , \\ \hat{U}_{\delta_2} \Psi_A(\vec{r}) = \Psi_A(\vec{r}) \ \ , \ \ \hat{U}_{\delta_2} \Psi_B(\vec{r}) = -\Psi_B(\vec{r}) \ \ .\surd \end{aligned} \tag{6.2}$$

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 $|\lambda\rangle$, $|\mu\rangle$,

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

where we have used that

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

With equation (6.1) we then find

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

In the following, we always assume that representation functions are normalised. The representation functions of a d-dimensional representation $\bar{\Gamma}$ span a d-dimensional subspace $\underline{V}^d$ of the Hilbert space $\underline{H}$. This is called a *representation space of* $\bar{\Gamma}$. A representation generally has an infinite number of representation spaces. Conversely, however, a representation space uniquely defines the corresponding representation (except for equivalence).

Proof

Let equation (6.1) be satisfied and then we choose another basis $|\lambda\rangle_2$ of the representation space, thus

$$|\lambda\rangle_2 = \sum_{\lambda'} U_{\lambda',\lambda}|\lambda'\rangle \ .$$

C_2	E	δ_2
A	1	1
B	1	-1

Table 6.1: Character table of the group C_2

Then,

$$\hat{U}_a|\lambda\rangle_2 = \sum_{\lambda'} U_{\lambda',\lambda}\hat{U}_a|\lambda'\rangle \overset{(6.1)}{=} \sum_{\lambda',\mu'} U_{\lambda',\lambda}\Gamma_{\mu',\lambda'}|\mu'\rangle \ .$$

We can now also express the state $|\mu'\rangle$ in reverse by $|\mu\rangle_2$,

$$|\mu'\rangle = \sum_{\mu} \left(\tilde{U}^{-1}\right)_{\mu,\mu'} |\mu\rangle_2 \ .$$

This leads to

$$\hat{U}_a|\lambda\rangle_2 = \sum_{\mu} \Gamma'_{\mu,\lambda}|\mu\rangle_2$$

with

$$\bar{\Gamma}' = \tilde{U}^{-1}\bar{\Gamma}\tilde{U} \ ,$$

whch proves the statement.

6.1.3 Representation spaces and invariant subspaces

Every representation space is obviously a subspace of $\underline{H}$ invariant with respect to all operators $\hat{U}_a$. But the converse is also true, that every subspace $\underline{V}^d$ invariant with respect to all $\hat{U}_a$ is a representation space.

Proof

Let $|\lambda\rangle$ ($\lambda = 1, \ldots, d$) be a basis of $\underline{V}^d$. Then, the invariance means

$$\hat{U}_a|\lambda\rangle = \sum_{\lambda'} D_{\lambda',\lambda}(a)|\lambda'\rangle \ . \tag{6.3}$$

To prove the statement, only the representation properties of the matrices $\tilde{D}(a)$ have to be shown:

$$\begin{aligned}
\hat{U}_a\hat{U}_b|\lambda\rangle &= \sum_{\lambda''} D_{\lambda'',\lambda}(b)\hat{U}_a|\lambda''\rangle = \sum_{\lambda',\lambda''} D_{\lambda'',\lambda}(b)D_{\lambda',\lambda''}(a)|\lambda'\rangle \\
&= \hat{U}_{a\cdot b}|\lambda\rangle = \sum_{\lambda'} D_{\lambda',\lambda}(a\cdot b)|\lambda'\rangle
\end{aligned}$$

Therefore

$$D_{\lambda',\lambda}(a\cdot b) = \sum_{\lambda''} D_{\lambda',\lambda''}(a)D_{\lambda'',\lambda}(b) \ . \quad \surd \tag{6.4}$$

6.1.4 Irreducibility of representation spaces

A representation space $\underline{V}^d$ of dimension d is called reducible if it can be written as a direct sum of two representation spaces of smaller dimension, i.e.

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

Otherwise the space is called irreducible. It holds that $\underline{V}^d$ is reducible exactly when the same applies to the representation belonging to $\underline{V}^d$.

proof:

We have to do 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.

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

Without limiting generality, we can assume that the bases are orthogonal. Then the matrix $\tilde{S}$ is unitary. With this and equation (6.3) we find ($\tilde{D} \to \tilde{\Gamma}$)

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

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 $\bar{\Gamma}$. One can then easily show that in the base

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

the matrix elements $\langle\mu|\hat{U}_a|\mu'\rangle$ are block diagonal. ∎

As an example, let us look again at the group C_2. The two functions

$$\varphi_1(\vec{r}) \equiv (x+z) f(|\vec{r}|) \ , \tag{6.7}$$
$$\varphi_1(\vec{r}) \equiv (x-z) f(|\vec{r}|) \ . \tag{6.8}$$

form a two-dimensional representation space of this group. This space is obviously reducible, because it can also be spanned by the two irreducible (one-dimensional) representation spaces given by the states

$$\Psi_A(\vec{r}) = z \cdot f(|\vec{r}|) \quad \text{and} \quad \Psi_B(\vec{r}) = x \cdot f(|\vec{r}|)$$

which we have already introduced in Section 6.1.1.

6.1.5 The Expansion Theorem

If $\bar{\Gamma}^p$ ($p = 1, \ldots, r$) are the representations (of dimension d_p) of a group G of operators $\hat{U}_a$. Then every state $|\psi\rangle$ in the Hilbert space of these operators can be written as

$$|\psi\rangle = \sum_{p=1}^{r} \sum_{\lambda=1}^{d_p} |\lambda\rangle^p \ . \tag{6.9}$$

Here the states $|\lambda\rangle^p$ belong to the λ-th line of the representation $\bar{\Gamma}$. Before we prove the theorem, it is worth explaining a few things and looking at an example:

i) We first have to clarify what the statement *the states $|\lambda\rangle^p$ belong to the λ-th line of the representation* $\bar{\Gamma}$ in the theorem actually means. The meaning is that $d_p - 1$ *partner functions* $|\lambda_i\rangle$ exist which together with $|\lambda\rangle^p$ form a representation space of $\bar{\Gamma}^p$ and in which $|\lambda\rangle^p$ belongs to the λ-th row, as defined in Section 6.1.1.

ii) Not for each p and l a state $|\lambda\rangle^p$ has to appear in the expansion (6.9). Formally more precise would therefore be the formula

$$|\psi\rangle = \sum_{p=1}^{r}\sum_{\lambda=1}^{d_p} \alpha_\lambda^p |\lambda\rangle^p \ ,$$

with $\alpha_\lambda^p = 1$ or $\alpha_\lambda^p = 0$. In the literature, however, the shorter formula (6.9) has prevailed.

iii) The d_p states $|\lambda\rangle^p$ $(\lambda = 1, \ldots, d_p)$ in generally do not form a representation space. This can be seen in the following counterexample: As we will see in chapter ??, the three functions

$$p_{[x,y,z]} = [x, y, z] \cdot f(|\vec{r}|)$$

form a three-dimensional representation space of the group O_h. Then, for example,

$$\Psi(\vec{r}) \equiv x f_1(|\vec{r}|) + y f_2(|\vec{r}|) \equiv p_x^1 + p_y^2$$

is already of the form (6.9), but the two functions p_x^1, p_y^2 do not form a representation space unless $f_1(|\vec{r}|) = f_2(|\vec{r}|)$.

iv) We will find a practical way to set up the expansion (6.9) in the next section. However, in the example of group C_2, we can half-guess it. Given an arbitrary function $\Psi(\vec{r}) = \Psi(x, y, z)$. Then

$$\Psi(\vec{r}) = \underbrace{\frac{1}{2}\left[\Psi(x, y, z) + \Psi(-x, -y, z)\right]}_{\equiv \Psi_A(\vec{r})} + \underbrace{\frac{1}{2}\left[\Psi(x, y, z) - \Psi(-x, -y, z)\right]}_{\equiv \Psi_B(\vec{r})} \ .$$

Proof of equation (6.9):
With the elements $a_i \in G$ and $a_1 = E$ we define the g states

$$|\tilde{\Psi}_i\rangle \equiv \hat{U}_{a_i}|\Psi\rangle \ .$$

If the states $|\tilde{\Psi}_i\rangle$ are not orthormal, we orthonormalise them $(|\tilde{\Psi}_i\rangle \to |\Psi_i\rangle)$ keeping the first state constant $(|\tilde{\Psi}_1\rangle = |\Psi_1\rangle = |\Psi\rangle)$. The d-dimensional $(d \le g)$ subspace $\underline{V}^d$ of $\underline{H}$ spanned by the states $|\Psi_i\rangle$ or $|\tilde{\Psi}_1\rangle$ is invariant with respect to all $\hat{U}_a$, because

$$\hat{U}_a|\tilde{\Psi}_i\rangle = \hat{U}_{a\cdot a_i}|\Psi\rangle \in \underline{V}^d \ \ \forall i \ .$$

With section 6.1.2, $\underline{V}^d$ is thus a representation space of a representation $\bar{\Gamma}$ with representation matrices

$$\Gamma_{i,j} = \langle\Psi_i|\hat{U}_a|\Psi_j\rangle \ . \tag{6.10}$$

This representation is, in general, reducible,

$$\bar{\Gamma} \sim \sum_{p=1}^{r} n_p \bar{\Gamma}^p = \tilde{U}^\dagger \bar{\Gamma} \tilde{U} \tag{6.11}$$

with a unitary matrix [1]

$$U_{i,j} \equiv U_{i,(p,m,\lambda)}$$

whose second index is assigned to the irreducible representations ($m = 1, \ldots, n_p$). With this matrix, we define the states

$$|p,m,\lambda\rangle \equiv \sum_i U_{i,(p,m,\lambda)}|\Psi_i\rangle \qquad (m = 1,\ldots,n_p, \lambda = 1,\ldots,d_p)\ .$$

Since $\tilde{U}$ is unitary the inversion of this equation reads

$$|\Psi_i\rangle = \sum_{p,m,\lambda} U^*_{i,(p,m,\lambda)}|p,m,\lambda\rangle\ . \tag{6.12}$$

The states $\{|p,m,\lambda\rangle\}$ with fixed p, m and $\lambda = 1,\ldots,d_p$ span an irreducible representation space of G, as can be seen in the following way

$$\hat{U}_a|p,m,\lambda\rangle = \sum_i U_{i,(p,m,\lambda)}\hat{U}_a|\Psi_i\rangle \tag{6.13}$$

Since

$$\hat{U}_a|\Psi_i\rangle = \sum_j \Gamma_{j,i}(a)|\Psi_j\rangle \overset{(6.12)}{=} \sum_j \sum_{p',m',\lambda'} \Gamma_{j,i}(a)U^*_{j,(p',m',\lambda')}|p',m',\lambda'\rangle$$

we find

$$\begin{aligned}\hat{U}_a|p,m,\lambda\rangle &= \sum_{p',m',\lambda'}\sum_{i,j} U^*_{j,(p',m',\lambda')}\Gamma_{j,i}(a)U_{i,(p,m,\lambda)}|p',m',\lambda'\rangle \\ &\overset{(6.11)}{=} \sum_{\lambda'}\Gamma^p_{\lambda',\lambda}|p,m,\lambda'\rangle \ \checkmark\ . \end{aligned} \tag{6.14}$$

With equation (6.12) we can write the state $|\Psi\rangle = |\Psi_1\rangle$ as

$$|\Psi\rangle = \sum_{p,\lambda} \underbrace{\sum_{m=1}^{n_p} U^*_{1,(p,m,\lambda)}|p,m,\lambda\rangle}_{\equiv|\lambda\rangle^p} \tag{6.15}$$

This, formally, creates an expression of the form in equation (6.9). Of course, we still have to show that the state $|\lambda\rangle^p$ defined in (6.15) has the required properties. For this we identify the partner functions of $|\lambda\rangle^p$ as

$$|\bar{\lambda}\rangle^p \equiv \sum_{m=1}^{n_p} U_{1,(p,m,\lambda)}|p,m,\bar{\lambda}\rangle\ . \tag{6.16}$$

Note that on the right-hand side of this equation, the index 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

$$\hat{U}_a|\bar{\lambda}\rangle^p \overset{(6.16)}{=} \sum_{m=1}^{n_p} U_{1,(p,m,\lambda)}\hat{U}_a|p,m,\bar{\lambda}\rangle \tag{6.17}$$

$$\overset{(6.14)}{=} \sum_{\bar{\lambda}'}\Gamma^p_{\bar{\lambda}',\bar{\lambda}}U_{1,(p,m,\lambda)}|p,m,\bar{\lambda}'\rangle \overset{(6.16)}{=} \sum_{\bar{\lambda}'}\Gamma^p_{\bar{\lambda}',\bar{\lambda}}|\bar{\lambda}'\rangle^p \quad \checkmark\ . \tag{6.18}$$

[1] $\tilde{U}$ can be chosen unitary, since $\bar{\Gamma}$ is unitary and $\bar{\Gamma}^p$ can be assumed to be unitary (see section 4.1.1)

6.1.6 Projection Operators

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

$$\hat{P}^p_{\lambda,\lambda'} \equiv \frac{d_p}{g} \sum_a \left(\Gamma^p_{\lambda,\lambda'}(a)\right)^* \hat{U}_a \ . \tag{6.19}$$

For these applies

i) The d_p operators $\hat{P}^p_{\lambda,\lambda}$ are projection operators[2] and applied to an arbitrary state $|\Psi\rangle$ in (6.9), 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 of $|\lambda\rangle^p$.

Proof:

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

$$\left(\hat{P}^p_{\lambda,\lambda}\right)^\dagger \overset{(6.19)}{=} \frac{d_p}{g} \sum_a \underbrace{\Gamma^p_{\lambda,\lambda}(a)}_{=\left(\Gamma^p_{\lambda,\lambda}(a^{-1})\right)^*} \cdot \underbrace{\hat{U}^\dagger_a}_{=\hat{U}_{a^{-1}}} \overset{(a^{-1}\to a)}{=} \frac{d_p}{g} \sum_a \left(\Gamma^p_{\lambda,\lambda'}(a)\right)^* \hat{U}_a = \hat{P}^p_{\lambda,\lambda} \ ,$$

and

$$\left(\hat{P}^p_{\lambda,\lambda}\right)^2 = \frac{d_p^2}{g^2} \sum_{a,a'} \left(\Gamma^p_{\lambda,\lambda}(a)\right)^* \left(\Gamma^p_{\lambda,\lambda}(a')\right)^* \hat{U}_{a\cdot a'} \overset{(b\equiv a\cdot a')}{=} \frac{d_p^2}{g^2} \sum_{a,b} \left(\Gamma^p_{\lambda,\lambda}(a)\right)^* \left(\Gamma^p_{\lambda,\lambda}(a^{-1}\cdot b)\right)^* \hat{U}_b \ .$$

Since

$$\left(\Gamma^p_{\lambda,\lambda}(a^{-1}\cdot b)\right)^* = \sum_{\lambda'} \left(\Gamma^p_{\lambda,\lambda'}(a^{-1})\right)^* \left(\Gamma^p_{\lambda',\lambda}(b)\right)^*$$

we can evaluate the sum over a with the help of the orthogonality theorem (5.1) and thus it follows

$$\left(\hat{P}^p_{\lambda,\lambda}\right)^2 = \hat{P}^p_{\lambda,\lambda} \ .$$

It remains to be shown that

$$\hat{P}^p_{\lambda,\lambda}|\Psi\rangle = |\lambda\rangle^p \ .$$

We will do that this together with statement ii):

ii) To prove this statement we only have to apply $\hat{P}^p_{\mu,\lambda}$ to a general state (6.9)

$$\hat{P}^p_{\mu,\lambda}|\Psi\rangle \overset{(6.9)}{=} \sum_{p',\lambda'} \hat{P}^p_{\mu,\lambda}|\lambda'\rangle^{p'} \overset{(6.19)}{=} \sum_{p',\lambda'} \frac{d_p}{g} \sum_a \left(\Gamma^p_{\mu,\lambda}(a)\right)^* \hat{U}_a|\lambda'\rangle^{p'} \ . \tag{6.20}$$

With the partner functions $|\mu'\rangle^{p'}$ of $|\lambda'\rangle^{p'}$ we find

$$\hat{U}_a|\lambda'\rangle^{p'} \sum_{\mu'} \Gamma^p_{\mu',\lambda'}(a)|\mu'\rangle^{p'} \ .$$

If one uses this equation in (6.20) and again the orthogonality theorem (5.1), then follows

$$\hat{P}^p_{\mu,\lambda}|\Psi\rangle = |\mu\rangle^p \ .\surd$$

[2]A projection operator $\hat{P}$ has the properties $\hat{P}^\dagger = \hat{P}$ and $\hat{P}^2 = hatP$

With the operators $\hat{P}^p_{\lambda,\lambda}$ the following criterion obviously results: A state $|\Psi\rangle$ belongs exactly to the λ-th line of the representation $\bar{\Gamma}^p$ if

$$\hat{P}^p_{\lambda,\lambda}|\Psi\rangle = |\Psi\rangle \ .$$

To work with the operators $\hat{P}^p_{\lambda,\lambda}$ one needs the representation matrices $\Gamma_{\lambda,\lambda'}(a)$. If one only wants to generate a state that belongs to a representation space of the representation $\bar{\Gamma}^p$ (and not to a defined line) one can alternatively work with the projection operator

$$\hat{P}^p \equiv \sum_\lambda \hat{P}^p_{\lambda,\lambda} = \frac{d_p}{g}\sum_a \left(\chi^p(a)\right)^* \hat{U}_a \tag{6.21}$$

in which only the characters are needed. The calculation with such projection operators is described in great detail in the classic book on group theory in physics by Wigner [?].

As an example, let uns look again at the group C_2. Since here both irreducible representations are one-dimensional, the operators (6.19) and (6.21) are identical and given as

$$\hat{P}^A = \frac{1}{2}\left(\hat{1} + \hat{U}_{\delta_2}\right) \quad , \quad \hat{P}^B = \frac{1}{2}\left(\hat{1} - \hat{U}_{\delta_2}\right) \ .$$

They have the expected properties

$$\hat{P}^A\Psi(x,y,z) = \frac{1}{2}\left(\Psi(x,y,z) + \Psi(-x,-y,z)\right) \ , \tag{6.22}$$

$$\hat{P}^B\Psi(x,y,z) = \frac{1}{2}\left(\Psi(x,y,z) - \Psi(-x,-y,z)\right) \ . \tag{6.23}$$

6.1.7 Theorem on the orthogonality of representation spaces

If $|\lambda\rangle^p$ and $|\lambda'\rangle^{p'}$ belong to the λ-th and λ'-th row of the representations $\bar{\Gamma}^p$ and $\bar{\Gamma}^{p'}$, then they are orthogonal if $p \neq p'$ or $\lambda \neq \lambda'$.

Proof:

The proof is the same as in section 6.1.2.

6.2 Hamiltonians with symmetries

6.2.1 Reminder: degeneracies in quantum mechanics

Let us briefly recall how most textbooks and lectures on quantum mechanics identify the degeneracy of quantum mechanical spectra: Given the Hamiltonian $\hat{H}$ of a physical system. Then one searches for a complete set of observables $\hat{O}_i$ ($i = 1, \ldots, m$) commutating with $\hat{H}$ and with each other.[3] Then, there is a unique basis $|n, \alpha_1, \ldots, \alpha_n\rangle$ of the Hilbert space made up of eigenstates

$$\begin{aligned}\hat{H}|n,\alpha_1,\ldots,\alpha_n\rangle &= E_{n,\alpha_1,\ldots,\alpha_m}|n,\alpha_1,\ldots,\alpha_n\rangle \ , \\ \hat{O}_i|n,\alpha_1,\ldots,\alpha_n\rangle &= \alpha_i|n,\alpha_1,\ldots,\alpha_n\rangle \ .\end{aligned}$$

As an example, let us recall the case of a particle in a rotationally symmetric potential. Here there are two observables, with the above property, e.g., $\hat{O}_1 = \hat{\vec{L}}^2$ and $\hat{O}_1 = \hat{L}_z$ where $\hat{\vec{L}}$ is

[3] Completeness here means that there is no other such observable that cannot be written as a function of the $\hat{O}_i$.

the angular momentum vector operator. The eigenstates and eigenenergies are then given as $|n,l,m\rangle$, $E = E_{n,l}$ where

$$\begin{aligned}\hat{\vec{L}}^2|n,l,m\rangle &= l(l+1)|n,l,m\rangle \quad l = 0,1,\ldots,\infty\ ,\\ \hat{L}_z|n,l,m\rangle &= m|n,l,m\rangle \quad m = -l,\ldots,l\ .\end{aligned}$$

In this approach, the degeneracies of the spectrum and the symmetries of the eigenstates result only from the full diagonalisation of the Hamiltonians. Since one cannot diagonalise most Hamiltonians, it is, in general, of no pratical use. To gain insight into the qualitative nature of a Hamiltonian's spectrum without explicitely diagonalising it, group theory will help us decisively.

A distinction is usually made between *natural and accidental degeneracies*. While the former are preserved in the case of symmetry-preserving changes of $\hat{H}$, in the case of random degeneracies already infinitesimal changes lead to a splitting.

6.2.2 Group Theoretical Treatment

As we motivated in Chapter 1.1, a group of unitary operators $\hat{U}_a$ is called a symmetry group of a Hamiltonian $\hat{H}$ if

$$[\hat{U}_a, \hat{H}] = \quad \forall a\ .$$

The group is called a *maximal symmetry group* if it is not a subgroup of another symmetry group. It holds: If $|\Psi_p\rangle$ is an eigenstate of $\hat{H}$,

$$\hat{H}|\Psi_p\rangle = E_p|\Psi_p\rangle\ ,$$

then

$$|\Psi'_p\rangle \equiv \hat{U}_a|\Psi_p\rangle$$

is obviously also an eigenstate to the the same eigenvalue E_p. The subspace $\underline{V}^p$ to the eigenvalue E_p is therefore invariant subspace with respect to all $\hat{U}_a$. Thus, because of (6.1.3) $\underline{V}^p$ is a representation space of G.

6.2.3 Irreducibility Postulate

Let $\underline{V}^p$ be an eigenspace to the eigenvalue E_p of $\hat{H}$ and thus a representation space to each symmetry group of $\hat{H}$. Then it holds

i) $\underline{V}^p$ is irreducible with respect to the maximum symmetry group, provided the degeneracy is not accidental.

ii) With respect to a non-maximal symmetry group $\underline{V}^p$ is, in general, reducible.

The postulate states that every eigenspace of a Hamiltonian is associated with exactly one irreducible representation of its maximal symmetry group. Therefore, one can classify the eigenstates of a Hamiltonian operator as $|p, m_p, \lambda_p$, where

i) p, as usual, is the index for the irreducible representation.

ii) $m_p = 0,1,\ldots,\infty$ numbers the representation spaces to the same p. In Hilbert spaces of finite dimension there is of course only a finite number of such representation spaces. It can also be $m_p = 0$, i.e. not every irreducible representation has to be realised in the spectrum of a Hamiltonian.

iii) $\lambda_p = 1, \ldots, d_p$ where the dimension of the representation d_p is identical with the degeneracy of the eigenspace.

In the following we will refer to the maximum symmetry group as the symmetry group of $\hat{H}$ for the sake of simplicity.

6.2.4 Example: a particle in a one-dimensional potential

We consider the text-book example of particle in a one-dimensional potential described by the Hamiltonian

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x})$$

with a symmetric potential $V(-x) = V(x)$. The symmetry group of $\hat{H}$ is $C_i = \{E, I\}$. This is isomorphic to C_2 and therefore has the irreducible representations $\bar{\Gamma}^A$ and $\bar{\Gamma}^B$ shown in table 12.1. With the results of this chapter we find the following:

i) Concerning the eigenstates we can conclude: Since the representations are one-dimensional, $\hat{H}$ cannot have any degenerate eigenstates. The eigenstates $\Psi^p(x)$ are either symmetric under inversion ($p = A$) or antisymmetric ($p = B$).

ii) The expansion theorem (6.9) says here that every function $\Psi(x)$ can be written as a linear combination of a symmetric and an antisymmetric function

$$\Psi(x) = \underbrace{\frac{1}{2}\left(\Psi(x) + \Psi(-x)\right)}_{\text{symmetric}} + \underbrace{\frac{1}{2}\left(\Psi(x) - \Psi(-x)\right)}_{\text{antisymmetric}} \tag{6.24}$$

iii) The projection operators that give us the two components in Equation (6.24) are here

$$\hat{P}^A = \frac{1}{2}(1 + I) \quad , \quad \hat{P}^A = \frac{1}{2}(1 - I)$$

6.2.5 Diagonalization of Hamiltonians

In practice, one usually diagonalises a Hamiltonian $\hat{H}$ by choosing a basis $|\varphi_i\rangle$ and then trying to diagonalise the (generally infinite dimensional) Hamiltonian matrix with the elements

$$H_{i,j} = \langle\varphi_i|\hat{H}|\varphi_j\rangle \ .$$

Group theory now helps us to find a suitable basis. Let G be the symmetry group of $\hat{H}$ with the r irreducible representations $\bar{\Gamma}^p$. Then according to section 6.2.3 the Hamiltonian can be written as

$$\hat{H} = \sum_{q, m_q, \lambda_q} E(q, m_q)|q, m_q, \lambda_q\rangle\langle q, m_q, \lambda_q|$$

with the unknown eigenfunctions $|q, m_q, \lambda_q\rangle$ and eigenvalues $E(q, m_q)$ of $\hat{H}$. We now choose a basis $|\varphi_{p,m,\lambda}\rangle$ of the Hilbert space which consists of orthogonal representation spaces with respect to G with irreducible representations $\bar{\Gamma}^p$. Then

$$\begin{aligned} \langle\varphi_{p,m_p,\lambda_p}|\hat{H}|\varphi_{p',m_{p'},\lambda_{p'}}\rangle &= \sum_{q, m_q, \lambda_q} E(q, m_q)\langle\varphi_{p,m_p,\lambda_p}|q, m_q, \lambda_q\rangle\langle q, m_q, \lambda_q|\varphi_{p',m_{p'},\lambda_{p'}}\rangle \\ &\overset{(6.1.7)}{=} \delta_{p,p'}\delta_{\lambda_p,\lambda_{p'}} H^{(p,\lambda)}_{m_p,m_{p'}} \ , \end{aligned} \tag{6.25}$$

where we have introduced

$$H^{(p,\lambda)}_{m_p,m_{p'}} = \langle \varphi_{p,m_p,\lambda_p} | \hat{H} | \varphi_{p',m_{p'},\lambda_{p'}} \rangle \,. \tag{6.26}$$

With equation (6.25), the maximum possible block diagonality due to the symmetry is established. In numerical practice, of course, the procedure introduced here is only worthwhile if $\tilde{H}^{(p,\lambda)}$ can be determined analytically. Applied to the one-dimensional potential in 6.2.4, equation 6.26 means that one can diagonalise the Hamiltonian independently in the space of symmetric and antisymmetric wave functions.

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 quantisation 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

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

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 $(y = 0)$. Therefore, the symmetry group of the molecule is c_{2v}. It has 4 (of course one-dimensional) irreducible representations, which are shown in the character table 6.2. To use equation (6.25), we need a basis of representation spaces. We can determine this with the projection operators 6.21. In this case it is sufficient to take one of the four states $|i\rangle$ and apply the 4 operators $\hat{P}^p$ to it,

$$\begin{aligned}
\hat{P}^{A_1}|1\rangle &\overset{(6.2)}{=} \frac{1}{4}\Big(\hat{U}_E|1\rangle + \hat{U}_{\delta_2}|1\rangle + \hat{U}_{\sigma_1}|1\rangle + \hat{U}_{\sigma_2}|1\rangle\Big) \\
&= \frac{1}{4}\left(|1\rangle + |4\rangle + |2\rangle + |3\rangle\right) \equiv \sqrt{4}|\Psi_{A_1}\rangle \\
\hat{P}^{A_2}|1\rangle &= \frac{1}{4}\left(|1\rangle + |4\rangle - |2\rangle - |3\rangle\right) \equiv \sqrt{4}|\Psi_{A_2}\rangle \equiv \sqrt{4}|\Psi_{A_2}\rangle \\
\hat{P}^{B_1}|1\rangle &= \frac{1}{4}\left(|1\rangle - |4\rangle + |2\rangle - |3\rangle\right) \equiv \sqrt{4}|\Psi_{B_1}\rangle \\
\hat{P}^{B_2}|1\rangle &= \frac{1}{4}\left(|1\rangle - |4\rangle - |2\rangle + |3\rangle\right) \equiv \sqrt{4}|\Psi_{B_2}\rangle \,.
\end{aligned}$$

where the factor $\sqrt{4}$ has been introduced to normalise 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 (6.26) here are one-dimensional with respect to $m_p, m_{p'}$,

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

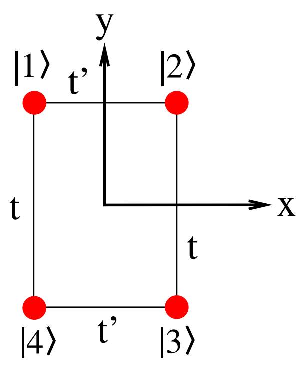

Figure 6.2: A rectangular 'molecule' with one orbital per site.

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

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

Chapter 7

Irreducible representations of the point groups in solids

7.1 Character table with representation functions

In the examples so far, we have mostly considered simple point groups with one-dimensional representations. For more complicated groups, we might need the explicit form of the representation matrices in addition to the character tables. In the literature this information is usually conveyed differently, namely by giving examples of representation spaces in the character table. In Table 7.1 we see this extended character table for the largest of our point groups O_H. In addition to the characters, examples of representation spaces are given here. These are more descriptive than the representation matrices and in principle one can determine the representation matrices from the representation functions with equation (6.10) [1].

We need to discuss this table in more detail:

i) We have only specified representation functions that are linear, quadratic, or cubic in the x, y, z. For the other representations we need higher order functions. As we will see in chapter xxx, the linear, quadratic, or cubic functions are relevant for atoms whose filled shells are p, d, or orbitals. All orders beyond 3 are therefore irrelevant in solid-state

[1] All representations of the 32 point groups can be found on https://www.cryst.ehu.es/

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

Table 7.1: Character table of the group O_H

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	$\begin{cases} 1 \\ 1 \end{cases}$	$\begin{matrix} \mathrm{i} \\ -\mathrm{i} \end{matrix}$	$\begin{matrix} -1 \\ -1 \end{matrix}$	$\begin{matrix} -\mathrm{i} \\ \mathrm{i} \end{matrix}$

Table 7.2: Character table of the group C_4

physics. The missing functions in the table of order $3-6$ are

$$
\begin{aligned}
A_{2\mathrm{u}} &: \ xyz \qquad (7.1)\\
A_{2\mathrm{g}} &: \ x^4(y^2-z^2)+y^4(z^2-x^2)+z^4(x^2-y^2)\\
A_{1\mathrm{u}} &: \ xyz\left[x^4(y^2-z^2)+y^4(z^2-x^2)+z^4(x^2-y^2)\right]\\
E_{\mathrm{u}} &: \ xyz\left[(x^2-y^2, 3z^2-r^2)\right]\\
T_{1\mathrm{g}} &: \ xy(x^2-y^2), xz(x^2-z^2), yz(y^2-z^2)
\end{aligned}
\qquad (7.2)
$$

ii) The following convention has emerged for the designation of the representations: One-dimensional representations are referred to as A or B. The difference between A and B refers to the positive or negative character in the proper rotations around the main symmetry axis. Two- and three-dimensional representations are denoted as E and T, respectively. If $I \in G$, the subscript 'g' or 'u' denotes that the representation is symmetric or antisymmetric under the inversion. Representations such as A' and A'' differ in terms of symmetry or antisymmetry concerning the mirro plane perpendicular to the main symmetry axis.

iii) For groups with complex-valued characters, we need to take a closer look at the character tables. An example is the group C_4, whose character table we have given in table 7.2. Since the group C_4 is Abelian, the four irreducible representations are one-dimensional. Nevertheless, the two representations with complex characters in the character tables are denoted as two-dimensional, which we will further explain here: the two functions

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

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

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

These representation matrices, however, are reducible and are diagonalised via the transformation

$$\Psi_+ \equiv p_x + \mathrm{ip_y} \ , \ \Psi_- \equiv \mathrm{p_x} - \mathrm{ip_y} \ .$$

In this basis the representation matrices are

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

These are exactly the two (conjugate complex) representations that we find in the character table 7.2.

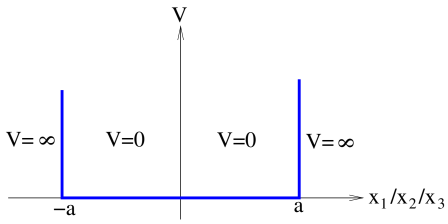

Figure 7.1: Potential of a quantum mechanical particle in a cubic box.

A Hamiltonian in the two-dimensional subspace of p_x and p_y that leads to non-degenerate eigenstates is

$$\hat{H} = \varepsilon \left(|p_x\rangle\langle p_x| + |p_y\rangle\langle p_y| \right) + \mathrm{i}\Omega \left(|\mathrm{p_x}\rangle\langle \mathrm{p_y}| - |\mathrm{p_y}\rangle\langle \mathrm{p_x}| \right)$$

with $\Delta \in \mathbb{R}$. The symmetry group of $\hat{H}$ is still C_4, as one can easily check, and the eigenstates are $\Psi_\pm$ with eigenvalues

$$E_\pm = \varepsilon \pm \Omega \ .$$

However, one-particle Hamiltonians in physics

$$\hat{H}_{\mathrm{sp}} = -\frac{\hbar^2}{2m}\Delta + V(\vec{r})$$

are real, i.e.

$$\langle p_x|\hat{H}_{\mathrm{sp}}|p_y\rangle$$

must be real too which means that $\Delta = 0$ in $\hat{H}$. This leads to a twofold degeneracy, which would not be expected from the point group theory. In most (physical) character tables, one therefore assumes real Hamiltonian operators and denotes such representations discussed as two-dimensional.

This fact that $\hat{H}_{\mathrm{sp}}$ is real means mathematically that $\hat{H}_{\mathrm{sp}}$ commutes with the *conjugation operator* $\hat{K}$. $\hat{K}$ is defined by

$$\hat{K}\Psi(\vec{r}) = \Psi(\vec{r})^* \ .$$

Since the operator $\hat{K}$ is not unitary but anti-unitary,

$$\langle \hat{K}\Psi_1|\hat{K}\Psi_2\rangle = \langle \Psi_2|\Psi_1\rangle \ ,$$

we cannot incorporate it directly into our previous representation theory.

7.2 Example: A particle in a cubic box

As an example of a system with the point group O_h, we consider a quantum mechanical particle in a cubic box with infinitely high potential walls. The Hamiltonian is then given as

$$\hat{H} = \sum_{i=1}^{3} \hat{H}_i \tag{7.3}$$

with

$$\hat{H}_i = \frac{\hat{p}_i^2}{2m} + V(\hat{x}_i)$$

and the potential

$$V(x) = \begin{cases} 0 & \text{if} \ \ |x| \le a \\ \infty & \text{if} \ \ |x| > a \end{cases} \ .$$

To solve the eigenvalue problem

$$\hat{H}\Psi(\vec{r}) = E\Psi(\vec{r}) \tag{7.4}$$

we use the product Ansatz

$$\Psi_{n_1,n_2,n_3}(\vec{r}) \equiv \prod_{i=1}^{3} \Psi_{n_i}(x_i)$$

which, inserted into (7.4), yields the three decoupled equations

$$\hat{H}_i \Psi_{n_i}(x_i) = E_{n_i} \Psi_{n_i}(x_i) \; .$$

This one-dimensional eigenvalue problem (with the boundary conditions $\Psi_{n_i}(\pm a) = 0$) is solved in almost all textbooks on quantum mechanics, and leads to the eigenstates ($n = 1, 2, \ldots$)

$$\Psi_n(x) = \begin{cases} \cos\left(\frac{\pi}{2a} n x\right) & \text{for odd } n \\ \sin\left(\frac{\pi}{2a} n x\right) & \text{for even } n \end{cases}$$

and eigenvalues

$$E_{n_1,n_2,n_3} = \alpha(n_1^2 + n_2^2 + n_3^2) \qquad \left(\alpha = \frac{h^2}{2ma^2}\right) \; .$$

In the following we consider the eigenspaces of lowest energy and try to find the corresponding irreducible representations with the help of table 7.1:

i) $E = 3\alpha$:

$$\Psi_{1,1,1}(\vec{r}) \sim \cos(x_1)\cos(x_2)\cos(x_3) \qquad \left(\frac{\pi}{2a} \equiv 1\right) .$$

This function transform like $x^2 + y^2 + z^2$ and therefore belongs to the irreducible representation A_{1g}.

ii) $E = 6\alpha$:

$$\begin{aligned} \Psi_{1,1,2}(\vec{r}) &\sim \cos(x_1)\cos(x_2)\sin(2x_3) \; , \\ \Psi_{1,2,1}(\vec{r}) &\sim \cos(x_1)\sin(2x_2)\cos(x_3) \; , \\ \Psi_{2,1,1}(\vec{r}) &\sim \sin(2x_1)\cos(x_2)\cos(x_3) \; , \end{aligned}$$

These functions transform like those of the irreducible representation T_{1u}.

iii) $E = 9\alpha$:

$$\begin{aligned} \Psi_{1,2,2}(\vec{r}) &\sim \cos(x_1)\sin(2x_2)\sin(2x_3) \; , \\ \Psi_{2,2,1}(\vec{r}) &\sim \sin(2x_1)\sin(2x_2)\cos(x_3) \; , \\ \Psi_{2,1,2}(\vec{r}) &\sim \sin(2x_1)\cos(x_2)\sin(2x_3) \; , \end{aligned}$$

These functions transform like those of the irreducible representation T_{1g}.

iv) $E = 11\alpha$:

$$\begin{aligned} \Psi_{1,1,3}(\vec{r}) &\sim \cos(x_1)\cos(x_2)\sin(3x_3) \; , \\ \Psi_{1,3,1}(\vec{r}) &\sim \cos(x_1)\sin(3x_2)\cos(x_3) \; , \\ \Psi_{3,1,1}(\vec{r}) &\sim \sin(3x_1)\cos(x_2)\cos(x_3) \; , \end{aligned}$$

For this degenerate space, we do not find a corresponding irreducible representation in Table 7.1 or in (7.1)-(7.2). This means that

a) the eigenspace $\underline{V}^{[1,1,3]}$ must be reducible with respect to O_h,

b) O_h cannot be the maximum point group of the Hamiltonian (7.3) because we would otherwise contradict the postulate 6.2.3.

We start with point a) by introducing the basis transformation

$$\Psi_1^{[1,1,3]} \equiv \frac{1}{\sqrt{3}}(\Psi_{3,1,1} + \Psi_{1,3,1} + \Psi_{1,1,3}) \; ,$$

$$\Psi_2^{[1,1,3]} \equiv \frac{1}{\sqrt{2}}(\Psi_{3,1,1} - \Psi_{1,3,1}) \; , \tag{7.5}$$

$$\Psi_3^{[1,1,3]} \equiv \frac{1}{\sqrt{6}}(2\Psi_{1,1,3} - \Psi_{1,3,1} - \Psi_{3,1,1}) \; . \tag{7.6}$$

It is easy to see that $\Psi_1^{[1,1,3]}$ is another representation function of $A_{1\mathrm{g}}$, i.e.

$$\hat{U}_a \Psi_1^{[1,1,3]} = \Psi_1^{[1,1,3]} \quad \forall a \in G \; . \tag{7.7}$$

The two states $\Psi_2^{[1,1,3]}$,$\Psi_3^{[1,1,3]}$ form a representation space for the representation E_{g} and behave under transformations like $x^2 - y^2$ and $3z^2 - r^2$.

If O_h is not the maximum symmetry group of the Hamilton (7.3), it must commute with other unitary operators. These can readily be found because $\hat{H}$ commutes with all three $\hat{H}_i$. Therefore it also commutes with the unitary operator

$$\hat{U}_i(\alpha) \equiv \exp{(\mathrm{i}\alpha\hat{H}_i)}$$

for any $\alpha \in \mathbb{R}$. [2] Mathematically, the definition of $\hat{U}_i(\alpha)$ is somewhat problematic, considering that $V(x) = \infty$ for $|x| > a$. However, the additional symmetries (7.7) exist for every Hamiltonian of the form (7.3), i.e. also for a potential whose value is v_w just very large but not infinite for $|x| > a$. Then it is clear that the degeneracy cannot disappear in the limit $v_w \to \infty$.

[2] The effects of these additional symmetries are discussed in more detail in arxiv 1310.5136 and Am. J. Phys. 65 (1087).

Chapter 8

Group theory in stationary perturbation theory calculations

8.1 Reminder: Schrödinger's perturbation theory

The typical situation in perturbation theory is a Hamiltonian of the form

$$\hat{H} = \hat{H}_0 + \hat{V}$$

whose eigenvalue problem

$$\hat{H}|n\rangle = E_n|n\rangle$$

we want to solve approximately, whereby the eigenvalue problem

$$\hat{H}_0|n\rangle_0 = E_n^0|n\rangle_0$$

is assumed to be solved. Then we distinguish two cases

i) E_n^0 is non-degenerate. Then the eigenstates $|n\rangle$ and eigenvalues E_n result in the leading order in $\hat{V}$ as

$$\begin{aligned} E_n &= E_n^0 + {}_0\langle n|\hat{V}|n\rangle_0 + \sum_{n'(\neq n)} \frac{|{}_0\langle n|\hat{V}|n'\rangle_0|^2}{E_n^0 - E_{n'}^0} + \mathcal{O}(\hat{V}^3) \,, \\ |n\rangle &= |n\rangle_0 + \sum_{n'(\neq n)} \frac{{}_0\langle n'|\hat{V}|n\rangle_0}{E_n^0 - E_{n'}^0} |n'\rangle_0 + \mathcal{O}(\hat{V}^2) \,. \end{aligned}$$

The group-theoretical question that arises here is how to calculate the matrix elements ${}_0\langle n'|\hat{V}|n\rangle_0$ as simply as possible and, in particular, to identify those that are zero. In physics, the operators V are usually of a form where the Wigner-Eckhart theorem helps us in answering this question, see chapter 10.

ii) E_n^0 is degenerate, so

$$\hat{H}_0|n_i\rangle_0 = E_n^0|n_i\rangle_0 \quad (\text{for } n_i = 1, \ldots, d)$$

The first order energy splitting then results from the diagonalization of the matrix $\tilde{V}$ with the elements

$$V_{i,j} = {}_0\langle n_i|\hat{V}|n_j\rangle_0 \,.$$

The eigenfunctions $|\alpha\rangle$ of $\hat{V}$ with the eigenvalues ΔE_α are called *adapted 0-th order eigenfunctions* with the energies

$$E_\alpha = E_n^0 + \Delta E_\alpha \,.$$

The group-theoretical question that arises here, and which we will analyse in this chapter, is which splittings of the spectra are to be expected based solely on the symmetry groups of $\hat{H}$ and $\hat{H}_0$. Let G and G_0 be the symmetry groups of $\hat{H}$ and $\hat{H}_0$. Then the physically most important case is that G is a subgroup of G_0 (with the special case $G = G_0$). Of course we can also construct other situations:

– G_0 is a real subgroup of G, for example for a quantum-mechanical particle in three dimensions with the Hamiltonian

$$\hat{H}_0 = \frac{\hat{\vec{p}}^2}{2m} + \alpha(\hat{x}^2 + \hat{y}^2) \quad , \quad \hat{V} = \alpha\hat{z}^2$$

– There are elements $a \in G_0, b \in G$ for which $a \notin G, b \notin G_0$, e.g.

$$\hat{H}_0 = \frac{\hat{\vec{p}}^2}{2m} + \alpha(\hat{x}^2 + \hat{y}^2) \quad , \quad \hat{V} = \alpha(\hat{z}^2 - \hat{x}^2)$$

Such artificial cases, however, are (if at all) only of academic interest.

8.2 Subduced Representations

Let G be a subgroup of G_0 and $\bar{\Gamma}$a representation of G_0.[1] Then the matrix group of the representation matrices $\{\tilde{\Gamma}(a)\}$ with $a \in G$ is evidently a representation of G, the so-called subduced representation $\bar{\Gamma}^{(\mathrm{s})}$. Even if $\bar{\Gamma}$ is irreducible (with respect to G_0), $\bar{\Gamma}^{(\mathrm{s})}$is generally reducible with respect to G. In this case there is a reduction

$$\bar{\Gamma}^{(\mathrm{s})} = \sum_{p=1}^{r} n_p \bar{\Gamma}^p$$

where the $\bar{\Gamma}^p$ are the irreducible representations of G and n_p can be determined, as is usually the case, with equation (5.23).

As an example we consider $G_0 = D_3$ and $G = C_2$ with the character tables shown in 8.1. The irreducible representation E of the group D_3 is, with respect to C_2, a subduced representation that is reducible. The reduction results in

$$\begin{aligned} n_A &= \frac{1}{2}(\underbrace{2}_{(\chi^E_{C_2})^*} \cdot \underbrace{1}_{\chi^{(\mathrm{s})}_E} + \underbrace{0}_{(\chi^E_E)^*} \cdot \underbrace{1}_{\chi^{(\mathrm{s})}_E}) = 1 \ , \\ n_A &= \frac{1}{2}(2 \cdot 1 - 0 \cdot 1) = 1 \ , \end{aligned}$$

i.e.,

$$\bar{\Gamma}^{(\mathrm{s})}_E = \bar{\Gamma}^A \oplus \bar{\Gamma}^B \ .$$

The reduction of subduced representations are shown in correlation tables. As an example, we show in table 8.2 for $G_0 = O_h$ the reductions of the subduced representations of some subgroups of O_h. All other correlation tables can be found online (Ref. xx).

[1]We have changed our usual notation here for the obvious reason that in our coming discussion G_0/G will be symmetry groups of $\hat{H}_0/\hat{H}$

8.3 Degenerate Perturbation Theory

In the 0-th 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

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

where the $\underline{\tilde{V}}^{p_i}$ must be irreducible representations of $\hat{H} = \hat{H}_0 + \hat{V}$. The reason is that in the 0-th order only a base change is made in $\underline{V}^p$. The representations $\underline{\tilde{V}}^{p_i}$ that are involved then result, as in section 8.2, from the reduction of $\bar{\Gamma}^p$), i.e., with the help of the respective correlation tables.

As an example we consider again the particle in the cubic box from section 7.2. At least the first three eigenspaces are not reducible and can be considered here. We add $\hat{V} = \alpha \hat{z}^2$ to the Hamiltonian of the system. So we have $G_0 = O_h$ and $G = D_4$. The first eigenspace of $\hat{H}_0$ is not degenerate and therefore cannot split up energetically. We therefore consider the second and the third eigenspace:

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

$$T_{1\mathrm{u}} \overset{O_h \to D_{4h}}{\to} A_{2\mathrm{u}} \oplus E_{\mathrm{u}} \; .$$

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

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

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

$$T_{2\mathrm{g}} \overset{O_h \to D_{4h}}{\to} B_{2\mathrm{g}} \oplus E_{\mathrm{g}} \; .$$

where

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

The splitting into irreducible representation spaces $\underline{\tilde{V}}^{p_i}$ of G that resultins in 0-th order remains of course also valid beyond the perturbation-theoretic regime. Otherwise there would have to be a discontinuous transition into a qualitatively different eigenspace at some point, if $\hat{V}$ is continuously increasing. This can be surely be excluded, even without a formal proof.

D_3			E	$2C_3$	$3C_2$
$x^2 + y^2, z^2$		A_1	1	1	1
	z	A_2	1	1	1
(zx, yz), $(x^2 - y^2, xy)$	(x, y)	E	2	-1	0

C_2			E	$2C_2$
x^2, y^2, z^2, xy	z	A	1	1
zx, yz	x, y	B	1	-1

Table 8.1:

8.4 Application: Splitting of atomic orbitals in crystal fields

Let the orbitals $(s, p, d, \ldots)$ of an atom be given. Then the question is: what happens qualitatively with these, if the atom is in an environment which is no longer fully rotationally symmetric (e.g. in a solid). So we consider a Hamiltonian of the form

$$\hat{H} = \underbrace{\frac{\hat{\vec{p}}^2}{2m} + V(|\vec{r}|)}_{\text{atom}} + \underbrace{V_{\text{cf}}(\vec{r})}_{\text{crystal-field}} \equiv \hat{H}_0 + V_{\text{cf}}(\vec{r})$$

The symmetry group G_0 of H_0 is not finite, unlike all other groups dealt with in this book. We can, however, forego dealing with such infinite groups in detail here by using our knowledge of the spectrum of $\hat{H}_0$:

8.4.1 The Atomic Problem

Remainder: Atomic Spectra

We briefly repeat the essential results for the spectrum of $\hat{H}_0$, which are derived in every textbook on quantum mechanics:

It is $[\hat{H}_0, \hat{L}_i] = 0$ for all three components $\hat{L}_i$ of the orbital angular momentum $\hat{\vec{L}}$. One then shows in general that $\hat{\vec{L}}^2$ and $\hat{L}_z$ have common eigenstates $|l, m\rangle$, with

$$\begin{aligned}
\hat{\vec{L}}^2|l,m\rangle &= l(l+1)|l,m\rangle \qquad l = 0, 1, 2, \ldots \\
\hat{L}_z|l,m\rangle &= m|l,m\rangle \qquad m = -l, -l+1, \ldots l-1, l \;.
\end{aligned}$$

Since $[\hat{H}_0, \hat{\vec{L}}^2] = 0$ and $[\hat{H}_0, \hat{L}_z] = 0$ we can find common eigenstates of all three operators,

$$\hat{H}_0|n,l,m\rangle = E_{n,l,m}|n,l,m\rangle \;.$$

With the creation and annihilation operators $\hat{L}_\pm$,

$$\hat{L}_\pm|n,l,m\rangle \sim |n,l,m\pm 1\rangle$$

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

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

O_h	O	T_d	T_h	D_{4h}	D_{3d}
A_{1g}	A_1	A_1	A_g	A_{1g}	A_{1g}
A_{2g}	A_2	A_2	A_g	B_{1g}	A_{2g}
A_{1u}	A_1	A_2	A_u	A_{1u}	A_{1u}
A_{2u}	A_2	A_1	A_u	B_{1u}	A_{2u}
E_g	E	E	E_g	$A_{1g} \oplus B_{1g}$	E_g
E_u	E	E	E_u	$A_{1u} \oplus B_{1u}$	E_u
T_{1g}	T_1	T_1	T_g	$A_{2g} \oplus E_g$	$A_{2g} \oplus E_g$
T_{2g}	T_2	T_2	T_g	$B_{2g} \oplus E_g$	$A_{1g} \oplus E_g$
T_{1u}	T_1	T_2	T_u	$A_{2u} \oplus E_u$	$A_{2u} \oplus E_u$
T_{2u}	T_2	T_1	T_u	$B_{2u} \oplus E_u$	$A_{1u} \oplus E_u$

Therefore all states $|n, l, m\rangle$ ($m = -l, \dots, l$) 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

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

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 the following considerations. The wave functions for the lowest values of l are

- $l = 0$, s-orbitals: $Y_{0,0} \sim \text{const}$
- $l = 1$, p-orbitals: $Y_{1,\pm 1} \sim \sin^2(\theta) e^{\pm \mathrm{i}\varphi}$, $Y_{1,0} \sim \cos(\theta)$
- $l = 2$, d-orbitals: $Y_{2,\pm 2} \sim \sin^2(\theta) e^{2\pm \mathrm{i}\varphi}$, $Y_{2,\pm 1} \sim \sin(\theta)\cos(\theta) e^{\pm \mathrm{i}\varphi}$, $Y_{2,0} \sim (3\cos^2(\theta) - 1)$.

Group-theoretical treatment of the problem

The symmetry group of $\hat{H}_0$ is $O(3)$ and consists of all operators $\hat{U}_{\tilde{D}}$ with arbitrary orthogonal matrices $\tilde{D}$. We now want to answer the question of what the representation matrices and (more importantly) the characters of this group are. In order to avoid dealing with infinite groups, we proceed pragmatically and use the results from Section (8.4.1):

Since $O(3)$ is the maximum symmetry group of $\hat{H}_0$, the functions $Y_{l,m}(\theta, \varphi)$ ($m = -l, \dots, l$) must form a $(2l+1)$-dimensional representation space of $O(3)$ according to our postulate from Section 6.2.3. This allows us to determine the representation matrices and the associated characters.

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

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

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

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

With the help of the well-known geometric sum formula, follows for the character

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

With other axes of rotation, the representation matrices are not diagonal. The characters are obviously independent of the axis (with the same angle of rotation α). Since we only need these in the following, we do not have to deal with 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

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

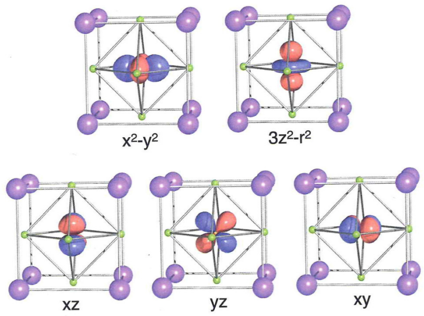

Figure 8.1: $e_{\rm g}$ and $t_{2\rm g}$ orbitals

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

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

In particular, in the special case of a reflection on a plane, it is $\bar{\chi}^l(\alpha = \pi) = 1$.

8.4.2 Splitting of orbital energies in crystal fields

With the results for the characters of the group Oh and the character tables of our 32 point groups, we can now evaluate the qualitative splitting of the atomic orbitals with the help of equation (5.23). We consider the example of the group $G = O_h$. The reduction of the subduced representation of the first 4 atomic eigenspace then results in

$$\begin{aligned}
\Gamma^{(\rm s)}_{l=0} &= A_{\rm g} \ , \\
\Gamma^{(\rm s)}_{l=1} &= T_{1\rm u} \ , \\
\Gamma^{(\rm s)}_{l=2} &= E_{\rm g} + T_{2\rm g} \ , \\
\Gamma^{(\rm s)}_{l=2} &= A_{2\rm u} + T_{1\rm u} + T_{2\rm u} \ .
\end{aligned}$$

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

$$\begin{aligned}
\phi_\xi(r,\theta,\varphi) &= \frac{\rm i}{\sqrt{2}} R_{t_{2\rm g}}(r)\left[Y_{2,1}(\theta,\varphi) + Y_{2,-1}(\theta,\varphi)\right] \sim y \cdot z \ , \\
\phi_\eta(r,\theta,\varphi) &= \frac{-1}{\sqrt{2}} R_{t_{2\rm g}}(r)\left[Y_{2,1}(\theta,\varphi) - Y_{2,-1}(\theta,\varphi)\right] \sim x \cdot z \ , \\
\phi_\rho(r,\theta,\varphi) &= \frac{-\rm i}{\sqrt{2}} R_{t_{2\rm g}}(r)\left[Y_{2,2}(\theta,\varphi) - Y_{2,-2}(\theta,\varphi)\right] \sim x \cdot y \ ,
\end{aligned}$$

and the double degenerate $e_{\rm g}$-orbitals

$$\begin{aligned}
\phi_u(r,\theta,\varphi) &= R_{e_{\rm g}}(r) Y_{2,0}(\theta,\varphi) \sim (3z^2 - r^2) \ , \\
\phi_v(r,\theta,\varphi) &= \frac{1}{\sqrt{2}} R_{e_{\rm g}}(r)\left[Y_{2,2}(\theta,\varphi) + Y_{2,-2}(\theta,\varphi)\right] \sim (x^2 - y^2) \ .
\end{aligned}$$

In Fig. 8.1 we show the shape of these orbitals.

Chapter 9

Material Tensors and Tensor Operators

9.1 Material Tensors

9.1.1 Physical Motivation

The reaction of solids to external fields is described by material tensors. For example, applying an electric field $\vec{E}$ in leading linear order results in a dipole moment

$$\vec{P} = \tilde{\alpha}^{(2)} \cdot \vec{E}$$

where the three-dimensional matrix $\tilde{\alpha}^{(2)}$ is denoted as the *polarization tensor*. In general, of course, $\vec{P} = \vec{P}(\vec{E})$ is a non-linear function and one can do a Taylor expansion

$$P_i \approx \sum_j \alpha^{(2)}_{i,j} E_j + \sum_{j,k} \alpha^{(3)}_{i,j,k} E_j E_k + \dots \tag{9.1}$$

with *tensors* $\alpha^{(n)}_{i_1,\dots,i_n}$ *of rank* n . The central question in this chapter will be which of the tensor components are independent and how they are related to the dependent components. This is important both in experimental and theoretical physics, since one only needs to measure or calculate the independent components in order to determine the entire tensor.

9.1.2 Transformation of Tensors

We now consider the contribution of rank n in an expansion of the form (9.1),

$$P^{(n)}_{i_1} = \sum_{i_2,\dots,i_n} \alpha^{(n)}_{i_1,\dots,i_n} E_{i_2} \cdots E_{i_n} \tag{9.2}$$

where $\vec{P}$ and $\vec{E}$ are three-dimensional polar vectors. Here's a quick reminder of the difference between polar and axial vectors: whereas axial vectors (e.g. the magnetic field $\vec{B}$) transform like

$$\begin{aligned} \vec{B}' &= \tilde{D} \cdot \vec{B} \quad (\text{if } |\tilde{D}| = 1) \ , \\ \vec{B}' &= -\tilde{D} \cdot \vec{B} \quad (\text{if } |\tilde{D}| = -1) \ . \end{aligned}$$

We will first look at the case of polar vectors and at the end of section 9.3 briefly explain how the entire formalism can also be applied to axial vectors.

In a rotated coordinate system, analogously to (9.2), we have a relationship of the form

$$P_{l_1}^{(n)'} = \sum_{l_2,\dots,l_n} \alpha_{l_1,\dots,l_n}^{(n)'} E'_{l_2} \cdots E'_{l_n} \ . \tag{9.3}$$

We now want to derive the relationship between $\tilde{\alpha}^{(n)}$ and $\tilde{\alpha}^{(n)'}$. For this we apply (9.3) to (**??**),

$$\sum_{i_1} D_{l_1,i_1} P_{i_1}^{(n)} = \sum_{\substack{i_2,\dots,i_n \\ l_2,\dots,l_n}} \alpha_{l_1,\dots,l_n}^{(n)'} D_{l_2,i_2} \cdots D_{l_n,i_n} E_{i_2} \cdots E_{i_n} \ . \ .$$

Both sides are multiplied with by D_{l_1,j_1} and the sum over l_1 is carried out. The left side then becomes

$$\sum_{i_1,l_1} \underbrace{D_{l_1,j_1}}_{=\left(\tilde{D}^{-1}\right)_{j_1,l_1}} D_{l_1,i_1} P_{i_1}^{(n)} = \delta_{i_1,j_1} P_{i_1}^{(n)} \ .$$

A comparison with (9.2) yields

$$\alpha_{i_1,\dots,i_n}^{(n)} = \sum_{l_1,\dots,l_n} D_{l_1,i_1} \cdots D_{l_n,i_n} \alpha_{l_1,\dots,l_n}^{(n)'} \ .$$

Under symmetry transformations of a solid, $\tilde{\alpha}^{(n)}$ should not change its form, i.e. for all g elements $\tilde{D}$ of the symmetry group it is

$$\alpha_{i_1,\dots,i_n}^{(n)} = \sum_{l_1,\dots,l_n} D_{l_1,i_1} \cdots D_{l_n,i_n} \alpha_{l_1,\dots,l_n}^{(n)} \ . \tag{9.4}$$

These are g equations that connect the components of $\tilde{\alpha}^{(n)}$. Before we can analyze this relationship in more detail, we need the concept of a *product representation.*

9.2 Product Representations

9.2.1 Definition of Product Representations

Let $\bar{\Gamma}^p, \Gamma^{p'}$ be irreducible representations of a group G. Then the product representation is defined as

$$\Gamma_{(ik),(jl)}^{p\otimes p'}(a) \equiv \Gamma_{i,j}^{p}(a) \cdot \Gamma_{k,l}^{p'}(a) \tag{9.5}$$

for all $a \in G$. The proof of the representation property is simple,

$$\begin{aligned} \Gamma_{(ik),(jl)}^{p\otimes p'}(a\cdot b) &\overset{(9.5)}{=} \Gamma_{i,j}^{p}(a\cdot b)\cdot\Gamma_{k,l}^{p'}(a\cdot b) \\ &= \sum_{n,m} \Gamma_{i,n}^{p}(a)\Gamma_{n,j}^{p}(b)\Gamma_{k,m}^{p'}(a)\Gamma_{m,l}^{p'}(b) \\ &\overset{(9.5)}{=} \sum_{n,m} \Gamma_{(ik),(nm)}^{p\otimes p'}(a)\Gamma_{(nm),(jl)}^{p\otimes p'}(b) \end{aligned}$$

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 write this as $\bar{\Gamma} \otimes \bar{\Gamma}'$. In this chapter we will mainly consider such product representations.

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

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

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 equation (5.23). For this we need the characters of the product representation

$$\chi^{p\otimes p'}(a) = \sum_{k,l} \Gamma^{p\otimes p}_{(kl),(kl)}(a) \stackrel{(9.5)}{=} \sum_{k,l} \Gamma^p_{k,k}(a)\Gamma^{p'}_{l,l}(a) = \chi^p(a)\cdot\chi^{p'}(a) \;. \tag{9.6}$$

With (5.23) we then find

$$c(p,p'|\tilde{p}) = \frac{1}{g}\sum_i r_i\cdot\chi_i^{p\otimes p'}\cdot\chi_i^{\tilde{p}} \stackrel{(9.6)}{=} \frac{1}{g}\sum_i r_i\cdot\chi_i^p\cdot\chi_i^{p'}\cdot\chi_i^{\tilde{p}} \;.$$

With this equation and with the help of the character tables, we can find all the coefficients of interest. As an example we consider the group D_3, and use its character table 8.1 to find, for example, for the reduction of $\bar{\Gamma}^{E\otimes E}$:

$$\begin{aligned}
c(E,E|A_1) &= \frac{1}{6}(\underbrace{1}_{=r_1}\cdot\underbrace{2\cdot 2}_{=\chi_1^{E\otimes E}}\cdot\underbrace{1}_{=\chi_1^{A_1}}+2\cdot(-1)\cdot(-1)\cdot 1+3\cdot 0\cdot 0\cdot 1) = 1\;,\\
c(E,E|A_2) &= \frac{1}{6}(1\cdot 2\cdot 2\cdot 1+2\cdot(-1)\cdot(-1)\cdot 1+3\cdot 0\cdot 0\cdot 1) = 1\;,\\
c(E,E|E) &= \frac{1}{6}(1\cdot 2\cdot 2\cdot 2+2\cdot(-1)\cdot(-1)\cdot(-1)+3\cdot 0\cdot 0\cdot 0) = 1\;.
\end{aligned}$$

So we find

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

The reduction of product representations from irreducible representations are shown in so-called *multiplication tables*, e.g., in table 9.1 for the group D_3.

The multiple product presentations 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

$$\Gamma_{I,L}(a) \equiv \Gamma_{(i_1,\ldots,i_n),(l_1,\ldots,l_n)}(a) \equiv \Gamma_{i_1,l_1}(a)\cdot\Gamma_{i_2,l_2}(a)\cdots\Gamma_{i_n,l_n}(a) \tag{9.7}$$

and the multiple indices

$$I \equiv (i_1,\ldots,i_n), L \equiv (l_1,\ldots,l_n)\;. \tag{9.8}$$

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

Table 9.1: The multiplication table for the irreducible representations of the group D_3.

9.3 Independent Tensor Components

We now return to equation (9.4) which we can write, using the multiple indices (9.8), as

$$\alpha_I = \sum_L \Gamma_{L,I}(a)\alpha_L \tag{9.9}$$

where[1]

$$\Gamma_{(l_1,\ldots,l_n),(i_1,\ldots,i_n)}(a) \equiv D_{l_1,i_1}(a)\cdots D_{l_n,i_n}(a)\ .$$

Let

$$\bar\Gamma = \sum_p n_p \bar\Gamma^p$$

be the reduction of g and be generated by the orthogonal matrix $S_{I,(p,m_p,\lambda_p)}$, ($m_p = 1,\ldots,n_p$, $\lambda_p = 1,\ldots,d_p$), i.e.,

$$\tilde S^\dagger \bar\Gamma \tilde S = \begin{pmatrix} \bar\Gamma^1 & & & & & & 0 \\ & \ddots & & & & & \\ & & \bar\Gamma^1 & & & & \\ & & & \ddots & & & \\ & & & & \bar\Gamma^r & & \\ & & & & & \ddots & \\ 0 & & & & & & \bar\Gamma^r \end{pmatrix}\ . \tag{9.10}$$

With the matrix $\tilde S$ we define the new tensor components

$$\beta_{(p,m_p,\lambda_p)} \equiv \sum_I S_{I,(p,m_p,\lambda_p)}\alpha_I$$

the inverse of which is given by

$$\alpha_I = \sum_p \sum_{m_p=1}^{n_p} \sum_{\lambda_p=1}^{d_p} S^*_{I,(p,m_p,\lambda_p)}\beta_{(p,m_p,\lambda_p)}\ . \tag{9.11}$$

We now want to analyze which of the tensor components $\beta_{(p,m_p,\lambda_p)}$ can be nonzero without violating equations (9.4) or (9.9). For this we put equation (9.11) into (9.9),

$$\sum_{p,m_p,\lambda_p} S^*_{I,(p,m_p,\lambda_p)}\beta_{(p,m_p,\lambda_p)} = \sum_{L,p,m_p,\bar\lambda_p} \Gamma_{L,I}(a) S^*_{L,(p,m_p,\bar\lambda_p)}\beta_{(p,m_p,\bar\lambda_p)}\ . \tag{9.12}$$

We multiply this equation with $S_{I,(p',m_{p'},\lambda_{p'})}$ and sum over I. Then, with the orthogonality of $\tilde S$ and equation (9.10), it follows

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

If we summarize the components in a vector

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

[1] Recall that the three-dimensional rotation matrices of a point group are also a (generally reducible) representation

we recognize the meaning of the equation (9.12), namely that $\vec{\beta}_{p,m_p}$ is an eigenvector of every matrix $\tilde{\Gamma}^p(a)$ with an eigenvalue 1. As we now show, it follows from this that $\vec{\beta}_{p,m_p} = 0$ $(\forall p \neq 1)$, where $p = 1$ is the trivial representation A_1, i.e. the one-dimensional representation with $\Gamma^1(a) = 1$ $(\forall a)$.
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 section 4.1.2.

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

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

which proves the statement.

With that we can now summarize

i) There are exactly n_1 independent tensor components β_{1,m_1}, i.e. as many as the number of occurrence of the representation $\bar{\Gamma}^1$ in the product representation (9.7).

ii) The tensor α_I can then be written as

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

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

As an example we consider a polarizability tensor $\tilde{\alpha}^{(2)}$ of the 2nd order. This leads to the 9-dimensional representation matrices

$$\Gamma_{(i,j),(k,l)}(a) = D_{i,k}(a) D_{j,l}(a) \; . \tag{9.13}$$

With that 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 in a class C_i. The number n_1 then results in

$$n_1 = \frac{1}{g} \sum_i r_i \underbrace{(\chi_i^1)^*}_{=1} \cdot \bar{\chi}_i^2 \; . \tag{9.14}$$

The characters $\bar{\chi}(a)$ or $\bar{\chi}_i$ can be calculated with the equation

$$\sum_i D_{i,i}(a) = \pm(2\cos\alpha + 1)$$

from section 3.3 where α is the rotation angle.

As an example, we consider the point groups C_2, C_i, and O_h. Although the two groups C_2 and C_i are isomorphic, the results are different in this context. So this is a first example that shows that the classification of groups according to isomorphism alone is not helpful in physics.

i) For the group C_2 we have the matrices

$$\tilde{D}(E) = \tilde{1} \ , \ \tilde{D}(\delta_2) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

which leads to

$$\bar{\chi}(E) = 3 \ , \ \bar{\chi}(\delta_2) = -1 \ .$$

So with equation (9.14) we have

$$n_1 = \frac{1}{2}(3^2 + 1) = 5$$

independent elements in $\tilde{\alpha}^{(2)}$. In order to determine the relationship between these components and those from $\tilde{\alpha}^{(2)}$, we have to reduce the product representation (9.13). This is easily possible here, because

$$\Gamma_{(i,j),k,l}(a) D_{i,k}(a) D_{j,l}(a) = \delta_{i,k}\delta_{j,l} D_{i,i} D_{l,l}$$

is automatically diagonal. With the arrangement

$$\begin{aligned} (i,j) \ = \ & (1,1) = 1 \ , \ , (2,2) = 2 \ , \ (3,3) = 3 \ , \ (1,2) = 4 \ , \ (2,1) = 5 \ , \\ & (1,3) = 6 \ , \ (3,1) = 7 \ , \ (2,3) = 8 \ , \ (3,2) = 9 \ , \end{aligned}$$

we find

$$\tilde{\Gamma}(E) = \tilde{1} \ , \ \tilde{\Gamma}(\delta_2) = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 \end{pmatrix}$$

With this we can assign the independent tensor components,

$$\alpha_{1,1} = \beta_{(p=1,1)} \ , \ \alpha_{2,2} = \beta_{(p=1,2)} \ , \ldots , \alpha_{2,1} = \beta_{(p=1,5)}$$

whereas

$$\alpha_{1,3} = \beta_{(p=2,1)} = 0 \ , \ \alpha_{3,1} = \beta_{(p=2,2)} = 0 \ , \ \alpha_{2,3} = \beta_{(p=2,3)} = 0 \ , \ \alpha_{3,2} = \beta_{(p=2,4)} = 0 \ .$$

The polarizability tensor $\tilde{\alpha}^{(2)}$ therefore has the general form

$$\tilde{\alpha}^{(2)} = \begin{pmatrix} \alpha_{1,1} & \alpha_{1,2} & 0 \\ \alpha_{2,1} & \alpha_{2,2} & 0 \\ 0 & 0 & \alpha_{3,3} \end{pmatrix}$$

At first glance it seems strange that here $\alpha_{1,2} \neq \alpha_{2,1}$. However, if we consider, for example a body as in Figure 6.1, i.e., an area in the x-y plane with C_2 symmetry, over which there is a pyramid in $z - direction$. If we apply an electric field in x or in y direction to a solid with such a symmetry, it is obvious that the dipole moments

$$\vec{P}_x = \tilde{\alpha}^{(2)} \vec{E}_x \ , \ \vec{P}_y = \tilde{\alpha}^{(2)} \vec{E}_y$$

do not include an angle $\pi/2$. So it is clear that $\alpha_{1,2} \neq \alpha_{2,1}$.

ii) Let us now consider the group C_i. Here is

$$\tilde{D}(E) = \tilde{1} \ , \ \ \tilde{D}(I) = -\tilde{1}$$

and thus

$$\bar{\chi}(E) = 3 \ , \ \ \bar{\chi}(I) = -3 \ .$$

This gives us

$$n_1 = \frac{1}{2}(3^2 + (-3)^2) = 9$$

for the number of independent tensor components, i.e., there are no dependencies in the tensor $\tilde{\alpha}^{(2)}$ for this group.

iii) Without proof, which is easily possible with equation (9.14), we only give the result for the group O_h that $n_1 = 1$. Thus,

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

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

We conclude this section with a brief consideration of tensors with axial components, for example the magnetic susceptibility $\tilde{\chi}^{(2)}$,

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

which describes the relationship between the magnetic moment and an applied magnetic field in leading order, which are both axial vectors. Here one can proceed in exactly the same way as in our previous considerations, since the matrices $\tilde{D}'(a)$, defined as

$$\begin{aligned} \tilde{D}'(a) &\equiv \tilde{D}(a) \ \text{ for } |\tilde{D}(a)| = 1 \text{ (i.e. } a \in G_0) \\ \tilde{D}'(a) &\equiv -\tilde{D}(a) \ \text{ for } |\tilde{D}(a)| = -1 \text{ (i.e. } a \in L_0) \end{aligned}$$

are also a representation of the point group, because

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

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

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

i) $a, b \in L_0$:

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

9.4 Tensor Operators

9.4.1 Definition of Tensor Operators

We consider a quantum mechanical system with a symmetry group G, described by unitary operators $\hat{U}_a$. A set of operators $\hat{T}_{i_1,\ldots,i_n}$ is then called *tensor operators of rank* n if they transform as follows

$$\hat{U}_a \hat{T}_{i_1,\ldots,i_n} \hat{U}_a^\dagger = \sum_{l_1,\ldots,l_n} \Gamma_{l_1,i_1}(a) \cdots \Gamma_{l_n,i_n}(a) \hat{T}_{l_1,\ldots,l_n} \ , \tag{9.15}$$

where $\bar{\Gamma}$ is a (mostly reducible) representation of G. As examples, we consider operators in the Hilbert space of square-integrable functions.

i) *Vector operators* are tensor operators of rank $n = 1$. An example are the three components $\hat{x}_i$ of the position vector operator $\hat{\vec{r}}$. They transform like **proof: exercise xx**

$$\hat{U}_{\tilde{D}} \cdot \hat{\vec{r}} \cdot \hat{U}^{\dagger}_{\tilde{D}} = \tilde{D} \cdot \hat{\vec{r}} \tag{9.16}$$

or expressed in components

$$\hat{U}_{\tilde{D}} \cdot \hat{x}_i \cdot \hat{U}^{\dagger}_{\tilde{D}} = \sum_j D_{i,j} \cdot \hat{x}_j$$

This equation actually corresponds to (9.15), since $D_{i,j} = (\tilde{D}^{-1})^*_{j,i}$ and the set of matrices $(\tilde{D}^{-1})^*$ also represent a representation of a point group.

i) One can also consider the case $n = 0$ (*scalar operators*) which transform like

$$\hat{U}_{\tilde{D}} \hat{T}_0 \hat{U}^{\dagger}_{\tilde{D}} = \hat{T}_0 (= \underbrace{1}_{\tilde{\Gamma}(\tilde{D})=1\ \forall \tilde{D}} \hat{T}_0)$$

for all orthogonal matrices $\tilde{D}$, i.e. for all elements of any point group. An example is

$$\hat{\vec{r}}^2 = \hat{x}_1^2 + \hat{x}_2^2 + \hat{x}_3^2$$

because

$$\hat{U}_{\tilde{D}} \cdot (\hat{\vec{r}} \cdot \hat{\vec{r}}) \cdot \hat{U}^{\dagger}_{\tilde{D}} = \hat{U}_{\tilde{D}} \cdot \hat{\vec{r}} \cdot \underbrace{\hat{U}^{\dagger}_{\tilde{D}} \cdot \hat{U}_{\tilde{D}}}_{=1} \cdot \hat{\vec{r}} \cdot \hat{U}^{\dagger}_{\tilde{D}} \overset{(9.16)}{=} (\tilde{D} \cdot \vec{r}) \cdot (\tilde{D} \cdot \vec{r}) = \hat{\vec{r}}^2 \ .$$

9.4.2 Irreducible Tensor Components

Vector Operators

For simplicity, we consider vector operators $\hat{T}_i$ first. The generalization for general tensor operators will then be straightforward.

As is known, the rotation matrices of a point group are themselves a representation of the group,

$$\tilde{\Gamma}(\tilde{D}) \equiv \tilde{D} \ .$$

In general, we can reduce this representation, mediated by the matrix $S_{i,(p,m_p,\lambda_p)}$, i.e.

$$\sum_{i,j} S_{j,(p',m_{p'},\lambda'_{p'})} \Gamma_{j,i} S_{i,(p,m_p,\lambda_p)} = \delta_{p,p'} \delta_{m_p,m_{p'}} \Gamma^p_{\lambda'_p,\lambda_p} \ . \tag{9.17}$$

With this matrix we define the *irreducible tensor components*

$$\hat{T}_{p,m_p,\lambda_p} \equiv \sum_i S_{i,(p,m_p,\lambda_p)} \hat{T}_i \ . \tag{9.18}$$

The inversion of this equation reads

$$\hat{T}_i = \sum_{p,m_p,\lambda_p} S^*_{i,(p,m_p,\lambda_p)} \hat{T}_{p,m_p,\lambda_p} \ . \tag{9.19}$$

The irreducible tensor components transform exactly according to the respective irreducible representation matrices, because

$$\begin{aligned}\hat{U}_a \hat{T}_{p,m_p,\lambda_p} \hat{U}_a^\dagger &\overset{(9.18)}{=} \sum_i S_{i,(p,m_p,\lambda_p)} \hat{U}_a \hat{T}_i \hat{U}_a^\dagger \overset{(9.15)}{=} \sum_i S_{i,(p,m_p,\lambda_p)} \sum_j \Gamma_{j,i} \hat{T}_j \\ &\overset{(9.19)/(9.17)}{=} \sum_{\lambda'_p} \Gamma^p_{\lambda'_p,\lambda_p} \hat{T}_{p,m_p,\lambda'_p} \end{aligned} \tag{9.20}$$

As an example we consider again the vector operator $\hat{\vec{r}}$ and the group $G = C_2$. This group has two elements

$$C_2 = \left\{ \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \right\}$$

which, viewed as representations, are already reduced in this case, i.e.,

$$\bar{\Gamma} = \bar{\Gamma}^A + 2\bar{\Gamma}^B \, .$$

In this case the operators $\hat{x}_i$ themselves are already irreducible, namely

$$\begin{aligned} p = A \quad &: \quad \hat{T}_{A,1,1} = \hat{x}_3 \;\; \text{(symmetric under } \delta_2\text{-rotations)} \\ p = B \quad &: \quad \hat{T}_{B,1,1} = \hat{x}_1 \;\; \text{(antisymmetric under } \delta_2\text{-rotations)} \\ p = B \quad &: \quad \hat{T}_{B,2,1} = \hat{x}_2 \;\; \text{(antisymmetric under } \delta_2\text{-rotations)} \end{aligned}$$

General Tensor Operators

The generalization to arbitrary tensor operators is simple. So we consider an operator that satisfies (9.15). Let's summarize the indices again as $I = (i_1, \ldots, i_n)$, $L = (l_1, \ldots, l_n)$. Then equation (9.15) reads

$$\hat{U}_a \hat{T}_I \hat{U}_a^\dagger = \sum_L \left[\bar{\Gamma}(a) \otimes \bar{\Gamma}(a) \cdots \otimes \bar{\Gamma}(a) \right]_{L,I} \hat{T}_L \, .$$

The product representation in this equation can also be reduced by means of a matrix $S_{I,(p,m_p,\lambda_p)}$. With this we again define the irreducible tensor components

$$\hat{T}_{p,m_p,\lambda_p} \equiv \sum \sum_I S_{I,(p,m_p,\lambda_p)} \hat{T}_I$$

with the inverse

$$\hat{T}_I = \sum_{p,m_p,\lambda_p} S^*_{I,(p,m_p,\lambda_p)} \hat{T}_{p,m_p,\lambda_p} \, .$$

So we can summarize that every component of a tensor operator can be expressed as a linear combination of its irreducible components with respect to the symmetry group of a system. We will use this in the next chapter to evaluate matrix elements.

Chapter 10

Matrix Elements of Tensor Operators: The Wigner-Eckart Theorem

10.1 Motivation: Time-Dependent Perturbation Theory

In the time-dependent perturbation theory one usually considers Hamiltonian of the form

$$\hat{H}(t) = \hat{H}_0 + f(t)\hat{V} \ .$$

Let $|p, m_p, \lambda_p\rangle$ be the eigenstates of $\hat{H}_0$. Then one is mostly interested in transition probabilities

$$W_{(p,m_p,\lambda_p)\to(p',m_{p'},\lambda_{p'})} \sim \langle p', m_{p'}, \lambda_{p'}|\hat{V}|p, m_p, \lambda_p\rangle \ .$$

In practice one often has to work with operators $\hat{V}$, which can be expressed by components of tensor operators, e.g.

$$\hat{V} = \vec{E} \cdot \hat{\vec{r}} \quad \text{or} \quad \hat{V} = \vec{A} \cdot \hat{\vec{p}}$$

Since tensor operators can always be represented by their irreducible components, the general question arises, how one can evaluate matrix elements of the form $\langle p, \lambda|\hat{T}_{p',\lambda'}|p'', \lambda''\rangle$ with group-theoretical methods.[1]

10.2 Coupling coefficients

The reduction of a product representation of two irreducible representations $\bar{\Gamma}^p$ and $\bar{\Gamma}^{p'}$

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

[1]As we will see, the labels $m_p, m_{p'}, m_{p''}$ for the eigenspaces or the different irreducible tensor components are irrelevant here and are therefore droped in the following.

is mediated by the unitary matrix $\tilde{S}$, i.e.

$$\tilde{S}^\dagger \cdot \bar{\Gamma}^{p\otimes p'} \cdot \tilde{S} = \begin{pmatrix} \bar{\Gamma}^1 & & & & & & & 0 \\ & \ddots & & & & & & \\ & & \bar{\Gamma}^1 & & & & & \\ & & & \bar{\Gamma}^2 & & & & \\ & & & & \ddots & & & \\ & & & & & \bar{\Gamma}^r & & \\ & & & & & & \ddots & \\ 0 & & & & & & & \bar{\Gamma}^r \end{pmatrix} \tag{10.1}$$

The representation $\bar{\Gamma}^{\tilde{p}}$ appears in the matrix exactly $C(p,p'|\tilde{p})$ times. The elements of $\tilde{S}$ are usually written as

$$S_{((p,\lambda),(p',\lambda_{p'})),(\tilde{p},f_{\tilde{p}},\lambda_{\tilde{p}})} = \left(\begin{array}{cc|cc} p & p' & \tilde{p} & f_{\tilde{p}} \\ \lambda & \lambda' & \tilde{\lambda} & \end{array} \right) \quad (f_{\tilde{p}} = 1, \ldots, C(p,p'|\tilde{p}))$$

and are called *coupling coefficients*.

10.3 The Wigner-Eckhart Theorem

We now want to derive the *Wigner-Eckhart theorem* for evaluating matrix elements of the form

$$W^{p,p',p''}_{\lambda,\lambda',\lambda''} \equiv \langle p,\lambda|\hat{T}_{p',\lambda'}|p'',\lambda''\rangle = \langle p,\lambda|\underbrace{\hat{U}_a^\dagger \hat{U}_a}_{1}\hat{T}_{p',\lambda'}\underbrace{\hat{U}_a^\dagger \hat{U}_a}_{1}|p'',\lambda''\rangle$$

With (6.14) and (9.20) we can evaluate the right hand side of this equation,

$$W^{p,p',p''}_{\lambda,\lambda',\lambda''} = \sum_{\bar{\lambda},\bar{\lambda}',\bar{\lambda}''} \left(\Gamma^p_{\bar{\lambda},\lambda}(a)\right)^* \underbrace{\Gamma^{p'}_{\bar{\lambda}',\lambda'}(a)\Gamma^{p''}_{\bar{\lambda}'',\lambda''}(a)}_{(x)} \langle p,\bar{\lambda}|\hat{T}_{p',\bar{\lambda}'}|p'',\bar{\lambda}''\rangle \,. \tag{10.2}$$

Using equation (10.1) the term (x) can be written as

$$(x) = \sum_{p_0}\sum_{f_{p_0}}\sum_{\lambda_0,\lambda_0'} \left(\begin{array}{cc|cc} p'' & p' & p_0 & f_{p_0} \\ \lambda'' & \lambda' & \lambda_0 & \end{array} \right) \left(\begin{array}{cc|cc} p'' & p' & p_0 & f_{p_0} \\ \bar{\lambda}'' & \bar{\lambda}' & \lambda_0' & \end{array} \right) \Gamma^{p_0}_{\lambda_0,\lambda_0'}(a) \tag{10.3}$$

Since the left side of (10.2) is independent of a, the same applies to the right side. Therefore we can perform the operation

$$1 = \frac{1}{g}\sum_a$$

on both sides. The a-dependence then only exists in the two green matrix elements in (10.2) and (10.3). With the help of the orthogonality theorem (5.2) we then find the *Wigner-Eckart theorem*

$$W^{p,p',p''}_{\lambda,\lambda',\lambda''} = \sum_{f_p} \left(\begin{array}{cc|cc} p'' & p' & p & f_p \\ \lambda'' & \lambda' & \lambda & \end{array} \right) \Omega(p,p';p'',f_p)$$

with

$$\Omega(p,p';p'',f_p) \equiv \frac{1}{d_p}\sum_{\bar{\lambda},\bar{\lambda}',\bar{\lambda}''} \left(\begin{array}{cc|cc} p'' & p' & p & f_p \\ \bar{\lambda}'' & \bar{\lambda}' & \bar{\lambda} & \end{array} \right) \,.$$

The essential meaning of this theorem is that the dependency with respect to $\lambda, \lambda', \lambda''$ is exclusively in the coupling coefficients and independent of the specific form of the operator $\hat{T}_{p',\lambda'}$ and the eigenstates $|p,\lambda\rangle$, $|p'',\lambda''\rangle$. This means that one only has to determine the (smaller) number of properties $\Omega(p,p';p'',f_p)$ (theoretically or experimentally) in order to calculate the set of all matrix elements $W^{p,p',p''}_{\lambda,\lambda',\lambda''}$.

As an example we consider again the three operators $(\hat{x},\hat{y},\hat{z})$ and the group $G = C_2$. Here there are the irreducible representations and representation functions

$$p = A \quad : \quad |p_z\rangle \tag{10.4}$$
$$p = B \quad : \quad |p_x\rangle, |p_y\rangle \; . \tag{10.5}$$

The multiplication table yields $A \otimes A = A, A \otimes B = B \otimes A = B, B \otimes B = A$. Hence, it is $C(p,p'|\tilde{p}) > 0$ only if

i) all $p, p', \tilde{p} = A$, or

ii) two of the $p, p', \tilde{p}$ are B, one is A.

Thus the following matrix elements are zero

$$\begin{aligned}
&\langle p_z|\,\{\hat{x},\hat{y}\}\,|p_z\rangle \; , \\
&\langle p_z|\hat{z}|p_i\rangle \; , \; \langle p_i|\hat{z}|p_z\rangle \;\; i \in \{x,y\} \\
&\langle p_i|\,\{\hat{x},\hat{y}\}\,|p_j\rangle \quad (i,j \in (x,y)) \; .
\end{aligned}$$

Chapter 11

Double Groups and their representations

11.1 Particles with spin 1/2

For an electron with a spin 1/2, we obtain the Hilbert space with basis states

$$\Psi_{i,\sigma} = \Psi_i(\vec{r})\chi$$

with the basis of spatial wave function $\Psi_i(\vec{r})$ and the spinor states

$$\chi = \alpha_\uparrow|\uparrow\rangle + \alpha_\downarrow|\downarrow\rangle \ ,$$

where $|\uparrow\rangle, |\downarrow\rangle$ are the eigenstates of the spin operator in z-direction $\hat{S}_z = \frac{1}{2}\tilde{\sigma}_3$ and $\tilde{\sigma}_i$ the well-known Pauli matrices. As shown in textbooks on quantum mechanics, a spinor $|\sigma\rangle$ transforms like

$$\tilde{T}_{\vec{\alpha}}|\sigma\rangle = \exp\left(\mathrm{i}\frac{1}{2}\vec{\alpha}\cdot\hat{\vec{\sigma}}\right)|\sigma\rangle$$

under a rotation. Here, $\vec{\alpha}$ is the rotation vector, i.e. the direction of $\vec{\alpha}$ is the axis of rotation and $|\vec{\alpha}|$ is the angle of the rotation. The vector $\hat{\vec{\sigma}}$ consists of the three Pauli matrices. The 2×2-matrix $\tilde{T}_{\vec{\alpha}}$ can be evaluated via its Taylor expansion and the algebra of the $\tilde{\sigma}_i$ with the result

$$\tilde{T}_{\vec{\alpha}} = \cos\left(\frac{1}{2}|\vec{\alpha}|\right)\tilde{1} + \mathrm{i}\sin\left(\frac{1}{2}|\vec{\alpha}|\right)\frac{\vec{\alpha}}{|\vec{\alpha}|}\cdot\hat{\vec{\sigma}} \ . \tag{11.1}$$

For a rotation around the angle 2π we find for example

$$\tilde{T}_{2\vec{\pi}}|\sigma\rangle = -|\sigma\rangle$$

i.e. such a rotation $\tilde{T}_{2\vec{\pi}} \equiv E^-$ cannot be the group's identity element anymore when applied to a spinor. The identity element results from a rotation with the angle 4π,

$$\tilde{T}_{4\vec{\pi}} = \tilde{T}^2_{2\vec{\pi}} = E \ .$$

11.2 Definition of Double Groups

Obviously we have to distinguish between angles $\varphi \in (0, 2\pi)$ and $\varphi \in (2\pi, 4\pi)$ for proper rotations. This doubles the number of elements in a point group in all three cases: