12

GROUP THEORY—AN OUTLINE

IT is difficult to exaggerate the role played in paramagnetic resonance by symmetry considerations, from which alone a tremendous amount of theoretical information can be obtained. Fortunately there exists a mathematical tool made to measure, as it were, for the task of extracting this information and translating it into quantitative results; this tool is the theory of group representations. Considered not so long ago as a somewhat sophisticated branch of mathematics, this theory has become accessible to physicists in a number of books written for them rather than for mathematicians. This poses the problem of on what level group theory should be treated in a book on paramagnetic resonance, in which perhaps the only certainty is that it cannot be ignored altogether.

Group-theoretical considerations enter the subject in both rather simple and rather complicated ways, as well as lying behind a number of statements contained in elementary books on atomic theory. For example, when it is said that the orbital angular momentum is a good quantum number, or that **L** and **S** are coupled together to give a resultant **J**, use is being made (consciously or unconsciously) of the theory of the representations of the rotation group, which we shall consider in the next chapter. On a simpler level, group theory is hardly needed to predict that in a field of cubic symmetry the three wave-functions xy, yz, zx will correspond to states of the same energy; or, that if the field has a distortion along the z-axis, the function xy will have an energy different from the other two. On the other hand, without any knowledge of group theory it would hardly be possible to predict that a level with $J = \frac{15}{2}$ would split in a cubic field into two doublets and three quartets.

Given that group theory cannot be excluded, one may either assume that the reader already has a working knowledge of the subject, or attempt to give sufficient information to enable those unfamiliar with group theory to follow its applications in the field of paramagnetic resonance. Not without some hesitation, we have decided on the latter course. Apart from our desire to make this book reasonably self-contained, we felt (perhaps mistakenly) that, being ourselves more interested in paramagnetic resonance than in group theory *per se*, our account of the latter might be useful to readers sharing the same interest. In this chapter we shall therefore attempt to outline the main results of group theory relevant to our subject, and in subsequent chapters to apply them first to the free atom or ion and later more specifically to the conditions of lower symmetry experienced by paramagnetic ions in solids.

12.1. Invariance and degeneracy

The definition of a group is well known and will not be reproduced here. Consider a system defined by a set of dynamical variables $x_1, \ldots, x_n$, and assume that its Hamiltonian $\mathscr{H}$ is unchanged by all the transformations $\mathscr{R}$ of a group $\mathscr{G}$ which take a point of the set of variables $\mathbf{x} = (x_1, \ldots, x_n)$ into a point $\mathbf{x}' = \mathscr{R}\mathbf{x} = (x_1', \ldots, x_n')$. Let $\Psi(\mathbf{x})$ be a function of $(x_1, \ldots, x_n)$ and define $\Psi'(\mathbf{x})$ as the function

$$\Psi'(\mathbf{x}) = R\Psi = \Psi(\mathscr{R}^{-1}\mathbf{x}), \tag{12.1}$$

that is, the function that takes a value equal to $\Psi(\mathbf{x})$ at the point $\mathbf{x}'$ into which $\mathscr{R}$ transforms $\mathbf{x}$. We have written symbolically $\Psi' = R\Psi$, the meaning of this symbol being given by (12.1). The transformation R is a linear operator acting on the function Ψ and it is easy to see that the operators R form a group G that is isomorphous with $\mathscr{G}$. The relationship between G and $\mathscr{G}$ is a little more complicated when the electron spin is introduced, as will appear later on. Since $\mathscr{H}$ is invariant under G, $R(\mathscr{H}\Psi) = \mathscr{H}(R\Psi)$ for all Ψ and hence $\mathscr{H}$ commutes with all operators of G. This invariance entails the following fundamental property: unless all the operators R of the group commute with each other (abelian group) the system necessarily has degenerate levels: the proof of this is as follows.

Let R and S be two non-commuting operators of G, and let Ψ be an eigenfunction of $\mathscr{H}$ with eigenvalue W. Then

$$\mathscr{H}(R\Psi) = R\mathscr{H}\Psi = RW\Psi = W(R\Psi),$$

$$\mathscr{H}(S\Psi) = S\mathscr{H}\Psi = SW\Psi = W(S\Psi),$$

from which it is clear that $R\Psi$ and $S\Psi$ are eigenstates of $\mathscr{H}$ with the same eigenvalue W. If the system has no degenerate levels the three functions Ψ, $R\Psi$ and $S\Psi$ will represent the same state and differ by constant phase factors only. It follows that $[R, S]\Psi = 0$ for all eigenfunctions of the system. Since these functions form a complete set, $[R, S] = 0$, in contradiction with the initial assumption.

12.2. Linear representations, equivalence, and irreducibility

Let $\Psi_1, \Psi_2, \ldots, \Psi_p$ be a set of orthogonal, normalized eigenstates spanning the manifold of a p-fold degenerate energy level.

As we have seen, any state $\Phi_i = R\Psi_i$ is also an eigenstate of $\mathscr{H}$ with the same energy W, and it must therefore be a linear combination of the Ψ_k which we write as

$$R\Psi_i = \sum_k \Psi_k D_{ki}(R). \tag{12.2}$$

The linear operators $\mathscr{D}(R)$ represented by the matrices $D_{ki}(R)$ form what is known as a linear representation of the group G. We shall review briefly the properties of the linear representations that are of importance for the understanding of properties of paramagnetic ions in crystals. The groups of interest to us are certain finite groups, that is groups with a finite number of elements and also one infinite group, the group of spatial rotations.

A linear, p-dimensional representation of a group G establishes a correspondence between every element R of the group and a matrix $D(R)$, with a non-vanishing determinant, that transforms any vector $\mathbf{X}$ of a p-dimensional vector space $\mathscr{E}$ into a vector $\mathbf{Y} = D(R)\mathbf{X}$ of the same space through the formula

$$Y_i = \sum_j X_j D_{ji}(R), \tag{12.3}$$

with the isomorphism condition

$$D(R_1R_2) = D(R_1)D(R_2). \tag{12.4}$$

If in the space $\mathscr{E}$ we make a change of coordinate axes $\mathbf{X} = S\mathbf{X}'$ and $\mathbf{Y} = S\mathbf{Y}'$, the relationship $\mathbf{Y} = D(R)\mathbf{X}$ becomes

$$\mathbf{Y}' = D'\mathbf{X}' = S^{-1}DS\mathbf{X}'. \tag{12.5}$$

The two representations $\mathscr{D}'$ and $\mathscr{D}$ related by the similarity transformation (12.5) are said to be equivalent. For all finite groups and for the rotation group it can be shown (and we assume it without proof) that every linear representation has an equivalent representation that is unitary, i.e. formed of unitary matrices. From now on we shall consider unitary representations only.

A unitary representation $\mathscr{D}$ of dimension p is said to be reducible if through a similarity transformation all its matrices D can be transformed to the quasi-diagonal form

$$\begin{pmatrix} D_1 & 0 \\ 0 & D_2 \end{pmatrix}, \tag{12.6}$$

where the submatrices D_1 and D_2 have dimensions p_1 and p_2, with $p_1+p_2 = p$. Geometrically, the reducibility of the representation $\mathscr{D}$ corresponds to the fact that in the representation space $\mathscr{E}$ there are two invariant orthogonal subspaces $\mathscr{E}_1$ and $\mathscr{E}_2$ with dimensions p_1 and p_2, such that every vector of $\mathscr{E}_1$ is transformed by $\mathscr{D}$ into another vector of $\mathscr{E}_1$, and similarly for $\mathscr{E}_2$. A representation that cannot be reduced to the form (12.6) by a similarity transformation is said to be irreducible. If the matrices D_1 and/or D_2 are reducible the process can be carried further until all the matrices D are of the form:

$$\begin{pmatrix} D_1 & & & & \\ & D_2 & & & \\ & & \cdot & & \\ & & & \cdot & \\ & & & & \cdot \\ & & & & & D_q \end{pmatrix}$$

where all the submatrices are irreducible.

12.3. Orthogonality relations, characters, and classes

We shall make use of the following theorems, most of which are stated without proof.

(a) If a matrix M commutes with all the matrices of an irreducible representation it is a multiple of the unit matrix.

(b) For two irreducible non-equivalent representations $\mathscr{D}_1$ and $\mathscr{D}_2$ of a finite group G the following orthogonality relation holds whatever the values of the indices i, j, k, l,

$$\sum_S D_{1,ik}(S)D^*_{2,jl}(S) = 0, \tag{12.7}$$

where the summation is over all the elements S of the group.

Each group possesses as one irreducible representation the unit representation where to each operation of the group corresponds the multiplication by the number 1. Hence if in (12.7) we take $\mathscr{D}_2$ to be the unit representation we get

$$\sum_S D_{1,ik}(S) = 0. \tag{12.8}$$

(c) For every irreducible representation $\mathscr{D}$ of order p the following holds:

$$\sum_S D_{ik}(S)D^*_{jl}(S) = \frac{m}{p}\delta_{ij}\delta_{kl}, \tag{12.9}$$

where m is the number of elements of the group, also called the order of the group. For the rotation group, an infinite group, the orthogonality relations (12.7) and (12.9) are still valid provided the summation over the group elements is replaced by a suitable integration. It can be shown that if we define a rotation R by the three Euler angles α, β, γ the relations (12.7) and (12.9) adapted for the rotation group can be rewritten as

$$\int_0^{2\pi} \mathrm{d}\alpha \int_0^{2\pi} \mathrm{d}\gamma \int_0^{\pi} D_{ik}^*(\alpha, \beta, \gamma) D_{jl}(\alpha, \beta, \gamma) \sin\beta \, \mathrm{d}\beta = \delta_{ij}\delta_{kl}\frac{8\pi^2}{p}. \tag{12.10}$$

(d) The traces of the matrices of a linear representation are called its characters and are denoted by χ. Since the trace of a matrix is invariant under a similarity transformation such as (12.5), two equivalent representations have the same set of characters. From (12.7) and (12.9) we obtain immediately the relations

$$\begin{aligned} \sum_S \chi_1(S)\chi_2^*(S) &= 0, \\ \sum_S \chi_1(S)\chi_1^*(S) &= m. \end{aligned} \tag{12.11}$$

The concept of character is intimately connected with that of class: two elements A and B of a group are said to belong to the same class if the group contains a third element C such that

$$B = CAC^{-1}. \tag{12.12}$$

For instance, two rotations A and B through the same angle but around two different axes X and Y, belong to the same class provided that the element C in (12.12) is the rotation that converts X into Y. From the definition (12.12) it follows that the unit element of the group is in a class by itself. It also follows from that definition that all the matrices of a linear representation that belong to the same class have the same character.

If the group contains r different classes $C^{(k)}$ with g_k elements per class the relations (12.11) can be rewritten as

$$\begin{aligned} \sum_{k=1}^{r} \chi_1^{(k)}\chi_2^{(k)*} g_k &= 0, \\ \sum_{k=1}^{r} \chi_1^{(k)}\chi_1^{(k)*} g_k &= m. \end{aligned} \tag{12.13}$$

(e) A problem in the theory of linear representations of a finite group of paramount importance, for quantum mechanics in general and for paramagnetic resonance in particular, is the discovery of all the irreducible representations of a group G. Let $\mathscr{D}_1, \mathscr{D}_2, \ldots, \mathscr{D}_l$ be all the non-equivalent irreducible representations of a finite group G containing r classes. The number l is finite, as will appear presently. In a space $\mathscr{E}$ with r dimensions consider l vectors $\mathbf{X}_1, \mathbf{X}_2, \ldots, \mathbf{X}_l$, the r components of the vector $\mathbf{X}_i$ being the r numbers, with $k = 1, 2, \ldots, r$:

$$\chi_i^{(k)}\sqrt{\left(\frac{g_k}{m}\right)}.$$

It follows from (12.13) that these vectors are orthogonal and therefore linearly independent. Their number l cannot exceed the number r of dimensions of the space $\mathscr{E}$, and we must have $l \leqslant r$. It can also be shown (and we assume it without proof) that $l \geqslant r$ and thus $l = r$, which means that the number of non-equivalent irreducible representations of a finite group is equal to the number of its classes.

Let $l_1, l_2, \ldots, l_r$ be the dimensions of the r irreducible representations

$$\mathscr{D}_1, \mathscr{D}_2, \ldots, \mathscr{D}_r.$$

Consider one such representation $\mathscr{D}_p$ and the m matrix elements $D_{p,ij}(S)$ that correspond to the m elements S of the group. We can regard these numbers as the m components of a vector $\mathbf{X}_{p,ij}$ in a space $\mathscr{E}$ with m dimensions. The formula (12.7) shows that these vectors are all orthogonal and therefore their number $l_1^2+l_2^2+\ldots+l^2$ cannot be larger than the number of dimensions m of the space $\mathscr{E}$, which is the order of the finite group G.

Here again it can be shown that the following equality holds:

$$l_1^2+l_2^2+\ldots+l_r^2 = m, \tag{12.14}$$

which once more we assume to hold without proof.

12.4. Reduction of a representation and calculation of the characters

Let us assume that we know the characters of all the irreducible representations of a group G and let $\mathscr{D}$ be a reducible representation. We want to know the numbers of times $a_1, a_2, \ldots, a_r$ that each irreducible representation $\mathscr{D}_i$ is contained in $\mathscr{D}$. Let $\chi(S)$ be the character of the transformation S in the representation $\mathscr{D}$ and $\chi_1(S), \ldots, \chi_r(S)$ be the characters of S in the irreducible representations $\mathscr{D}_i$. From the very definition of reducibility and of the characters it is clear that

$$\chi(S) = \sum_{p=1}^{r} a_p \chi_p(S). \tag{12.15}$$

Multiplying each side of (12.15) by $\chi_q^*(S)$, where q is one of the indices $1, 2, \ldots, r$, and summing over all the group elements S, we obtain from (12.11)

$$a_q = \frac{1}{m}\sum_{S=1}^{m} \chi(S)\chi_q^*(S), \tag{12.16}$$

where a_q is necessarily an integer.

The prediction of the breakdown of a given representation into its irreducible components is therefore straightforward if the characters of all the irreducible representations are known. A straightforward answer to the question of how to find the characters of irreducible representations is to look them up in a table. Nevertheless we will indicate briefly the principle of their calculation.

If we consider the elements of the group as linear operators as explained in § 12.1 it follows from the definition (12.12) that the operator $\mathscr{C}^{(g)} = R_1+R_2+\ldots+R_g$, the sum of all elements of a given class (g) of the group, commutes with all the elements of the group and conversely that every operator that commutes with all the elements of the group is a sum of operators $\mathscr{C}^{(g)}$. It is clear, therefore, that the product $\mathscr{C}^{(p)}\mathscr{C}^{(q)}$ is also a sum of operators $\mathscr{C}$ which can be written as

$$\mathscr{C}^{(p)}\mathscr{C}^{(q)} = \sum_s a_{pq}^s \mathscr{C}^{(s)}. \tag{12.17}$$

The coefficients a_{pq}^s are obtained in a straightforward manner if the multiplication table of the group is known. Consider now an irreducible representation $\mathscr{D}_i$ of order l_i. The matrices representing the operators $\mathscr{C}^{(p)}$ commute with all the matrices of this representation and must therefore be multiples of the unit matrix. The operator $\mathscr{C}^{(p)}$ is represented by the matrix

$$C_i^{(p)} = \mathscr{C}_i^{(p)} I, \tag{12.18}$$

where I is the unit matrix and $\mathscr{C}_i^{(p)}$ a number.

Taking the trace of each side of (12.18) we get

$$\mathscr{C}_i^{(p)} = \chi_i^{(p)}\frac{g_p}{l_i} = \chi_i^{(p)}\frac{g_p}{\chi_i^{(1)}}, \tag{12.19}$$

where $\chi_i^{(1)} = l_i$ is the character of the class corresponding to the unit operator. Inserting this result into (12.17) we find

$$\frac{\chi^{(p)}}{\chi^{(1)}}\frac{\chi^{(q)}}{\chi^{(1)}}g_p g_q = \sum_{s=1}^{r} a_{pq}^s \frac{\chi^{(s)}}{\chi^{(1)}} g_s, \tag{12.20}$$

where we have dropped the index i of the particular representation $\mathscr{D}_i$.

With the notation $y^{(s)} = \chi^{(s)}/\chi^{(1)}$ where $y^{(1)} = 1$, (12.20) becomes

$$y^{(p)}y^{(q)}g_p g_q = \sum_{s=1}^{r} a_{pq}^{s} y^{(s)} g_s, \tag{12.21}$$

which can be solved for the values of y as follows. Consider a linear function

$$B = \sum_{s=1}^{r} \alpha_s y^{(s)}, \tag{12.22}$$

where we choose arbitrarily the coefficients α_s. According to (12.21) the successive powers $B^2, \ldots, B^r$ will also be linear functions of the $y^{(s)}$ of the form

$$\begin{cases} B^2 = \sum_{s=1}^{r} \beta_s y^{(s)} \\ \cdots\cdots\cdots\cdots \\ B^r = \sum_{s=1}^{r} \rho_s y^{(s)} \end{cases}, \tag{12.23}$$

where the $\beta_s, \ldots, \rho_s$ are deduced from the α_s by means of (12.21). From the $r+1$ linear equations (12.22), (12.23) and $y^{(1)} = 1$ we can eliminate the $y^{(s)}$, obtaining a secular equation of order r for B:

$$B^r + C_1 B^{r-1} + \ldots + C_r = 0, \tag{12.24}$$

where the coefficients $C_1, \ldots, C_r$ are known.

For each of the r roots of (12.24) we get from the sets of linear equations (12.22), (12.23) a set of values for the $y^{(s)}$ and thus also a set of characters if we know the $\chi_i^{(1)}$; that is, the dimensions l_i of the irreducible representation. The latter are often determined uniquely from the relation (12.14): $l_1^2 + \ldots + l_r^2 = m$.

We are now in a position to enumerate the irreducible representations of a group, to calculate their characters, and to break down every reducible representation into its irreducible components. These methods enable us to make predictions about the splitting of an energy level by a perturbation of known symmetry.

12.5. Splitting of a degenerate level by a perturbation of lower symmetry

Consider a Hamiltonian $\mathscr{H}_0$ which is invariant under all the transformations of a group G_0, and a level W_0 of that Hamiltonian with p-fold degeneracy. For instance, for a given level J of a free ion, the group G_0 will be the rotation group and the degeneracy is $p = 2J+1$. Under the operations of the group G_0, the p eigenfunctions Ψ_i that span the manifold $\mathscr{E}_0$ of the wave-functions with eigenvalue W_0 are transformed into each other as explained in § 12.2, and provide a linear representation $\mathscr{D}_0$ of order p of the group G_0, a representation that we shall initially assume to be irreducible. We introduce a perturbing Hamiltonian V of lower symmetry than $\mathscr{H}_0$. What is meant by lower symmetry is that only a fraction of the transformations belonging to G_0, namely a subgroup G of G_0, will leave V invariant. The linear transformation of the functions Ψ_i under the more restricted set of operations belonging to G, provides for this latter group a representation $\mathscr{D}$ that may not be irreducible. For, reducing the representation $\mathscr{D}_0$ of G_0 consisted of bringing by a similarity transformation all the matrices of $\mathscr{D}_0$ to the quasi-diagonal form (12.6), and our assumption of the irreducibility of $\mathscr{D}_0$ meant that this could not be done. On the other hand, since the representation $\mathscr{D}$ of G contains only a *fraction* of all the matrices of G_0, we have to 'quasi-diagonalize' fewer matrices by a similarity transformation and this may not be impossible.

We can also say that no sub-manifold $\mathscr{E}'$ of the manifold $\mathscr{E}_0$ was left invariant by all the transformations of the group G_0 but that it is not inconceivable that a fraction G of these transformations might leave such a sub-manifold invariant.

Let us assume then that $\mathscr{D}$, a linear representation of G, is reducible. We can reduce it by means of the formulae (12.15) and (12.16), which tell us how many times a given irreducible representation, say $\mathscr{D}_i$, of G is contained in $\mathscr{D}$. Assume for the sake of argument that $\mathscr{D}$ contains two irreducible representations $\mathscr{D}_1$ and $\mathscr{D}_2$ of dimensions p_1 and p_2 with $p_1+p_2 = p$. We can show that the level W will be split into two sublevels W_1 and W_2 with respective degeneracies of order p_1 and p_2. Let φ_i $(i = 1, 2, \ldots, p_1)$ be p_1 functions of the manifold $\mathscr{E}$ that transform by $\mathscr{D}_1$, and χ_j $(j = 1, 2, \ldots, p_2)$ those that transform by $\mathscr{D}_2$, and calculate the following matrix elements:

$$
\begin{aligned}
A_{ij} &= (\varphi_i|\ V\ |\chi_j),\\
B_{ii'} &= (\varphi_i|\ V\ |\varphi_{i'}),\\
C_{jj'} &= (\chi_j|\ V\ |\chi_{j'}).
\end{aligned}
$$

(Here of course χ_j has nothing to do with the quantity χ used to denote the character of a representation in § 12.3.)

The matrix element A_{ij} can be written

$$A_{ij} = \int \varphi_i^*(\mathbf{x})V(\mathbf{x})\chi_j(\mathbf{x})\,\mathrm{d}\tau. \tag{12.25}$$

Let R be an operation of group G that leaves V invariant, i.e.

$$A_{ij} = \int \varphi_i^*(\mathscr{R}^{-1}\mathrm{x}) V(\mathscr{R}^{-1}\mathrm{x}) \chi_j(\mathscr{R}^{-1}\mathrm{x}) \, \mathrm{d}\tau \tag{12.26}$$

(this involves just a change of variable in the integration). Making use of the definition (12.1) we find that

$$A_{ij} = \int (R\varphi_i)^* V(\mathrm{x})(R\chi_j) \, \mathrm{d}\tau = \frac{1}{m} \sum_R \int (R\varphi_i)^* V(\mathrm{x})(R\chi_j) \, \mathrm{d}\tau, \tag{12.27}$$

where m is the number of elements in the group.

From the formulae (12.2) and the orthogonality relations (12.7) we have

$$A_{ij} = \frac{1}{m} \sum_{k,l} \left(\int \varphi_k^* V \chi_l \, \mathrm{d}\tau \right) \sum_R \mathscr{D}_{1,ki}^*(R) \mathscr{D}_{2,lj}(R) = 0. \tag{12.28}$$

In particular, if in (12.25) we replace V by unity we find

$$\int \varphi_i^* \chi_j \, \mathrm{d}\tau = 0. \tag{12.29}$$

Thus two such functions belonging to two non-equivalent irreducible representations are orthogonal.

In the same way, with the help of (12.9), we find

$$\begin{aligned} B_{ii'} &= (\varphi_i| \, V \, |\varphi_{i'}) = \frac{\delta_{ii'}}{p_1} \sum_{k=1}^{p_1} (\varphi_k| \, V \, |\varphi_k), \\ C_{jj'} &= (\chi_j| \, V \, |\chi_{j'}) = \frac{\delta_{jj'}}{p_2} \sum_{l=1}^{p_2} (\chi_l| \, V \, |\chi_l). \end{aligned} \tag{12.30}$$

Equations (12.28) and (12.30) express precisely the fact that the functions φ_i and χ_j are the 'correct' zero-order wave-functions for the perturbation V, and that the level W is split into two levels W_1 and W_2 of respective multiplicity p_1 and p_2.

This may be generalized immediately to the case where $\mathscr{D}$ is reduced into q irreducible representations $\mathscr{D}_1, \ldots, \mathscr{D}_q$ of dimensions $p_1, \ldots, p_q$, all different. The level W is split into q sublevels $W_1, \ldots, W_q$ of multiplicity $p_1, \ldots, p_q$, and the correct zero-order wave-functions of the level W_q form a basis for the representation $\mathscr{D}_q$ and are determined from symmetry considerations alone. However, if a given irreducible representation occurs more than once in $\mathscr{D}$, the situation is rather more complicated.

Assume for the sake of argument that an irreducible representation $\mathscr{D}_1$ occurs twice in $\mathscr{D}$, spanned respectively by a set of functions

$\varphi_1, \ldots, \varphi_n$ and $\chi_1, \ldots, \chi_n$. We assume further that the φ_i and χ_j transform *exactly* by the same matrices D_1 and not only within a similarity transformation. We can establish as before that $B_{ii'}$ and $C_{jj'}$ vanish for $i \neq i'$ and $j \neq j'$ but we can no longer state that $(\varphi_i|\ V\ |\chi_i) = 0$ and indeed this cross-element will not, in general, be zero. φ_i and χ_i are not 'correct' zero-order wave-functions any more and the correct linear combinations as well as the energy splittings caused by the perturbation V are obtained from the secular equation

$$\begin{vmatrix} (\varphi_1|\ V\ |\varphi_1)-W & (\varphi_1|\ V\ |\chi_1) \\ (\chi_1|\ V\ |\varphi_1) & (\chi_1|\ V\ |\chi_1)-W \end{vmatrix}. \tag{12.31}$$

It follows from (12.30) that

$$\begin{aligned} (\varphi_1|\ V\ |\varphi_1) &= (\varphi_i|\ V\ |\varphi_i) \\ (\chi_1|\ V\ |\chi_1) &= (\chi_i|\ V\ |\chi_i). \end{aligned} \tag{12.32}$$

The same argument shows that

$$(\varphi_1|\ V\ |\chi_1) = \frac{1}{p}\sum_{l=1}^{p}(\varphi_l|\ V\ |\chi_l) = (\varphi_i|\ V\ |\chi_i). \tag{12.33}$$

We would therefore have obtained the same secular equation by choosing two other functions φ_i and χ_i instead of φ_1 and χ_1. The 'correct' zero-order wave-functions will be first a set of linear combinations

$$\alpha'\varphi_1+\beta'\chi_1,\ \alpha'\varphi_2+\beta'\chi_2,\ \ldots,\ \alpha'\varphi_p+\beta'\chi_p$$

spanning a first manifold of order p, with an energy W' that will be one of the roots of (12.31), and a second set orthogonal to it,

$$\alpha''\varphi_1+\beta''\chi_1,\ \ldots,\ \alpha''\varphi_p+\beta''\chi_p,$$

with an energy W'' that will be the second root of (12.31). The 'correct' zero-order wave-functions can no longer be obtained from symmetry considerations alone but involve the perturbing potential V explicitly.

More generally, if a representation $\mathscr{D}_q$ of dimension p_q occurs a_q times in $\mathscr{D}$, the original level W will be split into a_q sublevels $W_1, \ldots, W_q$ each of degeneracy p_q (and also into other sublevels). The energies $W_1, \ldots, W_q$ and the 'correct' zero-order wave-functions are obtained by solving a secular equation of order a_q.

In the foregoing discussion use has been made of first-order perturbation theory and one might ask whether a higher-order calculation might not lead to a further removal of degeneracy. The answer is no. Let us consider a total Hamiltonian $\mathscr{H}(\varepsilon) = \mathscr{H}_0+\varepsilon V$, where W_0 is a

p-fold degenerate level of $\mathscr{H}(0) = \mathscr{H}_0$ spanned by p eigenfunctions Ψ_i, which provide an irreducible representation $\mathscr{D}$ of the group G that leaves $\mathscr{H}_0$ invariant. We assume that G also leaves V invariant. We saw that first-order perturbation theory predicts then no splitting for the level W, and we shall show that this statement is correct to all orders. We assume that W_0 is split into two levels W_1 and W_2 spanned respectively by p_1 eigenfunctions φ_j and p_2 eigenfunctions χ_k. The p_1 functions φ_j provide a representation $\mathscr{D}'$ of G, irreducible or not, but which can neither contain $\mathscr{D}$ nor coincide with it since $p_1 < p$, nor be contained in it since $\mathscr{D}$ is irreducible. From the orthogonality relations it follows that the Ψ_i are orthogonal to all the φ_j and also to all the χ_k. The manifold of the functions (φ_j, χ_k) being orthogonal to the manifold Ψ_i cannot be made to coincide with it in a continuous manner when $\varepsilon \to 0$, and the two levels W_1 and W_2, if they do exist, do not originate from a splitting of W_0.

This takes us back to the assumption made at the beginning of this section (§ 12.5) that the representation $\mathscr{D}_0$ of the group G_0, which left $\mathscr{H}_0$ invariant and which can be represented by the eigenfunctions of a level W_0, was irreducible. Had it been reducible into, say, two representations $\mathscr{D}_0'$ and $\mathscr{D}_0''$, a perturbation of the same *symmetry* as $\mathscr{H}_0$ could have split W_0 into two levels W_0' and W_0''. A degeneracy of this type is called accidental and will be disregarded from now on.

12.6. The direct product of two representations

We consider now two dynamic systems S_1 and S_2, and to start with we assume them to have no mutual interaction, so that their Hamiltonians $\mathscr{H}_1$ and $\mathscr{H}_2$ commute with each other and are each invariant under operations of the same group G. Examples of this type are two electrons moving in the central potential of the same type of atom, or two nuclear spins in an applied magnetic field.

Let W_1 be a level of $\mathscr{H}_1$ spanned by p_1 functions φ_i and W_2 a level of $\mathscr{H}_2$ spanned by p_2 functions χ_j. The φ and the χ provide two representations $\mathscr{D}_1$ and $\mathscr{D}_2$, each of which, barring accidental degeneracy, we assume to be irreducible. It is clear that the products $\varphi_i\chi_j$ also provide a representation of G, which we shall denote as $\mathscr{D}_1 \times \mathscr{D}_2$ and shall call the direct product of the two representations $\mathscr{D}_1$ and $\mathscr{D}_2$. A matrix element of this representation is defined by the relations

$$\begin{aligned} R(\varphi_i\chi_j) &= \sum_{kl} \varphi_k\chi_l D_{1,ki}(R)D_{2,lj}(R), \\ (D_1 \times D_2)_{kl,ij} &= D_{1,ki}D_{2,lj}. \end{aligned} \tag{12.34}$$

The degeneracy of the level $W = W_1+W_2$ of the combined system S_1+S_2 is at most of order p_1p_2. (It may be less because of the limitations due to the Pauli principle.) If we introduce an interaction $\mathscr{H}_{12}$, between the two systems, invariant by the same group G, the degeneracy of the level W may be partially lifted, for $\mathscr{D}_1\times\mathscr{D}_2$ will not in general be an irreducible representation of the group G. We shall be able to bring it to a reduced form by means of the relations (12.15) and (12.16), since the character of a matrix

$$(D_1\times D_2)_{ij,kl} = D_{1,ik}D_{2,jl}$$

is clearly

$$\chi(D_1\times D_2) = \chi(D_1)\chi(D_2). \tag{12.35}$$

The problem of reduction of direct products of representations is closely connected with the calculation of matrix elements of various physical operators. A special case is the establishment of selection rules that correspond to the vanishing of certain matrix elements.

Consider first a function $\Psi_\alpha(\mathbf{r})$, which belongs to an irreducible representation $\mathscr{D}$ of a group G that is not the unit representation. It can be seen that $\int \Psi_\alpha(\mathbf{r})\,d\tau = 0$. Indeed, following the argument that led to the relation (12.28), we have, because of the relation (12.8),

$$\int\Psi_\alpha(\mathbf{r})\,d\tau = \frac{1}{m}\sum_R\int R\Psi_\alpha(\mathbf{r})\,d\tau = \frac{1}{m}\sum_R\sum_\beta D_{\beta\alpha}(R)\left(\int\Psi_\beta(\mathbf{r})\,d\tau\right) = 0. \tag{12.36}$$

Consider now a matrix element of the form

$$(\Psi_\alpha|\,V_\beta\,|\Phi_\gamma) = \int \Psi_\alpha^*(\mathbf{r})V_\beta(\mathbf{r})\Phi_\gamma(\mathbf{r})\,d\tau, \tag{12.37}$$

where Ψ_α, V_β, and Φ_γ transform according to irreducible representati ns $\mathscr{D}$, $\mathscr{D}'$, $\mathscr{D}''$ of a certain group. The product $\Psi_\alpha^*V_\beta\Phi_\gamma$ transforms according to the representation $\mathscr{D}^*\times\mathscr{D}'\times\mathscr{D}''$ which is, in general, a reducible representation of G, and the matrix element (12.37) will be different from zero only if the representation $\mathscr{D}^*\times\mathscr{D}'\times\mathscr{D}''$ contains the unit representation at least once.

Practically all the group representations that we shall encounter have real characters and are therefore equivalent to their complex conjugates; if this is the case for $\mathscr{D}$, the direct product $\mathscr{D}^*\times\mathscr{D}'\times\mathscr{D}''$ can be replaced by $\mathscr{D}\times\mathscr{D}'\times\mathscr{D}''$. We can show that, if all three representations $\mathscr{D}$, $\mathscr{D}'$, $\mathscr{D}''$ have real characters, the condition that $\mathscr{D}\times\mathscr{D}'\times\mathscr{D}''$ contains the unit representation can be replaced by the requirement that $\mathscr{D}\times\mathscr{D}'$ contains $\mathscr{D}''$. The proof is as follows. The number of times, n_1, that the unit representation is contained in the direct product

$\mathscr{D}_a \times \mathscr{D}_b$ of two irreducible representations $\mathscr{D}_a$ and $\mathscr{D}_b$ is unity if $\mathscr{D}_a$ and $\mathscr{D}_b$ are equivalent and zero if they are not, for n_1 is given by the following relation derived from (12.16) and (12.35):

$$n_1 = \frac{1}{m}\sum_R \chi^{(a\times b)}(R)\chi^1(R) = \frac{1}{m}\sum_R \chi^{(a)}(R)\chi^{(b)}(R) = \delta_{a,b}. \quad (12.38)$$

Thus $(\mathscr{D}\times\mathscr{D}')\times\mathscr{D}''$ contains the unit representation if and only if $(\mathscr{D}\times\mathscr{D}')$ contains $\mathscr{D}''$.

Let us assume now that Ψ_α and Φ_γ of (12.37) belong to the same representation $\mathscr{D} = \mathscr{D}''$. It is easily shown that the trace

$$T_\beta = \sum_\alpha (\Psi_\alpha|\, V_\beta\, |\Psi_\alpha)$$

vanishes unless V_β belongs to the unit representation. We can write

$$\begin{aligned} T_\beta &= \frac{1}{m}\sum_{R,\alpha}(R\Psi_\alpha|\, RV_\beta\, |R\Psi_\alpha) \\ &= \frac{1}{m}\sum_{R,\alpha,\alpha',\alpha'',\beta'} D^*_{\alpha'\alpha}(R)D_{\alpha''\alpha}(R)D'_{\beta'\beta}(R)(\Psi_{\alpha'}|\, V_{\beta'}\, |\Psi_{\alpha'}). \end{aligned} \quad (12.39)$$

Since the matrices D are unitary, $\sum_\alpha D^*_{\alpha'\alpha}(R)D_{\alpha''\alpha}(R) = \delta_{\alpha'\alpha''}$ and (12.39) can be rewritten:

$$T_\beta = \frac{1}{m}\sum_{R,\beta'} D'_{\beta'\beta}(R)T_{\beta'}, \quad (12.40\text{a})$$

which vanishes because of (12.8) unless V_β belongs to the unit representation. Let $\delta W_1^\beta, \ldots, \delta W_p^\beta$ be the energy changes produced in the degenerate level spanned by a set of functions Ψ_α belonging to the representation $\mathscr{D}$, by the perturbation V_β. Because of the invariance of the trace we have

$$\sum_i \delta W_i^\beta = T_\beta = 0, \quad (12.40\text{b})$$

which means that the mean position of the energy levels is unchanged by the perturbation that lifts the degeneracy.

If in the direct product (12.34) the two representations $\mathscr{D}_1$ and $\mathscr{D}_2$ of order p are the same $\mathscr{D}_1 = \mathscr{D}_2 = \mathscr{D}$, the set of functions $\varphi_k\chi_l$ that span the reducible representation $(\mathscr{D})^2 = \mathscr{D}\times\mathscr{D}$ can be broken up into a symmetrical subset $\frac{1}{2}\{\varphi_k\chi_l + \varphi_l\chi_k\}$ that contains $\frac{1}{2}p(p+1)$ terms, and into an antisymmetrical subset $\frac{1}{2}\{\varphi_k\chi_l - \varphi_l\chi_k\}$ that contains $\frac{1}{2}p(p-1)$ terms. It is clear that in the reduction of $(\mathscr{D})^2 = \mathscr{D}\times\mathscr{D}$ the two subsets do not mix and that in the decomposition

$$(\mathscr{D})^2 = \mathscr{D}_a + \mathscr{D}_b + \ldots + \mathscr{D}_l + \ldots + \mathscr{D}_r, \quad (12.41)$$

where the $\mathscr{D}_l$ are irreducible representations, each of them belongs either to the symmetrical or to the antisymmetrical part of $(\mathscr{D})^2$.

The following relations for the characters of the symmetrical and antisymmetrical parts of $(\mathscr{D})^2$ are easily established:

$$\chi^{\mathscr{D}^2}(R) = \sum_{i,j} D_{ii}(R)D_{jj}(R) = \{\chi^{\mathscr{D}}(R)\}^2, \tag{12.42}$$

$$\begin{cases} \chi_{\mathrm{S}}^{\mathscr{D}^2}(R) = \frac{1}{2}\sum\limits_{i,j}\{D_{ii}(R)D_{jj}(R)+D_{ij}(R)D_{ji}(R)\} = \frac{1}{2}\{\chi^{\mathscr{D}}(R)\}^2+\frac{1}{2}\{\chi^{\mathscr{D}}(R^2)\}, \\ \chi_{\mathrm{A}}^{\mathscr{D}^2}(R) = \frac{1}{2}\sum\limits_{i,j}\{D_{ii}(R)D_{jj}(R)-D_{ij}(R)D_{ji}(R)\} = \frac{1}{2}\{\chi^{\mathscr{D}}(R)\}^2-\frac{1}{2}\{\chi^{\mathscr{D}}(R^2)\}. \end{cases} \tag{12.43}$$

In (12.42), (12.43), R is any transformation of the group G and the suffixes S and A stand for the symmetrical and antisymmetrical parts of $\mathscr{D}^2$.