6

Application to Selection Rules and Direct Products

Our second general application of group theory to physical problems will be to selection rules. In considering selection rules we always involve some interaction Hamiltonian matrix $\mathcal{H}'$ that couples two states ψ_α and ψ_β. Group theory is often invoked to decide whether or not these states are indeed coupled and this is done by testing whether or not the matrix element $(\psi_\alpha, \mathcal{H}'\psi_\beta)$ vanishes by symmetry. The simplest case to consider is the one where the perturbation $\mathcal{H}'$ does not destroy the symmetry operations and is invariant under all the symmetry operations of the group of the Schrödinger equation. Since these matrix elements transform as scalars (numbers), then $(\psi_\alpha, \mathcal{H}'\psi_\beta)$ must exhibit the full group symmetry, and must therefore transform as the fully symmetric representation Γ_1. Thus, if $(\psi_\alpha, \mathcal{H}'\psi_\beta)$ does *not transform as a number, it vanishes.* To exploit these symmetry properties, we thus choose the wave functions ψ_α^* and ψ_β to be eigenfunctions for the unperturbed Hamiltonian, which are basis functions for irreducible representations of the group of Schrödinger's equation. Here $\mathcal{H}'\psi_\beta$ transforms according to an irreducible representation of the group of Schrödinger's equation. This product involves the direct product of two representations and the theory behind the direct product of two representations will be given in this chapter. If $\mathcal{H}'\psi_\beta$ is orthogonal to ψ_α, then the matrix element $(\psi_\alpha, \mathcal{H}'\psi_\beta)$ vanishes by symmetry; otherwise the matrix element need not vanish, and a transition between state ψ_α and ψ_β may occur.

6.1 The Electromagnetic Interaction as a Perturbation

In considering various selection rules that arise in physical problems, we often have to consider matrix elements of a perturbation Hamiltonian which lowers the symmetry of the unperturbed problem. For example, the Hamiltonian in the presence of electromagnetic fields can be written as

$$\mathcal{H} = \frac{1}{2m}\left(\boldsymbol{p} - \frac{e}{c}\boldsymbol{A}\right)^2 + V\,. \tag{6.1}$$

Then the proper form of the Hamiltonian for an electron in a solid in the presence of an electromagnetic field is

$$\mathcal{H} = \frac{(\boldsymbol{p} - e/c\boldsymbol{A})^2}{2m} + V(\boldsymbol{r}) = \frac{p^2}{2m} + V(\boldsymbol{r}) - \frac{e}{mc}\boldsymbol{p} \cdot \boldsymbol{A} + \frac{e^2 A^2}{2mc^2}\,, \tag{6.2}$$

in which $\boldsymbol{A}$ is the vector potential due to the electromagnetic fields and $V(\boldsymbol{r})$ is the periodic potential. Thus, the one-electron Hamiltonian without electromagnetic fields is

$$\mathcal{H}_0 = \frac{p^2}{2m} + V(\boldsymbol{r})\,, \tag{6.3}$$

and the electromagnetic perturbation terms $\mathcal{H}'_{\text{em}}$ are

$$\mathcal{H}'_{\text{em}} = -\frac{e}{mc}\boldsymbol{p} \cdot \boldsymbol{A} + \frac{e^2 A^2}{2mc^2}\,, \tag{6.4}$$

which is usually approximated by the leading term for the electromagnetic perturbation Hamiltonian

$$\mathcal{H}'_{\text{em}} \cong -\frac{e}{mc}\boldsymbol{p} \cdot \boldsymbol{A}\,. \tag{6.5}$$

Such a perturbation Hamiltonian is generally *not* invariant under the symmetry operations of the group of Schrödinger's equation which are determined by the symmetry of the unperturbed Hamiltonian $\mathcal{H}_0$. Therefore, we must consider the transformation properties of $\mathcal{H}'\psi_\beta$ where the eigenfunction ψ_β is chosen to transform as one of the partners $\psi_j^{(\Gamma_i)}$ (denoted by $|\Gamma_i j\rangle$ in Chap. 4) of an irreducible representation Γ_i of the unperturbed Hamiltonian $\mathcal{H}_0$. In general, the action of $\mathcal{H}'$ on $\psi_j^{(\Gamma_i)}$ will mix all other partners of the representation Γ_i since any arbitrary function can be expanded in terms of a complete set of functions $\psi_j^{(\Gamma_i)}$. In group theory, the transformation properties of $\mathcal{H}'\psi_j^{(\Gamma_i)}$ are handled through what is called the *direct product*. When $\mathcal{H}'$ does not transform as the totally symmetric representation (e.g., $\mathcal{H}'_{\text{em}}$ transforms as a vector x, y, z), then the matrix element $(\psi_k^{(\Gamma_i)}, \mathcal{H}'\psi_j^{(\Gamma_i)})$ will not in general vanish.

The discussion of selection rules in this chapter is organized around the following topics:

(a) summary of important symmetry rules for basis functions,
(b) theory of the Direct Product of Groups and Representations,
(c) the Selection Rule concept in Group Theoretical Terms,
(d) example of Selection Rules for electric dipole transitions in a system with full cubic point group symmetry.

6.2 Orthogonality of Basis Functions

The basis functions $\psi_\alpha^{(i)}$ where we here use the superscript i as an abbreviated notation for the superscript Γ_i for a given irreducible representation i are defined by (see (4.1))

$$\hat{P}_R \psi_\alpha^{(i)} = \sum_{j=1}^{\ell_i} D^{(i)}(R)_{j\alpha} \psi_j^{(i)} , \tag{6.6}$$

where $\hat{P}_R$ is the symmetry operator, $\psi_\alpha^{(i)}$ denotes the basis functions for an l_i-dimensional irreducible representation (i) and $D^{(i)}(R)_{j\alpha}$ is the matrix representation for symmetry element R in irreducible representation (i). To exploit the symmetry properties of a given problem, we want to find eigenfunctions which form basis functions for the irreducible representations of the group of Schrödinger's equation. We can find such eigenfunctions using the symmetry operator and projection operator techniques discussed in Chap. 4. In this chapter, we will then assume that the eigenfunctions have been chosen to transform as irreducible representations of the group of Schrödinger's equation for $\mathcal{H}_0$. The application of group theory to selection rules then depends on the following orthogonality theorem. This orthogonality theorem can be considered as the selection rule for the identity operator.

Theorem. *Two basis functions which belong either to different irreducible representations or to different columns (rows) of the same representation are orthogonal.*

Proof. Let $\phi_\alpha^{(i)}$ and $\psi_{\alpha'}^{(i')}$ be two basis functions belonging, respectively, to irreducible representations (i) and (i') and corresponding to columns α and α' of their respective representations. By definition:

$$\hat{P}_R \phi_\alpha^{(i)} = \sum_{j=1}^{\ell_i} D^{(i)}(R)_{\alpha j} \phi_j^{(i)} ,$$

$$\hat{P}_R \psi_{\alpha'}^{(i')} = \sum_{j'=1}^{\ell_{i'}} D^{(i')}(R)_{\alpha' j'} \psi_{j'}^{(i')} . \tag{6.7}$$

Because the scalar product (or the matrix element of unity taken between the two states) is independent of the coordinate system, we can write the scalar product as

$$\begin{aligned}\left(\phi_\alpha^{(i)}, \psi_{\alpha'}^{(i')}\right) &= \left(\hat{P}_{\mathrm{R}} \phi_\alpha^{(i)}, \hat{P}_{\mathrm{R}} \psi_{\alpha'}^{(i')}\right) \\ &= \sum_{j,j'} D^{(i)}(R)^*_{\alpha j} D^{(i')}(R)_{\alpha' j'} \left(\phi_j^{(i)}, \psi_{j'}^{(i')}\right) \\ &= \frac{1}{h} \sum_{j,j'} \sum_R D^{(i)}(R)^*_{\alpha j} D^{(i')}(R)_{\alpha' j'} \left(\phi_j^{(i)}, \psi_{j'}^{(i')}\right) ,\end{aligned} \tag{6.8}$$

since the left-hand side of (6.8) is independent of R, and h is the order of the group. Now apply the Wonderful Orthogonality Theorem (Eq. 2.52)

$$\frac{1}{h}\sum_{R} D^{(i)}(R)^{*}_{\alpha j} D^{(i')}(R)_{\alpha' j'} = \frac{1}{\ell_i}\delta_{ii'}\delta_{jj'}\delta_{\alpha\alpha'} \tag{6.9}$$

to (6.8), which yields:

$$\left(\phi^{(i)}_{\alpha}, \psi^{(i')}_{\alpha'}\right) = \frac{1}{\ell_i}\delta_{i,i'}\delta_{\alpha,\alpha'}\sum_{j=1}^{\ell_i}\left(\phi^{(i)}_{j}, \psi^{(i)}_{j}\right) . \tag{6.10}$$

Thus, according to (6.10), if the basis functions $\phi^{(i)}_{\alpha}$ and $\psi^{(i')}_{\alpha'}$ correspond to two different irreducible representations $i \neq i'$ they are orthogonal. If they correspond to the same representation ($i = i'$), they are still orthogonal *if* they correspond to different columns (or rows) of the matrix – i.e., if they correspond to different partners of representation i. We further note that the right-hand side of (6.10) is independent of α so that the *scalar product is the same for all components* α, thereby completing the proof of the orthogonality theorem. □

In the context of selection rules, the orthogonality theorem discussed above applies directly to the identity operator. Clearly, if a symmetry operator is invariant under all of the symmetry operations of the group of Schrödinger's equation then it transforms like the identity operator. For example, if

$$\mathcal{H}_0\psi^{(i')}_{\alpha'} = E^{(i')}_{\alpha'}\psi^{(i')}_{\alpha'} \tag{6.11}$$

then $E^{(i')}_{\alpha'}$ is a number (or eigenvalues) which is independent of any coordinate system.

If $\psi^{(i')}_{\alpha'}$ and $\phi^{(i)}_{\alpha}$ are both eigenfunctions of the Hamiltonian $\mathcal{H}_0$ and are also basis functions for irreducible representations (i') and (i), then the *matrix element* $(\phi^{(i)}_{\alpha}, \mathcal{H}_0\psi^{(i')}_{\alpha'})$ vanishes unless $i = i'$ and $\alpha = \alpha'$, which is a result familiar to us from quantum mechanics.

In general, selection rules deal with the matrix elements of an operator different from the identity operator. In the more general case when we have a perturbation $\mathcal{H}'$, the perturbation need not have the full symmetry of $\mathcal{H}_0$. In general $\mathcal{H}'\psi$ *transforms differently from* ψ.

6.3 Direct Product of Two Groups

We now define the *direct product of two groups*. Let $G_A = E, A_2, \ldots, A_{h_a}$ and $G_B = E, B_2, \ldots, B_{h_b}$ be two groups such that all operators A_R commute with all operators B_S. Then the direct product group is

$$G_A \otimes G_B = E, A_2, \ldots, A_{h_a}, B_2, A_2B_2, \ldots, A_{h_a}B_2, \ldots, A_{h_a}B_{h_b} \tag{6.12}$$

and has $(h_a \times h_b)$ elements. It is easily shown that if G_A and G_B are groups, then the direct product group $G_A \otimes G_B$ *is* a group. Examples of direct product groups that are frequently encountered involve products of groups with the group of inversions (group $C_i(S_2)$ with two elements E, i) and the group of reflections (group $C_\sigma(C_{1h})$ with two elements E, σ_h). For example, we can make a direct product group D_{3d} from the group D_3 by compounding all the operations of D_3 with (E, i) (to obtain $D_{3d} = D_3 \otimes C_i$), where i is the inversion operation (see Table A.13). An example of the group D_{3d} is a triangle with finite thickness. In general, we simply write the direct product group

$$D_{3d} = D_3 \otimes i\,, \tag{6.13}$$

when compounding the initial group D_3 with the inversion operation or with the mirror reflection in a horizontal plane (see Table A.14):

$$D_{3h} = D_3 \otimes \sigma_h\,. \tag{6.14}$$

Likewise, the full cubic group O_h is a direct product group of $O \otimes i$.

6.4 Direct Product of Two Irreducible Representations

In addition to *direct product groups* we have the *direct product of two representations* which is conveniently defined in terms of the direct product of two matrices. From algebra, we have the definition of the direct product of two matrices $A \otimes B = C$, whereby every element of A is multiplied by every element of B. Thus, the direct product matrix C has a double set of indices

$$A_{ij}B_{k\ell} = C_{ik,j\ell}\,. \tag{6.15}$$

Thus, if A is a (2×2) matrix and B is a (3×3) matrix, then C is a (6×6) matrix.

Theorem. *The direct product of the representations of the groups A and B forms a representation of the direct product group.*

Proof. We need to prove that

$$D^{(a)}_{ij}(A_i)D^{(b)}_{pq}(B_j) = (D^{(a\otimes b)}(A_iB_j))_{ip,jq}\,. \tag{6.16}$$

To prove this theorem we need to show that

$$D^{(a\otimes b)}(A_kB_\ell)\; D^{(a\otimes b)}(A_{k'}B_{\ell'}) = D^{(a\otimes b)}(A_iB_j)\,, \tag{6.17}$$

where

$$A_i = A_kA_{k'}\,, \quad B_j = B_\ell B_{\ell'}\,. \tag{6.18}$$

Since the elements of group A commute with those of group B by the definition of the direct product group, the multiplication property of elements in the direct product group is

$$A_k B_\ell \, A_{k'} B_{\ell'} = A_k A_{k'} \, B_\ell B_{\ell'} = A_i B_j \,, \tag{6.19}$$

where $A_k B_\ell$ is a typical element of the direct product group. We must now show that the representations reproduce this multiplication property. By definition:

$$\begin{aligned} &D^{(a\otimes b)}(A_k B_\ell) D^{(a\otimes b)}(A_{k'} B_{\ell'}) \\ &= [D^{(a)}(A_k) \otimes D^{(b)}(B_\ell)][D^{(a)}(A_{k'}) \otimes D^{(b)}(B_{\ell'})] \,. \end{aligned} \tag{6.20}$$

To proceed with the proof, we write (6.20) in terms of components and carry out the matrix multiplication:

$$\begin{aligned} &\left[D^{(a\otimes b)}(A_k B_\ell) D^{(a\otimes b)}(A_{k'} B_{\ell'})\right]_{ip,jq} \\ &= \sum_{sr} (D^{(a)}(A_k) \otimes D^{(b)}(B_\ell))_{ip,sr} (D^{(a)}(A_{k'}) \otimes D^{(b)}(B_{\ell'}))_{sr,jq} \\ &= \sum_s D^{(a)}_{is}(A_k) D^{(a)}_{sj}(A_{k'}) \sum_r D^{(b)}_{pr}(B_\ell) D^{(b)}_{rq}(B_{\ell'}) \\ &= D^{(a)}_{ij}(A_i) D^{(b)}_{pq}(B_j) = (D^{(a\otimes b)}(A_i B_j))_{ip,jq} \,. \end{aligned} \tag{6.21}$$

This completes the proof. □

It can be further shown that the direct product of two *irreducible* representations of groups G_A and G_B yields an *irreducible* representation of the direct product group so that all irreducible representations of the direct product group can be generated from the irreducible representations of the original groups before they are joined. We can also take direct products between two representations of the same group. Essentially the same proof as given in this section shows that the direct product of two representations of the same group is also a representation of that group, though in general, it is a reducible representation. The proof proceeds by showing

$$\left[D^{(\ell_1\otimes\ell_2)}(A) D^{(\ell_1\otimes\ell_2)}(B)\right]_{ip,jq} = D^{(\ell_1\otimes\ell_2)}(AB)_{ip,jq} \,, \tag{6.22}$$

where we use the short-hand notation ℓ_1 and ℓ_2 to denote irreducible representations with the corresponding dimensionalities. The direct product representation $D^{(\ell_1\otimes\ell_2)}(R)$ will in general be reducible even though the representations ℓ_1 and ℓ_2 are irreducible.

6.5 Characters for the Direct Product

In this section we find the characters for the direct product of groups and for the direct product of representations of the same group.

Theorem. *The simplest imaginable formulas are assumed by the characters in direct product groups or in taking the direct product of two representations:*

(a) If the direct product occurs between two groups, then the characters for the irreducible representations in the direct product group are obtained by multiplication of the characters of the irreducible representations of the original groups according to

$$\chi^{(a\otimes b)}(A_k B_\ell) = \chi^{(a)}(A_k)\,\chi^{(b)}(B_\ell)\,. \tag{6.23}$$

(b) If the direct product is taken between two representations of the same group, then the character for the direct product representation is written as

$$\chi^{(\ell_1\otimes\ell_2)}(R) = \chi^{(\ell_1)}(R)\,\chi^{(\ell_2)}(R)\,. \tag{6.24}$$

Proof. Consider the diagonal matrix element of an element in the direct product group. From the definition of the direct product of two groups, we write

$$D^{(a\otimes b)}(A_k B_\ell)_{ip,jq} = D^{(a)}_{ij}(A_k) D^{(b)}_{pq}(B_\ell)\,. \tag{6.25}$$

Taking the diagonal matrix elements of (6.25) and summing over these matrix elements, we obtain

$$\sum_{ip} D^{(a\otimes b)}(A_k B_\ell)_{ip,ip} = \sum_i D^{(a)}_{ii}(A_k) \sum_p D^{(b)}_{pp}(B_\ell)\,, \tag{6.26}$$

which can be written in terms of the traces:

$$\chi^{(a\otimes b)}(A_k B_\ell) = \chi^{(a)}(A_k)\chi^{(b)}(B_\ell)\,. \tag{6.27}$$

This completes the proof of the theorem for the direct product of two groups. □

The result of (6.27) holds equally well for classes (i.e., $R \to \mathcal{C}$), and thus can be used to find the character tables for direct product groups as is explained below.

Exactly the same proof as given above can be applied to find the character for the direct product of two representations of the same group

$$\chi^{(\ell_1\otimes\ell_2)}(R) = \chi^{(\ell_1)}(R)\chi^{(\ell_2)}(R) \tag{6.28}$$

for each symmetry element R. The direct product representation is irreducible only if $\chi^{(\ell_1\otimes\ell_2)}(R)$ for all R is identical to the corresponding characters for one of the irreducible representations of the group $\ell_1 \otimes \ell_2$.

In general, if we take the direct product between two irreducible representations of a group, then the resulting direct product representation will be reducible. If it is reducible, the character for the direct product can then be written as a linear combination of the characters for irreducible representations of the group (see Sect. 3.4):

$$\chi^{(\lambda)}(R)\chi^{(\mu)}(R) = \sum_{\nu} a_{\lambda\mu\nu}\chi^{(\nu)}(R)\,, \tag{6.29}$$

where from (3.20) we can write the coefficients $a_{\lambda\mu\nu}$ as

$$a_{\lambda\mu\nu} = \frac{1}{h}\sum_{\mathcal{C}_\alpha} N_{\mathcal{C}_\alpha}\chi^{(\nu)}(\mathcal{C}_\alpha)^* \left[\chi^{(\lambda)}(\mathcal{C}_\alpha)\chi^{(\mu)}(\mathcal{C}_\alpha)\right]\,, \tag{6.30}$$

where $\mathcal{C}_\alpha$ denotes classes and $N_{\mathcal{C}_\alpha}$ denotes the number of elements in class $\mathcal{C}_\alpha$. In applications of group theory to selection rules, constant use is made of (6.29) and (6.30).

Finally, we use the result of (6.27) to show how the character tables for the original groups G_A and G_B are used to form the character table for the direct product group. First, we form the elements and classes of the direct product group and then we use the character tables of G_A and G_B to form the character table for $G_A \otimes G_B$. In many important cases, one of the groups (e.g., G_B) has only two elements (such as the group C_i with elements E, i) and two irreducible representations Γ_1 with characters (1,1) and $\Gamma_{1'}$ with characters $(1, -1)$. We illustrate such a case below for the direct product group $C_{4h} = C_4 \otimes i$, a table that is not listed explicitly in Chap. 3 or in Appendix A. In the character table for group C_{4h} (Table 6.1) we use the notation g to denote representations that are even (German, *gerade*) under inversion, and u to denote representations that are odd (German, *ungerade*) under inversion.

We note that the upper left-hand quadrant of Table 6.1 contains the character table for the group C_4. The four classes obtained by multiplication of

Table 6.1. Character table for point group C_{4h}

	$C_{4h} \equiv C_4 \otimes i$				$(4/m)$				
	E	C_2	C_4	C_4^3	i	iC_2	iC_4	iC_4^3	
A_g	1	1	1	1	1	1	1	1	
B_g	1	1	-1	-1	1	1	-1	-1	even under
E_g	$\begin{cases}1\\1\end{cases}$	$\begin{matrix}-1\\-1\end{matrix}$	$\begin{matrix}i\\-i\end{matrix}$	$\begin{matrix}-i\\i\end{matrix}$	$\begin{matrix}1\\1\end{matrix}$	$\begin{matrix}-1\\-1\end{matrix}$	$\begin{matrix}i\\-i\end{matrix}$	$\begin{matrix}-i\\i\end{matrix}$	inversion (g)
A_u	1	1	1	1	-1	-1	-1	-1	
B_u	1	1	-1	-1	-1	-1	1	1	odd under
E_u	$\begin{cases}1\\1\end{cases}$	$\begin{matrix}-1\\-1\end{matrix}$	$\begin{matrix}i\\-i\end{matrix}$	$\begin{matrix}-i\\i\end{matrix}$	$\begin{matrix}-1\\-1\end{matrix}$	$\begin{matrix}1\\1\end{matrix}$	$\begin{matrix}-i\\i\end{matrix}$	$\begin{matrix}i\\-i\end{matrix}$	inversion (u)

the classes of C_4 by i are listed on top of the upper right columns. The characters in the upper right-hand and lower left-hand quadrants are the same as in the upper left hand quadrant, while the characters in the lower right-hand quadrant are all multiplied by (-1) to produce the odd (ungerade) irreducible representations of group C_{4h}.

6.6 Selection Rule Concept in Group Theoretical Terms

Having considered the background for taking direct products, we are now ready to consider the selection rules for the matrix element

$$(\psi_\alpha^{(i)}, \mathcal{H}'\phi_{\alpha'}^{(i')}) . \tag{6.31}$$

This matrix element can be computed by integrating the indicated scalar product over all space. Group theory then tells us that when any or all the symmetry operations of the group are applied, this *matrix element must transform as a constant.* Conversely, if the matrix element is not invariant under the symmetry operations which form the group of Schrödinger's equation, then the matrix element must vanish. We will now express the same physical concepts in terms of the direct product formalism.

Let the wave functions $\phi_\alpha^{(i)}$ and $\psi_{\alpha'}^{(i')}$ transform, respectively, as partners α and α' of irreducible representations Γ_i and $\Gamma_{i'}$, and let $\mathcal{H}'$ transform as representation Γ_j. Then if the direct product $\Gamma_j \otimes \Gamma_{i'}$ is orthogonal to Γ_i, the matrix element vanishes, or equivalently if $\Gamma_i \otimes \Gamma_j \otimes \Gamma_{i'}$ does not contain the fully symmetrical representation Γ_1, the matrix element vanishes. In particular, if $\mathcal{H}'$ transforms as Γ_1 (i.e., the perturbation does not lower the symmetry of the system), then, because of the orthogonality theorem for basis functions, either $\phi_\alpha^{(i')}$ and $\psi_{\alpha'}^{(i)}$ must correspond to the same irreducible representation and to the same partners of that representation or they are orthogonal to one another.

To illustrate the meaning of these statements for a more general case, we will apply these selection rule concepts to the case of electric dipole transitions in Sect. 6.7 below. First, we express the perturbation $\mathcal{H}'$ (in this case due to the electromagnetic field) in terms of the irreducible representations that $\mathcal{H}'$ contains in the group of Schrödinger's equation:

$$\mathcal{H}' = \sum_{j,\beta} f_\beta^{(j)} \mathcal{H}_\beta^{\prime(j)} , \tag{6.32}$$

where j denotes the irreducible representations Γ_j of the Hamiltonian $\mathcal{H}'$, and β denotes the partners of Γ_j. Then $\mathcal{H}'\phi_\alpha^{(i)}$, where (i) denotes irreducible representation Γ_i, transforms as the direct product representation formed by taking the direct product $\mathcal{H}_\beta^{'(j)} \otimes \phi_\alpha^{(i)}$ which in symmetry notation is $\Gamma_{j,\beta} \otimes \Gamma_{i,\alpha}$. The matrix element $(\psi_{\alpha'}^{(i')}, \mathcal{H}'\phi_\alpha^{(i)})$ vanishes if and only if $\psi_{\alpha'}^{(i')}$ is orthogonal to all the basis functions that occur in the decomposition of $\mathcal{H}'\phi_\alpha^{(i)}$ into irreducible representations. An equivalent expression of the same concept is obtained by considering the triple direct product $\psi_{\alpha'}^{(i')} \otimes \mathcal{H}'^{(j)}_\beta \otimes \phi_\alpha^{(i)}$. In order for the matrix element in (6.31) to be nonzero, this triple direct product must contain a term that transforms as a scalar or a constant number, or according to the irreducible representation Γ_1.

6.7 Example of Selection Rules

We now illustrate the group theory of Sect. 6.6 by considering electric dipole transitions in a system with O_h symmetry. The electromagnetic interaction giving rise to electric dipole transitions is

$$\mathcal{H}'_{\text{em}} = -\frac{e}{mc}\boldsymbol{p}\cdot\boldsymbol{A}\,, \tag{6.33}$$

in which $\boldsymbol{p}$ is the momentum of the electron and $\boldsymbol{A}$ is the vector potential of an external electromagnetic field. The momentum operator is part of the physical electronic "system" under consideration, while the vector $\boldsymbol{A}$ for the electromagnetic field acts like an external system or like a "bath" or "reservoir" in a thermodynamic sense. Thus $\boldsymbol{p}$ acts like an operator with respect to the group of Schrödinger's equation but $\boldsymbol{A}$ is invariant and does not transform under the symmetry operations of the group of Schrödinger's equation. Therefore, in terms of group theory, $\mathcal{H}'_{\text{em}}$ for the electromagnetic interaction transforms like a vector, just as p transforms as a vector, in the context of the group of Schrödinger's equation for the unperturbed system $\mathcal{H}_0\psi = E\psi$. If we have unpolarized radiation, we must then consider all three components of the vector $\boldsymbol{p}$ (i.e., p_x, p_y, p_z). In cubic symmetry, all three components of the vector transform as the same irreducible representation. If instead, we had a system which exhibits tetragonal symmetry, then p_x and p_y would transform as one of the two-dimensional irreducible representations and p_z would transform as one of the one-dimensional irreducible representations.

To find the particular irreducible representations that are involved in cubic symmetry, we consult the character table for $O_h = O \otimes i$ (see Table A.30). In the cubic group O_h the vector (x, y, z) transforms according to the irreducible representation T_{1u} and so does (p_x, p_y, p_z), because both are radial vectors and both are odd under inversion. We note that the character table for O_h (Table A.30) gives the irreducible representation for vectors, and the same is true for most of the other character tables in Appendix A. To obtain the character table for the direct product group $O_h = O \otimes i$ we note that each symmetry operation in O is also compounded with the symmetry operations E and i of group $C_i = S_2$ (see Table A.2) to yield 48 symmetry operations and ten classes.

Table 6.2. Characters for the direct product of the characters for the T_{1u} and T_{2g} irreducible representations of group O_h

E	$8C_3$	$3C_2$	$6C_2$	$6C_4$	i	$8iC_3$	$3iC_2$	$6iC_2$	$6iC_4$
9	0	1	−1	−1	−9	0	−1	1	1

For the O_h group there will then be ten irreducible representations, five of which are even and five are odd. For the even irreducible representations, the same characters are obtained for class $\mathcal{C}$ and class $i\mathcal{C}$. For the odd representations, the characters for classes $\mathcal{C}$ and $i\mathcal{C}$ have opposite signs. Even representations are denoted by the subscript g (gerade) and odd representations by the subscript u (ungerade). The radial vector $\boldsymbol{p}$ transforms as an odd irreducible representation T_{1u} since $\boldsymbol{p}$ goes into $-\boldsymbol{p}$ under inversion.

To find selection rules, we must also specify the initial and final states. For example, if the system is initially in a state with symmetry T_{2g} then the direct product $\mathcal{H}'_{\rm em} \otimes \psi_{T_{2g}}$ contains the irreducible representations found by taking the direct product $\chi_{T_{1u}} \otimes \chi_{T_{2g}}$. The characters for $\chi_{T_{1u}} \otimes \chi_{T_{2g}}$ are given in Table 6.2, and the direct product $\chi_{T_{1u}} \otimes \chi_{T_{2g}}$ is a reducible representation of the group O_h. Then using the decomposition formula (6.30) we obtain:

$$T_{1u} \otimes T_{2g} = A_{2u} + E_u + T_{1u} + T_{2u}\,. \tag{6.34}$$

Thus we obtain the selection rules that electric dipole transitions from a state T_{2g} can only be made to states with A_{2u}, E_u, T_{1u}, and T_{2u} symmetry. Furthermore, since $\mathcal{H}'_{\rm em}$ is an odd function, electric dipole transitions will couple only states with opposite parity. The same arguments as given above can be used to find selection rules between any initial and final states for the case of cubic symmetry. For example, from Table A.30, we can write the following direct products as

$$\left.\begin{aligned} E_g \otimes T_{1u} &= T_{1u} + T_{2u} \\ T_{1u} \otimes T_{1u} &= A_{1g} + E_g + T_{1g} + T_{2g} \end{aligned}\right\}.$$

Suppose that we now consider the situation where we lower the symmetry from O_h to D_{4h}. Referring to the character table for D_4 in Tables A.18 and 6.3, we can form the direct product group D_{4h} by taking the direct product between groups $D_{4h} = D_4 \otimes i$ where i here refers to group $S_2 = C_i$ (Table A.2).

We note here the important result that the vector in $D_{4h} = D_4 \otimes i$ symmetry does not transform as a single irreducible representation but rather as the irreducible representations:

$$\left.\begin{aligned} z &\rightarrow A_{2u} \\ (x,y) &\rightarrow E_u \end{aligned}\right\},$$

so that T_{1u} in O_h symmetry goes into: $A_{2u} + E_u$ in D_{4h} symmetry.

Table 6.3. Character table for the pint group D_4 (422)

D_4 (422)			E	$C_2 = C_4^2$	$2C_4$	$2C_2'$	$2C_2''$
x^2+y^2, z^2		A_1	1	1	1	1	1
	R_z, z	A_2	1	1	1	−1	−1
x^2-y^2		B_1	1	1	−1	1	−1
xy		B_2	1	1	−1	−1	1
(xz, yz)	$\left.\begin{matrix}(x,y)\\(R_x,R_y)\end{matrix}\right\}$	E	2	−2	0	0	0

Table 6.4. Initial and final states of group D_{4h} that are connected by a perturbation Hamiltonian which transform like z

initial state	final state
A_{1g}	A_{2u}
A_{2g}	A_{1u}
B_{1g}	B_{2u}
B_{2g}	B_{1u}
E_g	E_u
A_{1u}	A_{2g}
A_{2u}	A_{1g}
B_{1u}	B_{2g}
B_{2u}	B_{1g}
E_u	E_g

Furthermore a state with symmetry T_{2g} in the O_h group goes into states with E_g+B_{2g} symmetries in D_{4h} (see discussion in Sect. 5.3). Thus for the case of the D_{4h} group, electric dipole transitions will only couple an A_{1g} state to states with E_u and A_{2u} symmetries. For a state with E_g symmetry according to group D_{4h} the direct product with the vector yields

$$E_g \otimes (A_{2u}+E_u) = E_g \otimes A_{2u} + E_g \otimes E_u = E_u + (A_{1u}+A_{2u}+B_{1u}+B_{2u}) \,, \quad (6.35)$$

so that for the D_{4h} group, electric dipole transitions from an E_g state can be made to any odd parity state. This analysis points out that as we reduce the amount of symmetry, the selection rules are less restrictive, and more transitions become allowed.

Polarization effects also are significant when considering selection rules. For example, if the electromagnetic radiation is polarized along the z-direction in the case of the D_{4h} group, then the electromagnetic interaction involves only p_z which transforms according to A_{2u}. With the p_z polarization, the states listed in Table 6.4 are coupled by electric dipole radiation (i.e., by matrix elements of p_z).

If, on the other hand, the radiation is polarized in the x-direction, then the basis function is a single partner x of the E_u representation. Then if the initial state has A_{1g} symmetry, the electric dipole transition will be to a state which transforms as the x partner of the E_u representation. If the initial state has A_{2u} symmetry (transforms as z), then the general selection rule gives $A_{2u} \otimes E_u = E_g$ while polarization considerations indicate that the transition couples the A_{2u} level with the xz partner of the E_g representation. If the initial state has E_u symmetry, the general selection rule gives

$$(E_u \otimes E_u) = A_{1g} + A_{2g} + B_{1g} + B_{2g} \,. \tag{6.36}$$

The polarization x couples the partner E_u^x to $A_{1g}^{x^2+y^2}$ and $B_{1g}^{x^2-y^2}$ while the partner E_u^y couples to A_{2g}^{xy-yx} and B_{2g}^{xy}. We note that in the character table for group D_{4h} the quantity xy–yx transforms as the axial vector R_z or the irreducible representation A_{2u} and xy transforms as the irreducible representation B_{2g}. Thus polarization effects further restrict the states that are coupled in electric dipole transitions. If the polarization direction is not along one of the (x, y, z) directions, $\mathcal{H}'_{\mathrm{em}}$ will transform as a linear combination of the irreducible representations $A_{2u} + E_u$ even though the incident radiation is polarized.

Selection rules can be applied to a variety of perturbations $\mathcal{H}'$ other than the electric dipole interactions, such as uniaxial stress, hydrostatic pressure and the magnetic dipole interaction. In these cases, the special symmetry of $\mathcal{H}'$ in the group of Schrödinger's equation must be considered.

Selected Problems

6.1. Find the 4×4 matrix A that is the direct product $A = B \otimes C$ of the (2×2) matrices B and C given by

$$B = \begin{pmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{pmatrix} \quad \text{and} \quad C = \begin{pmatrix} c_{11} & c_{12} \\ c_{21} & c_{22} \end{pmatrix} .$$

6.2. (a) Show that if G_A with elements $E, A_2, \ldots, A_{h_a}$ and G_B with elements $E, B_2, \ldots, B_{h_b}$ are groups, then the direct product group $G_A \otimes G_B$ is also a group. Use the notation $B_{ij}C_{kl} = (B \otimes C)_{ik,jl}$ to label the rows and columns of the direct product matrix.

(b) In going from higher to lower symmetry, if the inversion operation is preserved, show that even representations remain even and odd representations remain odd.

6.3. (a) Consider electric dipole transitions in full cubic O_h symmetry for transitions between an initial state with A_{1g} symmetry (s-state in quantum mechanics notation) and a final state with T_{1u} symmetry (p-state in quantum mechanics notation). [Note that one of these electric dipole matrix elements is proportional to a term $(1|p_x|x)$, where $|1)$ denotes the

s-state and $|x)$ denotes the x partner of the p-state.] Of the nine possible matrix elements that can be formed, how many are nonvanishing? Of those that are nonvanishing, how many are equivalent, meaning partners of the same irreducible representation?

(b) If the initial state has E_g symmetry (rather than A_{1g} symmetry), repeat part (a). In this case, there are more than nine possible matrix elements. In solving this problem you will find it convenient to use as basis functions for the E_g level the two partners $x^2 + \omega y^2 + \omega^2 z^2$ and $x^2 + \omega^2 y^2 + \omega z^2$, where $\omega = \exp(2\pi i/3)$.

(c) Repeat part (a) for the case of electric dipole transitions from an s-state to a p-state in tetragonal D_{4h} symmetry. Consider the light polarized first along the z-direction and then in the x–y plane. Note that as the symmetry is lowered, the selection rules become less stringent.

6.4. (a) Consider the character table for group C_{4h} (see Sect. 6.5). Note that the irreducible representations for group C_4 correspond to the fourth roots of unity. Note that the two one-dimensional representations labeled E are complex conjugates of each other. Why must they be considered as one-dimensional irreducible representations?

(b) Even though the character table of the direct product of the groups $C_4 \otimes C_i$ is written out in Sect. 6.5, the notations C_{4h} and $(4/m)$ are used to label the direct product group. Clarify the meaning of C_{4h} and $(4/m)$.

(c) Relate the elements of the direct product groups $C_4 \otimes C_i$ and $C_4 \otimes C_{1h}$ (see Table A.3) and use this result to clarify why the notation C_{4h} and $(4/m)$ is used to denote the group $C_4 \otimes i$ in Sect. 6.5. How do groups $C_4 \otimes i$ and $C_4 \otimes \sigma_h$ differ?

6.5. Suppose that a molecule with full cubic symmetry is initially in a T_{2g} state and is then exposed to a perturbation $\mathcal{H}'$ inducing a magnetic dipole transition.

(a) Since $\mathcal{H}'$ in this case transforms as an axial vector (with the same point symmetry as angular momentum), what are the symmetries of the final states to which magnetic dipole transitions can be made?

(b) If the molecule is exposed to stress along a (111) direction, what is the new symmetry group? What is the splitting under (111) stress of the T_{2g} state in O_h symmetry? Use the irreducible representations of the lower symmetry group to denote these states. Which final states in the lower symmetry group would then be reached by magnetic dipole transitions?

(c) What are the polarization effects for polarization along the highest symmetry axes in the case of O_h symmetry and for the lower symmetry group?

6.6. Show that the factor group of the invariant subgroup (E, σ_h) of group C_{3h} is isomorphic to the group C_3. This is an example of how the C_3 group properties can be recovered from the $C_{3h} = C_3 \otimes \sigma_h$ group by factoring out the (E, σ_h) group.