Chapter 6

Groups and Representations in Quantum Mechanics

The universe is an enormous direct product of representations of symmetry groups.
—Steven Weinberg[1]

This chapter is devoted to applying the mathematical theory of groups and representations which we have developed in the preceding chapters to the quantum mechanical description of physical systems. The power of applying group theory to quantum mechanics is that it provides a framework for making *exact* statements about a physical system with a knowledge only of the symmetry operations which leave its Hamiltonian invariant, the so-called "group of the Hamiltonian." Moreover, when we apply the machinery of groups to quantum mechanics, we find that representations—and irreducible representations in particular—arise quite naturally, as do related concepts such as the importance of unitarity of representations and the connection between the symmetry of a physical system and the degeneracy of its eigenstates. We will follow the general sequence of the discussion in Sections 1.2 and 1.3,

[1]Steven Weinberg, Sheldon Glashow, and Abdus Salam were awarded the 1979 Nobel Prize in Physics for their incorporation of the weak and electromagnetic interactions into a single theory.

beginning with the group of the Hamiltonian, using this to establish the symmetry properties of the eigenfunctions, and concluding with a discussion of selection rules, which demonstrates the power and economy of using character tables. As a demonstration of the usefulness of these constructions, we will prove Bloch's theorem, the fundamental principle behind the properties of wavefunctions in periodic systems such as electrons and phonons (the quanta of lattice vibrations) in single crystals. The application of group theory to selection rules necessitates the introduction of the "direct product" of matrices and groups, though here, too, quantum mechanics provides a motivation for this concept.

6.1 The Group of the Hamiltonian

Recall the definition of a similarity transformation introduced in Section 3.3. Two matrices, or operators, A and B are related by a similarity transformation generated by a matrix (or operator) R if

$$B = RAR^{-1}\,.$$

The quantity B is therefore the expression of A under the transformation R. Consider now a Hamiltonian $\mathcal{H}$ and its transformation by an operation R

$$R\mathcal{H}R^{-1}\,.$$

The Hamiltonian is said to be *invariant* under R if

$$\mathcal{H} = R\mathcal{H}R^{-1}\,, \tag{6.1}$$

or, equivalently,

$$R\mathcal{H} = \mathcal{H}R\,. \tag{6.2}$$

Thus the *order* in which $\mathcal{H}$ and the R are applied is immaterial, so $\mathcal{H}$ and R commute: $[\mathcal{H}, R] = 0$. In this case, R is said to be a **symmetry operation** of the Hamiltonian.

Consider set of all symmetry operations of the Hamiltonian, which we will denote by $\{R_\alpha\}$. We now show that these operations form a group. To demonstrate closure, we observe that if R_α and R_β are two operations which satisfy (6.1), then

$$R_\alpha \mathcal{H} R_\alpha^{-1} = R_\alpha (R_\beta \mathcal{H} R_\beta^{-1}) R_\alpha^{-1} = (R_\alpha R_\beta)\mathcal{H}(R_\alpha R_\beta)^{-1} = \mathcal{H}\,.$$

Thus, the product $R_\alpha R_\beta = R_\gamma$ is also a symmetry operation of the Hamiltonian. Associativity is clearly obeyed since these operations represent transformations of coordinates and other variables of the Hamiltonian.[2] The unit element E corresponds to performing no operation at all and the inverse R_α^{-1} of a symmetry operation R_α is the application of the reverse operation to "undo" the original transformation. Thus, the set $\{R_\alpha\}$ forms a group, called the **group of the Hamiltonian**.

6.2 Eigenfunctions and Representations

There are a number of consequences of the discussion in the preceding section for the representations of the group of the Hamiltonian. Consider an eigenfunction φ of a Hamiltonian $\mathcal{H}$ corresponding to the eigenvalue E:

$$\mathcal{H}\varphi = E\varphi\,.$$

We now apply a symmetry operation R_α to both sides of this equation,

$$R_\alpha \mathcal{H}\varphi = E R_\alpha \varphi\,,$$

and use (6.2) to write

$$R_\alpha \mathcal{H}\varphi = \mathcal{H} R_\alpha \varphi\,.$$

Thus, we have

$$\mathcal{H}(R_\alpha \varphi) = E(R_\alpha \varphi)\,.$$

If the eigenvalue is nondegenerate, then $R_\alpha\varphi$ differs from φ by at most a phase factor:

$$R_\alpha \varphi = \mathrm{e}^{i\phi_\alpha}\varphi\,.$$

[2]The associativity of linear operations is discussed by Wigner in *Group Theory* (Academic, New York, 1959), p. 5.

The application of a second operation R_β then produces

$$R_\beta(R_\alpha\varphi) = \mathrm{e}^{i\phi_\beta}\mathrm{e}^{i\phi_\alpha}\varphi\,. \tag{6.3}$$

The left-hand side of this equation can also be written as

$$(R_\beta R_\alpha)\varphi = \mathrm{e}^{i\phi_{\beta\alpha}}\varphi\,, \tag{6.4}$$

Equating the right-hand sides of Eqs. (6.3) and (6.4), yields

$$\mathrm{e}^{i\phi_{\beta\alpha}} = \mathrm{e}^{i\phi_\beta}\mathrm{e}^{i\phi_\alpha}\,,$$

i.e., these phases preserve the multiplication table of the symmetry operations. Thus, the repeated application of all of the R_α to φ generates a *one-dimensional representation* of the group of the Hamiltonian.

The other case to consider occurs if the application of all of the symmetry operations to φ produces ℓ distinct eigenfunctions. These eigenfunctions are said to be ℓ-fold degenerate. If these are the *only* eigenfunctions which have energy E, this is said to be a **normal degeneracy**. If, however, there are other degenerate eigenfunctions which are not captured by this procedure, this is said to be an **accidental degeneracy**. The term "accidental" refers to the fact that the degeneracy is not due to symmetry. But an "accidental" degeneracy can also occur because a symmetry is "hidden," i.e., not immediately apparent, so the group of the Hamiltonian is not complete. One well-known example of this is the level degeneracy of the hydrogen atom.

For a normal degeneracy, there are orthonormal eigenfunctions φ_i, $i = 1, 2, \ldots, \ell$ which, upon application of one of the symmetry operations R_α are transformed into linear combinations of one another. Thus, if we denote by $\boldsymbol{\varphi}$ the ℓ-dimensional row vector

$$\boldsymbol{\varphi} = (\varphi_1, \varphi_2, \ldots, \varphi_\ell)\,,$$

we can write

$$R_\alpha\boldsymbol{\varphi} = \boldsymbol{\varphi}\Gamma(R_\alpha)\,,$$

where $\Gamma(R_\alpha)$ is an $\ell \times \ell$ matrix. In terms of components, this equation reads

$$R_\alpha\varphi_i = \sum_{k=1}^{\ell}\varphi_k[\Gamma(R_\alpha)]_{ki} \tag{6.5}$$

The successive application of operations R_α and R_β then yields

$$R_\beta R_\alpha \phi_i = R_\beta \sum_{k=1}^{\ell} \varphi_k [\Gamma(R_\alpha)]_{ki} = \sum_{k=1}^{\ell} (R_\beta \varphi_k)[\Gamma(R_\alpha)]_{ki} \,.$$

The operation $R_\beta \varphi_k$ can be written as in (6.5):

$$R_\beta \varphi_k = \sum_{j=1}^{\ell} \varphi_j [\Gamma(R_\beta)]_{jk} \,.$$

Thus,

$$\begin{aligned} R_\beta R_\alpha \phi_i &= \sum_{k=1}^{\ell} \sum_{j=1}^{\ell} \varphi_j [\Gamma(R_\beta)]_{jk} [\Gamma(R_\alpha)]_{ki} \\ &= \sum_{j=1}^{\ell} \varphi_j \left\{ \sum_{k=1}^{\ell} [\Gamma(R_\beta)]_{jk} [\Gamma(R_\alpha)]_{ki} \right\} . \end{aligned} \tag{6.6}$$

Alternatively, we can write

$$R_\beta R_\alpha \varphi_i = \sum_{j=1}^{\ell} \varphi_j [\Gamma(R_\beta R_\alpha)]_{ji} \,. \tag{6.7}$$

By comparing (6.6) and (6.7) and using the orthonormality of the wavefunctions, we conclude that

$$\Gamma(R_\beta R_\alpha) = \Gamma(R_\beta)\Gamma(R_\alpha) \,,$$

so the $\Gamma(R_i)$ form an ℓ-dimensional representation of the group of the Hamiltonian. Since the eigenfunctions can be made orthonormal, this representation can always be taken to be *unitary* (Problem Set 8). We will now show that this representation is also *irreducible*. We first consider the effect of replacing the φ_i by a linear combination of these functions, $\boldsymbol{\psi} = \boldsymbol{\varphi} U$. Then the effect of operating with R on the $\boldsymbol{\psi}$ is

$$R\boldsymbol{\psi} = R\boldsymbol{\varphi} U = \boldsymbol{\varphi}\Gamma U = \boldsymbol{\psi} U^{-1}\Gamma U \,,$$

i.e., the representation with the transformed wavefunctions is related by a similarity transformation to that with the original eigenfunctions, i.e., the two representations are *equivalent*. Suppose that this representation is reducible. Then there is a unitary transformation of the φ_j such that there are two or more subsets of the ψ_i that transform only among one another under the symmetry operations of the Hamiltonian. This implies that the application of the R_i to any eigenfunction generates eigenfunctions only in the same subset. The degeneracy of the eigenfunctions in the other subset is therefore *accidental*, in contradiction to our original assertion that the degeneracy is *normal*. Hence, the representation obtained for a normal degeneracy is *irreducible* and the corresponding eigenfunctions are said to *generate*, or form a **basis** for this representation.

We can summarize the results of this section as follows:

- To each eigenvalue of a Hamiltonian there corresponds a unique irreducible representation of the group of that Hamiltonian.
- The degeneracy of an eigenvalue is the dimensionality of this irreducible representation. Thus, the dimensionalities of the irreducible representations of a group are the possible degeneracies of Hamiltonians with that symmetry group.
- Group theory provides "good quantum numbers," i.e., labels corresponding irreducible representations to which eigenfunctions belong.
- Although these statements have been shown for *finite* groups, they are also valid for *continuous* groups.

6.3 Group Theory in Quantum Mechanics

The fact that eigenfunctions corresponding to an ℓ-fold degenerate eigenvalue form a basis for an ℓ-dimensional irreducible representation of the group of the Hamiltonian is one of the fundamental principles behind the application of group theory to quantum mechanics. In this section, we briefly describe the two main types of such applications, namely, where group theory is used to obtain *exact* results, and where it is used in conjunction with perturbation theory to obtain *approximate* results.

6.3.1 Exact Results

One of the most elegant applications of group theory to quantum mechanics involves using the group of the Hamiltonian to determine the (normal) degeneracies of the eigenstates, which are just the dimensions of the irreducible representations. Because such a classification is derived from the symmetry properties of the Hamiltonian, it can be accomplished without having to *solve* the Schrödinger equation. Among the most historically important of such applications is the classification of atomic spectral lines. The atomic Hamiltonian is comprised of the sum of the kinetic energies of the electrons and their Coulomb interactions, so an exact solution is impractical, even for few-electron atoms such as He. Nevertheless, the spherical symmetry of the Hamiltonian enables the identification of the irreducible representations of atomic states from which are derived the angular momentum addition rules and multiplet structures. This will be explored further when we discuss continuous groups. Another exact result is Bloch's theorem, which is the basis for many aspects of condensed matter physics. This theorem uses the translational invariance of perfect periodic crystals to determine the form of the eigenfunctions. As discussed in the next section, Bloch's theorem can be reduced to a statement about the (one-dimensional) irreducible representations and basis functions of cyclic groups.

The lowering of the symmetry of a Hamiltonian by a perturbation can also be examined with group theory. In particular, the question of whether the allowed degeneracies are affected by such a perturbation can be addressed by examining the irreducible representations of the groups of the original and perturbed Hamiltonians. Group theory can address not only whether degeneracies can change (from the irreducible representations of the two groups), but how irreducible representations of the original group are related to those of the perturbed group. Typically, when the symmetry of a system is lowered, the dimensionalities of the irreducible representations can also be lowered, resulting in a "splitting" of the original irreducible representations into lower-dimensional irreducible representations of the group of the perturbed system.

Finally, on a somewhat more practical level, group theory can be used to construct symmetrized linear combinations of basis functions to diagonalize a Hamiltonian. Examples where this arises is the lowering of the symmetry of a system by a perturbation, where the basis functions are the eigenfunctions of the original Hamiltonian, the bonding within molecules, where the basis functions are localized around the atomic sites within the molecule, and vibrations in molecules and solids, where the basis functions describe the displacements of atoms. These applications are discussed by Tinkham.[3]

6.3.2 Approximate Results

The most common application of group theory in approximate calculations involves the calculation of matrix elements in perturbation theory. A typical example is involved adding to a Hamiltonian $\mathcal{H}_0$ and perturbation $\mathcal{H}'$ due to an electromagnetic field which causes transitions between the eigenstates of the original Hamiltonian. The transition rate W is calculated from first-order time-dependent perturbation theory, with the result known as *Fermi's Golden Rule*:[4]

$$W = \frac{2\pi}{\hbar}\varrho_{if}|(i|\mathcal{H}'|f)|^2 ,$$

where ϱ_{if} is called the "joint density of states," which is a measure of the number of initial and final states which are available for the excitation, and $(i|\mathcal{H}'|f)$ is a matrix element of $\mathcal{H}'$ between the initial and final states. The application of group theory to this problem, which is the subject of Section 6.6, involves determining when this matrix element vanishes by reasons of symmetry.

6.4 Bloch's Theorem*

Bloch's theorem is of central importance to many aspects of electrons, phonons, and other excitations in crystalline solids. One of the main results of this theorem, namely, the form of the eigenfunctions, can be derived solely from group theory. We will work in one spatial dimension,

[3] M. Tinkham, *Group Theory and Quantum Mechanics* (McGraw–Hill, New York, 1964)

[4] L.I. Schiff, *Quantum Mechanics* 2nd edn (McGraw–Hill, New York, 1955)

but the discussion can be extended easily to higher dimensions. We consider a one-dimensional crystal where the distance between nearest neighbors is a and the number of repeat units is N (a large number for a macroscopic solid). Since this system is finite, it has no translational symmetry. However, by imposing a type of boundary condition known as *periodic*, whereby the Nth unit is identified with the first unit—effectively forming a circle from this solid—we now have N discrete symmetries. The Schrödinger equation for a particle of mass m moving in the periodic potential of this system is

$$\left[-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}+V(x)\right]\varphi = E\varphi\,,$$

where $V(x+a) = V(x)$.

6.4.1 The Group of the Hamiltonian

The translation of an eigenfunction by a will be denoted by R_a:

$$R_a\varphi(x) = \varphi(x+a)\,.$$

The basic properties of translations originate with the observation that a translation through na,

$$R_{na}\varphi(x) = \varphi(x+na)\,,$$

can be written as the n-fold product of R_a:

$$R_a^n\varphi(x) = \underbrace{R_aR_a\cdots R_a}_{n\,\text{factors}}\varphi(x) = \varphi(x+na)\,.$$

Moreover, because of the periodic boundary conditions, we identify the Nth unit with the first, so

$$R_a^N = R_0\,,$$

which means that no translation is carried out at all. Thus, the collection of all the translations can be written as the powers of a single element, R_a:

$$\{R_a, R_a^2, \ldots, R_a^N = E\}\,, \tag{6.8}$$

where E is the identity. This shows that the group of the Hamiltonian is a cyclic group of order N. In particular, since cyclic groups are Abelian, there are N one-dimensional irreducible representations of this group, i.e., each eigenvalue is nondegenerate and labelled by one of these irreducible representations.

6.4.2 Character Table and Irreducible Representations

Having identified the algebraic structure of the group of the Hamiltonian, we now construct the character table. Since $R_a^N = E$, and since all irreducible representations are one-dimensional, the character for R_a in each of these representations, $\chi^{(n)}(R_a)$ must obey this product:

$$\left[\chi^{(n)}(R_a)\right]^N = 1\,.$$

The solutions to this equation are the Nth roots of unity (cf. Problem 3, Problem Set 5):

$$\chi^{(n)}(R_a) = \mathrm{e}^{2\pi i n/N}, \qquad n = 0, 1, 2, \ldots N-1\,.$$

The character table is constructed by choosing one of these values for each irreducible representation and then determining the remaining entries from the multiplication table of the group (since each irreducible representation is one-dimensional). The resulting character table is:

	$\{E\}$	$\{R_a\}$	$\{R_a^2\}$	$\cdots$	$\{R_a^{N-1}\}$
Γ_1	1	1	1	$\cdots$	1
Γ_2	1	ω	ω^2	$\cdots$	ω^{N-1}
Γ_3	1	ω^2	ω^4	$\cdots$	$\omega^{2(N-1)}$
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$
Γ_N	1	ω^{N-1}	ω^{2N-2}	$\cdots$	$\omega^{(N-1)^2}$

where $\omega = \mathrm{e}^{2\pi i/N}$. If we denote the eigenfunction corresponding to the nth irreducible representation by φ_n, then applying R_a yields

$$R_a\varphi_n(x) = \omega^{n-1}\varphi_n(x) = \varphi_n(x+a)\,.$$

Since the characters of this group are pure phases, the moduli of the eigenfunctions are periodic functions:

$$|\varphi_n(x+a)|^2 = |\varphi_n(x)|^2 \,.$$

Thus, the most general form of the φ_n is

$$\varphi_n(x) = \mathrm{e}^{i\phi_n(x)} u_n(x) \,, \tag{6.9}$$

where $\phi_n(x)$ is a phase function, which we will determine below, and the u_n have the periodicity of the lattice: $u_n(x+a) = u_n(x)$. By combining this form of the wavefunction with the transformation properties required by the character table, we can write

$$R_a^m \varphi_n(x) = \omega^{m(n-1)} \varphi_n(x) = \omega^{m(n-1)} \mathrm{e}^{i\phi_n(x)} u_n(x) \,.$$

Alternatively, by applying the same translation operation directly to (6.9) yields

$$R_a^m \varphi_n(x) = \varphi_n(x+ma) = \mathrm{e}^{i\phi_n(x+ma)} u_n(x) \,.$$

By equating these two ways of writing $R_a^m \varphi_n(x)$, we find that their phase changes must be equal. This, in turn, requires that the phase function satisfies

$$\phi_n(x+ma) = \phi_n(x) + \frac{2\pi m(n-1)}{N} \,. \tag{6.10}$$

Thus, ϕ_n is a *linear* function of m and, therefore, also of $x+ma$, since ϕ_n is a function of only a single variable:

$$\phi_n(x) = Ax + B \,,$$

where A and B are constants to be determined. Upon substitution of this expression into both sides of (6.10),

$$A(x+ma) + B = Ax + B + \frac{2\pi m(n-1)}{N} \,,$$

and cancelling common factors, we obtain

$$\phi_n(x) = k_n x + B \,,$$

where

$$k_n = \frac{2\pi(n-1)}{Na} = \frac{2\pi(n-1)}{L}$$

and $L = Na$ is the size system. The wavefunction in (6.9) thereby reduces to

$$\varphi_n(x) = \mathrm{e}^{ik_n x} u_n(x)\,,$$

where we have absorbed the constant phase due to B into the definition of $u_n(x)$. This is called a **Bloch function**: a function $u_n(x)$ with the periodicity of the lattice modulated by a plane wave.[5] This is one of the two main results of Bloch's theorem, the other being the existence of energy gaps, which is beyond the scope of the discussion here.

6.5 Direct Products

The direct product provides a way of enlarging the number of elements in a group while retaining the group properties. Direct products occur in several contexts. For example, if a Hamiltonian or Lagrangian contains different types of coordinates, such as spatial coordinates for different particles, or spatial and spin coordinates, then the symmetry operations on the different coordinates commute with each other. If there is a coupling between such degrees of freedom, such as particle interactions or a spin-orbit interaction, then the direct product is required to determine the appropriate irreducible representations of the resulting eigenstates. In this section, we develop the group theory associated with direct products and their representations. We will then apply these concepts to selection rules in the following section.

[5]A related issue which can be addressed by group theory is the nature of the quantity $\hbar k_n$. Although it has units of momentum, it does not represent a true momentum, but is called the "crystal momentum." The true momentum $\hbar k$ labels the irreducible representations of the translation group, which is a continuous group and will be discussed in the next chapter. The discrete translations of a periodic potential form a subgroup of the full translation group, so the corresponding irreducible representations *cannot* be labelled by momentum.

6.5.1 Direct Product of Groups

Consider two groups

$$G_a = \{e, a_2, \ldots, a_{|G_a|}\}, \quad G_b = \{e, b_2, \ldots, b_{|G_b|}\}\,,$$

such that all elements in G_a commute with all elements in G_b:

$$a_i b_j = b_j a_i\,,$$

for $i = 1, 2, \ldots, |G_a|$ and $j = 1, 2, \ldots, |G_b|$. We have defined $a_1 = e$ and $b_1 = e$. The **direct product** of G_a and G_b, denoted by $G_a \otimes G_b$, is the set containing all elements $a_i b_j$:

$$G_a \otimes G_b = \{e, a_2, \ldots, a_{|G_a|}, b_2, \ldots, b_{|G_b|}, \ldots, a_i b_j, \ldots\}\,. \tag{6.11}$$

As shown in Problem 3 of Problem Set 8, the direct product is a group of order $|G_a||G_b|$.

Example 6.1. Consider the symmetry operations on an equilateral triangle that has a *thickness*, i.e., the triangle has become a "wedge." Thus, in addition to the original symmetry operations of the planar equilateral triangle, there is now also a reflection plane σ_h. There are now six vertices, which are labelled as in Example 2.1, except that we now distinguish between points which lie above, $\{1^+, 2^+, 3^+\}$, and below, $\{1^-, 2^-, 3^-\}$, the reflection plane. The original six operations do not transform points above and below the reflection plane into one another. The reflection plane, on the other hand, *only* transforms corresponding points above and below the plane into one another. Hence, the 6 operations of a planar triangle *commute* with σ_h.

The symmetry group of the equilateral wedge consists of the original 6 operations of a planar triangle, the horizontal reflection plane, and their products. Since the set with elements $\{E, \sigma_h\}$ forms a group (and each element commutes with the symmetry operations of an equilateral triangle), the appropriate group for the wedge is thereby obtained by taking the direct product

$$\{E, \sigma_{v,1}, \sigma_{v,2}, \sigma_{v,3}, C_3, C_3^2\} \otimes \{E, \sigma_h\}\,.$$

The 12 elements of this group are

$$\{E, \sigma_{v,1}, \sigma_{v,2}, \sigma_{v,3}, C_3, C_3^2, \sigma_h, \sigma_h\sigma_{v,1}, \sigma_h\sigma_{v,2}, \sigma_h\sigma_{v,3}, \sigma_h C_3, \sigma_h C_3^2\}\,.$$

∎

6.5.2 Direct Product of Matrices

The determination of the irreducible representations and the character table of a direct product group does not require a separate new calculation of the type discussed in the preceding chapter. Instead, we can utilize the irreducible representations of the two groups used to form the direct to obtain these quantities. To carry out these operations necessitates introducing the direct product of matrices.

The direct product C of two matrices A and B, written as $A \otimes B = C$, is defined in terms of matrix elements by

$$a_{ij} b_{kl} = c_{ik;jl} \,. \tag{6.12}$$

Note that the row and column labels of the matrix elements of C are *composite* labels: the row label, ik, is obtained from the row labels of the matrix elements of A and B and the column label, jl, is obtained from the corresponding column labels. The matrices need not have the same dimension and, in fact, need not even be square. However, since we will apply direct products to construct group representations, we will confine our discussion to square matrices. In this case, if A is an $n \times n$ matrix and B is an $m \times m$ matrix, C is an $mn \times mn$ matrix.

Example 6.2. For matrices A and B given by

$$A = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix}, \qquad B = \begin{pmatrix} b_{11} & b_{12} & b_{13} \\ b_{21} & b_{22} & b_{23} \\ b_{31} & b_{32} & b_{33} \end{pmatrix},$$

the direct product $C = A \otimes B$ is

$$A \otimes B = \begin{pmatrix} a_{11}b_{11} & a_{11}b_{12} & a_{11}b_{13} & a_{12}b_{11} & a_{12}b_{12} & a_{12}b_{13} \\ a_{11}b_{21} & a_{11}b_{22} & a_{11}b_{23} & a_{12}b_{21} & a_{12}b_{22} & a_{12}b_{23} \\ a_{11}b_{31} & a_{11}b_{32} & a_{11}b_{33} & a_{12}b_{31} & a_{12}b_{32} & a_{12}b_{33} \\ a_{21}b_{11} & a_{21}b_{12} & a_{21}b_{13} & a_{22}b_{11} & a_{22}b_{12} & a_{22}b_{13} \\ a_{21}b_{21} & a_{21}b_{22} & a_{21}b_{23} & a_{22}b_{21} & a_{22}b_{22} & a_{22}b_{23} \\ a_{21}b_{31} & a_{21}b_{32} & a_{21}b_{33} & a_{22}b_{31} & a_{22}b_{32} & a_{22}b_{33} \end{pmatrix}.$$

Another way of writing the direct product that more clearly displays its structure is

$$A \otimes B = \begin{pmatrix} a_{11}B & a_{12}B \\ a_{21}B & a_{22}B \end{pmatrix} .$$

∎

The notion of a direct product arises quite naturally in quantum mechanics if we consider the transformation properties of a product of two eigenfunctions. Suppose we have two eigenfunctions φ_i and $\varphi_{i'}$ of a Hamiltonian $\mathcal{H}$ which is invariant under some group of operations. As in Section 6.2, the action of these operations on the eigenfunctions of $\mathcal{H}$ is

$$R\varphi_i = \sum_{j=1}^{\ell} \varphi_j \Gamma_{ji}(R) ,$$

$$R\varphi_{i'} = \sum_{j'=1}^{\ell'} \varphi_{j'} \Gamma_{j'i'}(R) .$$

The question we now ask is: how does the *product* $\varphi_i \varphi_{i'}$ transform under the symmetry operations of the Hamiltonian? Given the transformation properties of φ_i and $\varphi_{i'}$ noted above, we first observe that

$$R(\varphi_i \varphi_{i'}) = R(\varphi_i) R(\varphi_{i'}) .$$

In other words, since R represents a coordinate transformation, its action on any function of the coordinates is to transform each occurrence of the coordinates. Thus,

$$\begin{aligned} R(\varphi_i \varphi_{i'}) &= \sum_{j=1}^{\ell} \sum_{j'=1}^{\ell'} \varphi_j \varphi_{j'} \Gamma_{ji}(R) \Gamma_{j'i'}(R) \\ &= \sum_{j=1}^{\ell} \sum_{j'=1}^{\ell'} \varphi_j \varphi_{j'} \Gamma_{jj';ii'}(R) , \end{aligned}$$

so $\varphi_i \varphi_{i'}$ transforms as the *direct product* of the irreducible representations associated with φ_i and $\varphi_{i'}$.

6.5.3 Representations of Direct Product Groups

Determining the representations of direct products and the construction of their character tables are based on the following theorem:

Theorem 6.1. The direct product of the representations of two groups is a representation of the direct product of these groups.

Proof. A typical product of elements in the direct product group in (6.11) is

$$(a_p b_q)(a_{p'} b_{q'}) = (a_p a_{p'})(b_q b_{q'}) = a_r b_{r'} \,.$$

A representation of the direct product group must preserve the multiplication table. We will use the notation that the matrix $A(a_p b_q)$ corresponds to the element $a_p b_q$. Thus, we must require that

$$A(a_p b_q) A(a_{p'} b_{q'}) = A(a_r b_{r'}) \,.$$

By using the definition of the direct product of two matrices in Equation (6.12), we can write this equation in terms of matrix elements as

$$\begin{aligned}
\Big[A(a_p b_q) A(a_{p'} b_{q'})\Big]_{ik;jl} &= \sum_{m,n} \underbrace{A(a_p b_q)_{ik;mn}}_{A(a_p)_{im} A(b_q)_{kn}} \, \underbrace{A(a_{p'} b_{q'})_{mn;jl}}_{(A(a_{p'})_{mj} A(b_{q'})_{nl}} \\
&= \underbrace{\bigg(\sum_m A(a_p)_{im} A(a_{p'})_{mj}\bigg)}_{A(a_p a_{p'})_{ij}} \underbrace{\bigg(\sum_n A(b_q)]_{kn} A(b_{q'})_{nl}\bigg)}_{A(b_p b_{p'})_{kl}} \\
&= A(a_r)_{ij} A(b_{r'})_{kl} \\
&= A(a_r b_{r'})_{ik;jl} \,.
\end{aligned}$$

Thus, the direct product of the representations preserves the multiplication table of the direct product group and, hence, is a representation of this group. ∎

In fact, as shown in Problem 4 of Problem Set 8, the direct product of irreducible representations of two groups is an irreducible representation of the direct product of those groups. An additional convenient feature of direct product groups is that the characters of its representations can be computed directly from the characters of the representations of the two groups forming the direct product. This statement is based on the following theorem:

Theorem 6.2. If $\chi(a_p)$ and $\chi(b_q)$ are the characters of representations of two groups G_a and G_b, the characters $\chi(a_pb_q)$ of the representation formed from the matrix direct product of these representations is

$$\chi(a_pb_q) = \chi(a_p)\chi(b_q)\,.$$

Proof. From the definition of the direct product, a representation of the direct product group is

$$A(a_pb_q)_{ij;kl} = A(a_p)_{ik}A(b_q)_{jl}\,.$$

Taking the trace of both sides of this expression yields

$$\underbrace{\sum_{i,j} A(a_pb_q)_{ij;ij}}_{\chi(a_pb_q)} = \underbrace{\Big(\sum_i A(a_p)_{ii}\Big)}_{\chi(a_p)}\underbrace{\Big(\sum_j A(b_q)_{jl}\Big)}_{\chi(b_q)}\,.$$

Thus,

$$\chi(a_pb_q) = \chi(a_p)\chi(b_q)\,,$$

which proves the theorem. ∎

Since the characters are associated with a given class, the characters for the classes of the direct product are computed from the characters of the classes of the original groups whose elements contribute to each class of the direct product. Moreover, the number of classes in the direct product group is the product of the numbers of classes in the original groups. This can be seen immediately from the equivalence classes in the direct product group. Using the fact that elements belonging to the different groups commute,

$$(a_ib_j)^{-1}(a_kb_l)(a_ib_j)^{-1} = (a_i^{-1}a_ka_i)(b_j^{-1}b_lb_j)\,.$$

Thus, equivalence classes in the direct product group must be formed from elements in equivalence classes in the original groups.

Example 6.3. Consider the direct product group of the equilateral wedge in Example 6.1. The classes of S_3 are (Example 2.9), in the notation of Example 5.5,

$$\{E\}, \qquad \{\sigma_{v,1}, \sigma_{v,2}, \sigma_{v,3}\}, \qquad \{C_3, C_3^2\}\,,$$

and the classes of the group $\{E, \sigma_h\}$ are

$$\{E\}, \qquad \{\sigma_h\}\,.$$

There are, therefore, six classes in the direct product group, which are obtained by taking the products of elements in the original classes, as discussed above:

$$\begin{gathered}\{E\}, \quad \{C_3, C_3^2\}, \ \{\sigma_{v,1}, \sigma_{v,2}, \sigma_{v,3}\}\,, \\ \{\sigma_h\}, \quad \sigma_h\{C_3, C_3^2\}, \ \sigma_h\{\sigma_{v,1}, \sigma_{v,2}, \sigma_{v,3}\}\,.\end{gathered}$$

∎

The structure of the character table of the direct product group can now be determined quite easily. We denote the character for the αth class of the jth irreducible representation of group G_a by $\chi_\alpha^j(a_p)$. Similarly, we denote the the character for the βth class of the lth irreducible representation of group G_a by $\chi_\beta^l(b_q)$. Since the direct products of irreducible representations of G_a and G_b are irreducible representations of $G_a \otimes G_b$ (Problem 4, Problem Set 8), and since the classes of $G_a \otimes G_b$ are formed from products of classes of G_a and G_b, the character table of the direct product group has the form

$$\chi_{\alpha\beta}^{jl}(a_p b_q) = \chi_\alpha^j(a_p)\chi_\beta^l(b_q)\,.$$

In other words, with the character tables regarded as square matrices, the character table of the direct product group $G_a \times G_b$ is constructed as a *direct product* of the character tables of G_a and G_b!

Example 6.4. For the direct product group in Example 6.3, the character tables of the original groups are

	E	$3\sigma_v$	$2C_3$
A_1	1	1	1
A_2	1	-1	1
E	2	0	-1

and

	E	σ_h
A_1	1	1
A_2	1	-1

The character table of the direct product group is, therefore, the direct product of these tables (cf. Example 6.1):

	E	$3\sigma_v$	$2C_3$	σ_h	$3\sigma_h\sigma_v$	$2\sigma_h C_3$
A_1^+	1	1	1	1	1	1
A_2^+	1	-1	1	1	-1	1
E^+	2	0	-1	2	0	-1
A_1^-	1	1	1	-1	-1	-1
A_2^-	1	-1	1	-1	1	-1
E^-	2	0	-1	-2	0	1

where the superscript on the irreducible representation refers to the parity under reflection through σ_h. ∎

6.6 Selection Rules

One common application of direct products and their representations is in the determination of selection rules. In this section, we will apply the techniques developed in this chapter to determine the conditions where symmetry requires that a matrix element vanishes.

6.6.1 Matrix Elements

As discussed in Section 6.3.2, the determination of selection rules is based on using group theory to ascertain when the matrix element

$$M_{if} = (i|\mathcal{H}'|f) = \int \varphi_i(x)^* \mathcal{H}' \varphi_f(x)\,\mathrm{d}x \tag{6.13}$$

vanishes by reasons of symmetry. In this matrix element, the initial state transforms according to an irreducible representation $\Gamma^{(i)}$ and the final state transforms according to an irreducible representation $\Gamma^{(f)}$. It only remains to determine the transformation properties of $\mathcal{H}'$. We do this by applying each of the operations of the group of the original Hamiltonian $\mathcal{H}_0$ to the perturbation $\mathcal{H}'$. If we retain only the distinct results of these operations we obtain, by construction, a representation of the group of the Hamiltonian, which we denote by Γ'. This representation may be either reducible or irreducible, depending on $\mathcal{H}'$ and on the symmetry of $\mathcal{H}_0$. If $\mathcal{H}'$ has the same symmetry as $\mathcal{H}_0$, then this procedure generates the identical representation. At the other extreme, if $\mathcal{H}'$ has *none* of the symmetry properties of $\mathcal{H}_0$, then this procedure generates a reducible representation whose dimensionality is equal to the order of the group.

We now consider the symmetry properties under transformation of the product $\mathcal{H}(x)\varphi_f(x)$. From the discussion in Section 6.5.2, we conclude that this quantity transforms as the direct product $\Gamma' \otimes \Gamma^{(f)}$. Since quantities that transform to different irreducible irreducible representations are orthogonal (Problem 6, Problem Set 8), the matrix element (6.13) vanishes if this direct product is either not equal to $\Gamma^{(i)}$ or, if it is reducible, does not include $\Gamma^{(i)}$ in its decomposition. We can summarize this result in the following theorem:

Theorem 6.3. The matrix element

$$(i|\mathcal{H}'|f) = \int \varphi_i(x)^* \mathcal{H}' \varphi_f(x)\,\mathrm{d}x$$

vanishes if the irreducible representation $\Gamma^{(i)}$ corresponding to φ_i is not included in the direct product $\Gamma' \otimes \Gamma^{(f)}$ of the representations Γ' and $\Gamma^{(f)}$ corresponding to $\mathcal{H}'$ and φ_f, respectively.

It is important to note that this selection rule only provides a condition that guarantees that the matrix element will vanish. It does *not* guarantee that the matrix element will not vanish even if the conditions of the theorem are fulfilled.

6.6.2 Dipole Selection Rules

As a scenario which illustrates the power of group theoretical methods, suppose that $\mathcal{H}'$ transforms as a vector, i.e., as (x, y, z). This situation arises when the transitions described by Fermi's Golden Rule (Section 6.3.2) are caused by an electromagnetic field. The form of $\mathcal{H}'$ in the presence of an electromagnetic potential $\boldsymbol{A}$ is obtained by making the replacement[6]

$$\boldsymbol{p} \to \boldsymbol{p} - e\boldsymbol{A}$$

for the momentum in the Hamiltonian. For weak fields, this leads to a perturbation of the form

$$\mathcal{H}' = \frac{e}{m}\boldsymbol{p} \cdot \boldsymbol{A} \tag{6.14}$$

Since the electromagnetic is typically uniform, we can write the matrix element M_{if} as

$$M_{if} \sim (i|\boldsymbol{p}|f) \cdot \boldsymbol{A}$$

so the transformation properties of $\boldsymbol{p} = (p_x, p_y, p_z)$, which are clearly those of a *vector*, determine the selection rules for electromagnetic transitions. These are called the **dipole selection rules.** The examination of many properties of materials rely on the evaluation of dipole matrix elements.

Example 6.6. Suppose the group of the Hamiltonian corresponds to the symmetry operations of an equilateral triangle, i.e., C_{3v}, the character table for which is (Example 5.5)

[6] H. Goldstein, *Classical Mechanics* (Addison–Wesley, Reading, MA, 1950)

C_{3v}	E	$3\sigma_v$	$2C_3$
A_1	1	1	1
A_2	1	-1	1
E	2	0	-1

To determine the dipole selection rules for this system, we must first determine the transformation properties of a vector $\boldsymbol{r} = (x, y, z)$. We take the x- and y-axes in the plane of the equilateral triangle and the z-axis normal to this plane to form a right-handed coordinate system. Applying each symmetry operation to $\boldsymbol{r}$ produces a *reducible* representation because these operations are either rotations or reflections through vertical planes. Thus, the z coordinate is invariant under every symmetry operation of this group which, together with the fact that an (x, y) basis generates the two-dimensional irreducible representation E, yields

$$\Gamma' = A_1 \oplus E$$

We must now calculate the characters associated with the direct products of between Γ' and each irreducible representation to determine the allowed final states given the transformation properties of the initial states. The characters for these direct products are shown below

$\Gamma' = A_1 \oplus E$

C_{3v}	E	$3\sigma_v$	$2C_3$
A_1	1	1	1
A_2	1	-1	1
E	2	0	-1
$A_1 \otimes \Gamma'$	3	1	0
$A_2 \otimes \Gamma'$	3	-1	0
$E \otimes \Gamma'$	6	0	0

Using the decomposition theorem, we find

$$A_1 \otimes \Gamma' = A_1 \oplus E$$

$$A_2 \otimes \Gamma' = A_2 \oplus E$$

$$E \otimes \Gamma' = A_1 \oplus A_2 \oplus 2E$$

Thus, if the initial state transforms as the identical representation A_1, the matrix element vanishes if the final state transforms as A_2. If the initial state transforms as the "parity" representation A_2, the matrix element vanishes if the final state transforms as A_1. Finally, there is no symmetry restriction if the initial state transforms as the "coordinate" representation E. ∎

6.7 Summary

This chapter has demonstrated how the mathematics of groups and their representations are used in quantum mechanics and, indeed, how many of the structures introduced in the preceding chapters appear quite naturally in this context. Apart from exact results, such as Bloch's theorem, we have focussed on the derivation of selection rules induced by perturbations, and derived the principles behind dipole selection rules. A detailed discussion of other applications of discrete groups to quantum mechanical problems is described in the book by Tinkham. Many of the proofs concerning the relation between quantum mechanics and representations of the group of the Hamiltonian are discussed by Wigner.