17

Permutation Groups and Many-Electron States

In this chapter we discuss the properties of permutation groups, which are known as "Symmetric Groups" in the mathematics literature. Although permutation groups are quite generally applicable to many-body systems, they are used in this chapter to classify the symmetry in many-electron states. This discussion applies to the symmetries of both the spin and orbital states. In Chap. 18 we apply the results of this chapter for the permutation groups to show a very different use of permutation groups, which is to classify the symmetry properties for tensors occuring in solid state physics in a powerful way.

The main application of the permutation group in this chapter is to describe atoms with full rotational symmetry. We give explicit results for two, three, four, and five electron systems. Whereas two electron systems can be handled without group theory, the power of group theory is evident for three, four, five, and even larger electron systems. With a five-electron system, we can treat all multielectron states arising from s, p, and d electrons, since five electrons fill half of a d level, and a more than half-filled level such as for eight d electrons can be treated as two d level holes, using concepts equivalent to the presence of hole states in solid state physics. To deal with all multielectron states that could be made with f electrons we would need to also consider the permutation groups for six and seven objects. In the solid state, multielectron states occur predominantly in the context of crystal fields, as for example the substitution of a transition metal ion (having d electrons) on a crystal site which experiences the symmetry of the crystal environment. The crystal field lowers the full rotational symmetry of the free ion giving rise to crystal field splittings. In this case the effect of the crystal field must be considered once the symmetry of the electronic configuration of the free ion has been determined using the permutation groups discussed in this chapter.

17.1 Introduction

In the physics of a many-electron atom or molecule we are interested in solutions to a Hamiltonian of the form

$$\mathcal{H}(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_n) = \sum_{i=1}^{n}\left(\frac{p_i^2}{2m}+V(\boldsymbol{r}_i)\right) + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{r_{ij}}, \tag{17.1}$$

where $V(\boldsymbol{r}_i)$ is a one-electron potential and the Coulomb electron–electron interaction term is explicitly included. The one-electron potential determines the rotational and translational symmetry of the Hamiltonian.

In addition to symmetry operations in space, the Hamiltonian in (17.1) is invariant under interchanges of electrons, i.e., permutation operations P of the type

$$P = \begin{pmatrix} 1 & 2 & \ldots n \\ a_1 & a_2 & \ldots & a_n \end{pmatrix}, \tag{17.2}$$

where the operation P replaces 1 by a_1, 2 by a_2, etc. and n by a_n. We have already seen that these permutation operations form a group (see Sect. 1.2), i.e., there exists the inverse operation

$$P^{-1} = \begin{pmatrix} a_1 & a_2 & \ldots & a_n \\ 1 & 2 & \ldots & n \end{pmatrix}, \tag{17.3}$$

and the identity element is given by

$$E = \begin{pmatrix} 1\,2\ldots n \\ 1\,2\ldots n \end{pmatrix}, \tag{17.4}$$

which leaves the n electrons unchanged. Multiplication involves sequential permutation operations of the type given by (17.2). The number of symmetry operations in a permutation group of n objects is $n!$, which gives the order of the permutation group to be $n!$. Thus the group $P(3)$ in Sect. 1.2 has $h = 3! = 3 \cdot 2 \cdot 1 = 6$ elements.

The wave function solutions of the many-electron Hamiltonian (17.1) are denoted by $\Psi_{\Gamma_i}(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_n)$. Since all electrons are indistinguishable, the permutation P commutes with the Hamiltonian, and we, therefore, can classify the wave functions of the group of the Schrödinger equation according to an irreducible representation Γ_i of the permutation or the symmetric group. Some permutations give rise to symmetric states, others to antisymmetric states, and the remainder are neither. In some cases, all possible states are either symmetric or antisymmetric, and there are no states that are neither fully symmetric nor fully antisymmetric.

For the permutation group of n objects amongst the various possible irreducible representations, there are two special one-dimensional irreducible representations: one that is *symmetric* and one that is *antisymmetric* under the interchange of two particles. The basis function for the *symmetric* representation Γ_1^s of an orbital state is just the product wave function

$$\Psi_{\Gamma_1^s}(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_n) = \frac{1}{\sqrt{n!}} \sum_{\text{permutations}} \psi_1(\boldsymbol{r}_1)\psi_2(\boldsymbol{r}_2)\ldots\psi_n(\boldsymbol{r}_n). \qquad (17.5)$$

The total wave function for a many-electron system is the product of the orbital and spin wave functions. The basis function for the antisymmetric representation Γ_1^a is conveniently written in terms of the Slater determinant [6]:

$$\Psi_{\Gamma_1^a}(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \psi_1(\boldsymbol{r}_1, \sigma_1) & \psi_1(\boldsymbol{r}_2, \sigma_2) & \ldots & \psi_1(\boldsymbol{r}_n, \sigma_n) \\ \psi_2(\boldsymbol{r}_1, \sigma_1) & \psi_2(\boldsymbol{r}_2, \sigma_2) & \ldots & \psi_2(\boldsymbol{r}_n, \sigma_n) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_n(\boldsymbol{r}_1, \sigma_1) & \psi_n(\boldsymbol{r}_2, \sigma_2) & \ldots & \psi_n(\boldsymbol{r}_n, \sigma_n) \end{vmatrix}, \qquad (17.6)$$

where $\boldsymbol{x}_i$ denotes a generalized coordinate, consisting of $\boldsymbol{r}_i$, the spatial coordinate and σ_i, the spin coordinate. When written in this form, the many-body wave function automatically satisfies the Pauli principle since the repetition of either a row or a column results in a zero determinant, thereby guaranteeing that every electron is in a different state.

The higher dimensional irreducible representations of the permutation group are also important in determining many-electron states which satisfy the Pauli principle. For example, in the $\boldsymbol{L} \cdot \boldsymbol{S}$ coupling scheme for angular momentum, one must take combinations of n spins to get the total S. These must be combined with the orbital angular momentum combinations to get the total L. Both the spin states and the orbital states will transform as some irreducible representation of the permutation group. When combined to make a total J, only those combinations which transform as the antisymmetric representation Γ_1^a are allowed by the Pauli principle. We will illustrate these concepts with several examples in this chapter, including the three-electron p^3 state and the four-electron p^4 state.

In this chapter we will use the permutation groups to yield information about the symmetry and the degeneracy of the states for a many-electron system. We emphasize that in contrast to the case of rotational invariance, the ground state of (17.1) does not transform as the totally symmetric representation of the permutation group Γ_1^s. But rather for electrons (or half integral spin (Fermion) particles), the ground state and all allowed excited states transform as the antisymmetric one-dimensional irreducible representation Γ_1^a since any physical perturbation $\mathcal{H}'$ will not distinguish between like particles. The perturbation $\mathcal{H}'$ itself transforms as the totally symmetric

irreducible representation of the permutation group. Only integral spin particles (Bosons) have ground states that transform as the totally symmetric irreducible representation Γ_1^s.

Mathematicians also study another aspect of permutations called braids [36], where both the permutation and the ordered sequence of the permutation is part of the definition of the group element. The group theory and application of braids to solid state physics is not considered in this chapter.

In this chapter we first discuss the classes of the permutation groups (Sect. 17.2), their irreducible representations (Sect. 17.2), and their basis functions (Sect. 17.3). Applications of the permutation groups are then made (Sect. 17.4) to classify two-electron, three-electron, four-electron and five-electron states.

17.2 Classes and Irreducible Representations of Permutation Groups

Of particular interest to the symmetry properties of permutation groups are cyclic permutations.

Definition 26. *A cyclic permutation is here defined in terms of an example:*

If a permutation group has n objects, one of the group elements of a cyclic permutation of n objects is

$$\begin{pmatrix} 1\ 2\ 3\ \ldots\ (n-1)\ n \\ 2\ 3\ 4\ \ldots\ \quad n\quad\ 1 \end{pmatrix} \equiv (23\ldots n1)\,,$$

where the permutation $(1\,2\,3\ldots n)$ denotes the identity element. It is clear that the n cyclic permutations of n identical objects are all related to one another by an equivalence transformation

$$(1\,2\,3\ldots n) = (2\,3\,4\ldots n\,1) = (3\,4\ldots n\,1\,2) = \text{etc.} \qquad (17.7)$$

Since all of these group elements are identical, and all these cyclic permutations have $1 \to 2$, $2 \to 3$, $3 \to 4$, all are the same permutation of n identical objects, all are related by an equivalence transformation, i.e., all of these cyclic permutations represent the same physics.

Theorem. *Any permutation can be decomposed into cycles.*

Proof. The decomposition of a given permutation is demonstrated by the following example.

$$P_i = \begin{pmatrix} 1\ 2\ 3\ 4\ 5\ 6\ 7 \\ 4\ 3\ 2\ 5\ 7\ 6\ 1 \end{pmatrix} \equiv (1\ 4\ 5\ 7)(2\ 3)(6) \qquad (17.8)$$

can be decomposed into three cycles as indicated in (17.8). The decomposition of a permutation into cycles is unique, since different arrangements of cycles correspond to different permutations. $\qquad\square$

Definition 27. *Length of a cycle.*

Let us assume that a permutation of n objects is decomposed into cycles as follows: there are λ_1 cycles of one element, i.e., of length $1, \lambda_2$ cycles of length $2, \ldots, \lambda_q$ cycles of length q:

$$n = \lambda_1 + 2\lambda_2 + \cdots + q\lambda_q. \qquad (17.9)$$

It is easily seen that there are

$$\frac{n!}{1^{\lambda_1}\lambda_1!\, 2^{\lambda_2}\lambda_2!\ldots q^{\lambda_q}\lambda_q!} \qquad (17.10)$$

permutations that have the same cycle structure. An example of the length of the cycle for permutation group $P(4)$ will be given after the next theorem.

Theorem. *Permutations with the same cycle structure belong to the same class.*

Proof. Consider two permutations P and P' with the same cycle structure given by

$$P = (a_1 a_2 \ldots a_{\lambda_1})(b_1 b_2 \ldots b_{\lambda_2}) \ldots (d_1 d_2 \ldots d_{\lambda_r})$$
$$P' = (a'_1 a'_2 \ldots a'_{\lambda_1})(b'_1 b'_2 \ldots b'_{\lambda_2}) \ldots (d'_1 d'_2 \ldots d'_{\lambda_r}). \qquad (17.11)$$

Here P takes $a_1 \rightarrow a_2$, etc. $b_1 \rightarrow b_2$, etc., $d_1 \rightarrow d_2$, etc. while P' does the corresponding permutation for the primed quantities. Now we introduce the permutation operation T which takes the primed quantities into the unprimed quantities (e.g., $a'_i \rightarrow a_i$)

$$T = \begin{pmatrix} a'_1 \ldots a'_{\lambda_1}\ b'_1 \ldots b'_{\lambda_2} \ldots d'_1 \ldots d'_{\lambda_r} \\ a_1 \ldots a_{\lambda_1}\ b_1 \ldots b_{\lambda_2} \ldots d_1 \ldots d_{\lambda_r} \end{pmatrix} \qquad (17.12)$$

and T^{-1} takes $a_i \rightarrow a'_i$. Thus $T^{-1}PT$ does the following sequence: $a'_i \rightarrow a_i$, $a_i \rightarrow a_{i+1}$ and finally $a_{i+1} \rightarrow a'_{i+1}$. But this is equivalent to $a'_i \rightarrow a'_{i+1}$ which is precisely the permutation P'. Therefore,

$$T^{-1}PT = P'.$$

P' is related to P by conjugation, thus completing the proof of the theorem. The number of elements in each class is found from (17.10). $\qquad\square$

From the above theorem it follows that the number k of different classes (and hence the number of irreducible representations) of the permutation group of n objects is the number of different cycle structures that can be formed. Thus, the number of classes is just the number of ways in which the number n can be written as the sum of positive integers. For example, $n = 4$ objects can be constituted into five different cycle structures as enumerated below:

$$
\begin{aligned}
n = 4 \quad & 4 = 4 && (1, 2, 3, 4) \\
& 4 = 3 + 1 && (1, 2, 3)(4) \\
& 4 = 2 + 1 + 1 && (1, 2)(3)(4) && (17.13) \\
& 4 = 2 + 2 && (1, 2)(3, 4) \\
& 4 = 1 + 1 + 1 + 1 && (1)(2)(3)(4)
\end{aligned}
$$

giving rise to five classes and the number of members in each class can be found from (17.10).

As an example of this theorem consider the cycle structure $(abc)(d)$ of the permutation group $P(4)$, which is isomorphic to the point group T_d for the symmetry operations of a regular tetrahedron. The cycle structure $(abc)(d)$ in $P(4)$ corresponds to the rotation about a threefold axis, which also forms a class. The number of symmetry operations k in this class according to (17.10) is

$$
\frac{4!}{(1^1)(1!)(3^1)(1!)} = 8 \,,
$$

which is in agreement with the number of elements in $8C_3$ in the group T_d. Another example is finding the number of symmetry operations in the class $(ab)(cd)$ of the point group $P(4)$, corresponding to the twofold axes around x, y, z, would be $4!/[(2^2)(2!)] = 3$ from (17.10), as expected for k from the isomorphism of $(ab)(cd)$ of $P(4)$ and $3C_2$ in T_d.

In the same way, $n = 5$ objects can be constituted in seven different cycle structures giving rise to 7 classes. Correspondingly $q = 6$ gives rise to 11 classes, $q = 7$ gives rise to 15 classes, $q = 8$ gives rise to 22 classes, etc. as further discussed in Problem 17.1(a).

Since the number of classes is equal to the number of irreducible representations, we can construct Table 17.1 where $P(n)$ labels the permutation group of n objects. Since the permutation groups are finite groups, we can appeal to our experience regarding finite groups and use the Theorem (3.40)

$$
h = \sum_i \ell_i^2 \,, \tag{17.14}
$$

where ℓ_i is the dimensionality of the representation i, and h is the order of the group. For a permutation group of n objects, the order of the group is $h = n!$. From Table 17.1 we note that $P(3)$ is isomorphic with group C_{3v} or alternatively with group D_3. Similarly $P(4)$ is isomorphic with the tetrahedral group T_d. Although the groups $P(5)$ and I_h both have 120 symmetry

Table 17.1. The number of classes and a listing of the dimensionalities of the irreducible representations

group	classes	number of group elements $\sum_i \ell_i^2$
$P(1)$	1	$1! = 1^2 = 1$
$P(2)$	2	$2! = 1^2 + 1^2 = 2$
$P(3)$	3	$3! = 1^2 + 1^2 + 2^2 = 6$
$P(4)$	5	$4! = 1^2 + 1^2 + 2^2 + 3^2 + 3^2 = 24$
$P(5)$	7	$5! = 1^2 + 1^2 + 4^2 + 4^2 + 5^2 + 5^2 + 6^2 = 120$
$P(6)$	11	$6! = 1^2 + 1^2 + 5^2 + 5^2 + 5^2 + 5^2 + 9^2 + 9^2 + 10^2 + 10^2 + 16^2 = 720$
$P(7)$	15	$7! = 1^2 + 1^2 + 6^2 + 6^2 + 14^2 + 14^2 + 14^2 + 14^2 + 15^2 + 15^2$
		$\qquad + 21^2 + 21^2 + 35^2 + 35^2 + 20^2 = 5040$
$P(8)$	22	$8! = 1^2 + 1^2 + 7^2 + 7^2 + 14^2 + 14^2 + 20^2 + 20^2 + 21^2 + 21^2$
		$\qquad + 28^2 + 28^2 + 35^2 + 35^2 + 56^2 + 56^2 + 64^2 + 64^2 + 70^2 + 70^2$
		$\qquad + 42^2 + 90^2 = 40320$

$\vdots$

operations, $P(5)$ is *not* isomorphic to the icosahedral group I_h since the two groups have different numbers of classes. The number of classes of $P(5)$ is seven while the number of classes of I_h is 10. The dimensions ℓ_i of the seven classes in the group $P(5)$ are listed in Table 17.1, and include two irreducible representations with $\ell_i = 1$, two with $\ell_i = 4$, two with $\ell_i = 5$ icosahedral group I_h, and one with $\ell_i = 6$. The 10 irreducible representations of I_h have the following dimensionalities: $2[1+3+3+4+5]$ (the 2 refers to two irreducible representations for each dimensionality arising from the inversion symmetry). Making use of the isomorphism of $P(3)$ and $P(4)$ mentioned above, matrix representations for the symmetry operations of these groups are easily written down.

17.3 Basis Functions of Permutation Groups

The basis functions considered here are for the particular application of permutation groups to many-particle systems. For example, the one-electron Hamiltonian

$$\mathcal{H}_0(\boldsymbol{r}_1) = \frac{p_1^2}{2m} + V(\boldsymbol{r}_1) \tag{17.15}$$

has one-electron solutions $\psi_0(\boldsymbol{r}_1)$, $\psi_1(\boldsymbol{r}_1)$, etc. Thus the solutions of the many-electron problem can be expanded in terms of products of the one-electron wave functions for the Hamiltonian in (17.15). Below, we write down the ground state many-electron wave function formed by putting all electrons in the ground state, and the lowest excited states are formed by putting one electron in an excited state.

Since electrons are Fermions, we present the discussion more generally in terms of particles. We will first consider the ground state of lowest energy which is a fully symmetric state with Γ_1^s symmetry. Every n-particle (electron) system also has one fully antisymmetric state with Γ_1^a symmetry. Because of the Pauli principle, we know that every allowed Fermion state must have Γ_1^a symmetry and thus we always look for the product of orbital and spin states that transform as Γ_1^a.

Ground State: (Boson gas)

The many-particle ground state wave function Ψ_0 is found by putting all the particles into the one-particle ground state:

$$\Psi_0 = \psi_0(\boldsymbol{r}_1)\psi_0(\boldsymbol{r}_2)\ldots\psi_0(\boldsymbol{r}_n) \rightarrow \Gamma_1^s \qquad (17.16)$$

and from a group theoretical point of view, this orbital state transforms at the totally symmetric representation Γ_1^s.

Single Excitation: (e.g., "phonons" or "magnons")

To form the first excited state, consider the functions g_i found by placing the ith particle in the first excited state $\psi_1(\boldsymbol{r}_i)$:

$$\psi_1(\boldsymbol{r}_1)\psi_0(\boldsymbol{r}_2)\ldots\psi_0(\boldsymbol{r}_n) = g_1\,,$$

$$\psi_0(\boldsymbol{r}_1)\psi_1(\boldsymbol{r}_2)\ldots\psi_0(\boldsymbol{r}_n) = g_2\,,$$

$$\vdots$$

$$\psi_0(\boldsymbol{r}_1)\psi_0(\boldsymbol{r}_2)\ldots\psi_1(\boldsymbol{r}_n) = g_n\,. \qquad (17.17)$$

The basis functions given by (17.17) transform as an n-dimensional reducible representation. Decomposition of this reducible representation yields

$$\Gamma_n(\text{reducible}) = \Gamma_1^s + \Gamma_{n-1}\,,$$

where Γ_1^s refers to the totally symmetric representation, with basis functions is given by

$$\Psi_{\Gamma_1^s}' = \frac{1}{\sqrt{n}} \sum_{i=1}^{n} g_i \rightarrow \Gamma_1^s \qquad (17.18)$$

and Γ_{n-1} is the $(n-1)$ dimensional irreducible representation, the basis functions depending on the ensemble of phase factors forming all possible n^{th} roots of unity

$$\Psi_{\Gamma_{n-1}}' = \left\{ \begin{array}{c} \dfrac{1}{\sqrt{n}} \displaystyle\sum_{i=1}^{n} \omega^{(i-1)} g_i \\[2mm] \dfrac{1}{\sqrt{n}} \displaystyle\sum_{i=1}^{n} \omega^{2(i-1)} g_i \\[2mm] \vdots \\[2mm] \dfrac{1}{\sqrt{n}} \displaystyle\sum_{i=1}^{n} \omega^{n(i-1)} g_i \end{array} \right\} \rightarrow \Gamma_{n-1} \qquad (17.19)$$

where ω are phase factors given by $\omega = e^{2\pi i/n}$. For the special case $n = 2$, where $\omega = -1$, we obtain

$$\Psi'_{\Gamma_1 = \Gamma_1^a} = \frac{1}{\sqrt{2}} [\psi_1(r_1)\psi_0(r_2) - \psi_0(r_1)\psi_1(r_2)].$$

For the case $n = 3$, where $\omega = e^{2\pi i/3}$, we obtain

$$\Psi'_{\Gamma_2} = \frac{1}{\sqrt{3}} \{\psi_1(r_1)\psi_0(r_2)\psi_0(r_3) + \omega\psi_0(r_1)\psi_1(r_2)\psi_0(r_3)$$

$$+\omega^2\psi_0(r_1)\psi_0(r_2)\psi_1(r_3)\}$$

and its partner

$$\Psi''_{\Gamma_2} = \frac{1}{\sqrt{3}} (\psi_1(r_1)\psi_0(r_2)\psi_0(r_3) + \omega^2\psi_0(r_1)\psi_1(r_2)\psi_0(r_3)$$

$$+\omega\psi_0(r_1)\psi_0(r_2)\psi_1(r_3))$$

for the two-dimensional irreducible representation.

The $(n-1)$ cyclic permutations $(1)(2\,3\ldots n)$, $(1)(n\,2\,3\ldots(n-1))$, ... all commute with each other. Hence the eigenfunctions can be chosen so that these matrices are brought into diagonal form. This means that the $(n-1)$ diagonal terms become eigenvalues, given by

$$e^{\frac{2\pi i}{n}(\frac{n-2}{2})}, \ldots, e^{\frac{-2\pi i}{n}(\frac{n-2}{2})}.$$

This Γ_{n-1} irreducible representation is present in every permutation group $P(n)$.

Irreducible Representation Γ_1^a. Also present in every permutation group is a one-dimensional irreducible representation Γ_1^a which is totally antisymmetric and Γ_1^a can be found from the regular representation which contains every irreducible representation (see Sect. 3.7) of the group in accordance with its dimensionality.

Regular Representation. Since all n electrons are in distinct states, they have different eigenfunctions. The Slater determinant (Sect. 17.1) formed from these eigenfunctions is distinct, and does not vanish. Furthermore the Slater determinant forms the basis function for the antisymmetric representation Γ_1^a. For the case where all n one-electron functions are distinct, the $n!$ functions form a regular representation of the permutation group, and the character for the identity element for the regular representation is the order of the group and according to (3.42) we have

$$\chi^{\text{regular}} = \sum_{j}^{n} \ell_j \, \chi^{\Gamma_j} = h = n!, \tag{17.20}$$

where ℓ_j is the dimension of the irreducible representation Γ_j and each representation occurs a number of times which is equal to the dimension of the representation, and h is the order of the group $= n!$.

17.4 Pauli Principle in Atomic Spectra

We will in the following subsections of this section apply the results in Sect. 17.3 to specify the symmetry of many-body wave-functions formed by two electrons, three electrons, etc. For each case, we will point out the states corresponding to the representations Γ_1^s, Γ_1^a, and Γ_{n-1} discussed in Sect. 17.3.

17.4.1 Two-Electron States

For the case of two electrons, the use of group theory is not especially needed for selecting the proper linear combinations of wave functions. The same results can be found just from consideration of even and odd states, since there are only two classes and two irreducible representations for $P(2)$. We discuss this case here largely for review and pedagogic reasons. The Slater determinant for the two-electron problem can be written as

$$\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_1(\boldsymbol{r}_1, \sigma_1) & \psi_1(\boldsymbol{r}_2, \sigma_2) \\ \psi_2(\boldsymbol{r}_1, \sigma_1) & \psi_2(\boldsymbol{r}_2, \sigma_2) \end{vmatrix}, \tag{17.21}$$

where $\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2)$ denotes the many-electron wave function for the case of two electrons. The wave-functions $\psi_i(\boldsymbol{r}_j, \sigma_j)$, $j = 1, 2$ denote the one-electron wave functions with each electron having spatial r_j and spin σ_j coordinates. The subscript i ($i = 1, 2$) refers to two distinct electron states that obey the Pauli Principle. We use the vector $\boldsymbol{x}_i$ to denote both the orbital and spin variables $(\boldsymbol{r}_i, \sigma_i)$. The two electron state defined by the Slater determinant in (17.21) has Γ_1^a symmetry.

The lowest energy state for the two-electron problem is achieved by putting both electrons in $1s$ orbital states, taking the *symmetric* (s) linear combination of spatial orbitals and taking the spins antiparallel. This choice provides two different states for the two electrons by the Pauli Principle, and minimizes the energy. Multiplying out the Slater determinant in this case yields

$$\Psi(1, 2) = \frac{1}{\sqrt{2}} \psi_s^{1s}(1) \psi_s^{1s}(2) [\alpha_1 \beta_2 - \alpha_2 \beta_1], \tag{17.22}$$

where the spin up state is denoted by α or $\uparrow$ and the spin down state by β, or $\downarrow$, and $\Psi(1, 2)$ denotes the two-electron ground state. The function $[\alpha_1 \beta_2 - \alpha_2 \beta_1]$ denotes the antisymmetric spin function where the subscripts refer to the individual electrons.

Let us now consider the transformation properties of these two electrons more generally, including their excited states. The possible spin states for two electrons are $S = 0, 1$ where capital S denotes the total spin for the many electron system. The phase factor for the two-electron problem is $\omega = e^{2\pi i/2} = -1$ so that the linear combinations simply involve ± 1. For the two-electron problem we can form a symmetric and an antisymmetric combination of α and β as given in Table 17.2.

Table 17.2. Transformation properties of two-electron states under permutations

configuration	state	irreducible representations	allowed states
$(\alpha_1\beta_2 - \beta_1\alpha_2)/\sqrt{2}$	$S = 0$	Γ_1^a	
$(\alpha_1\alpha_2 + \alpha_2\alpha_1)/\sqrt{2}, \ldots$	$S = 1$	Γ_1^s	
s^2	$L = 0$	Γ_1^s	^1S
$1s2s$	$L = 0$	$\Gamma_1^s + \Gamma_1^a$	$^1S, \, ^3S$
sp	$L = 1$	$\Gamma_1^s + \Gamma_1^a$	$^1P, \, ^3P$
p^2	$L = 0$	Γ_1^s	^1S
p^2	$L = 1$	Γ_1^a	^3P
p^2	$L = 2$	Γ_1^s	^1D
pd	$L = 1$	$\Gamma_1^s + \Gamma_1^a$	$^1P + {}^3P$
pd	$L = 2$	$\Gamma_1^s + \Gamma_1^a$	$^1D + {}^3D$
pd	$L = 3$	$\Gamma_1^s + \Gamma_1^a$	$^1F + {}^3F$
d^2	$L = 0$	Γ_1^s	^1S
d^2	$L = 1$	Γ_1^a	^3P
d^2	$L = 2$	Γ_1^s	^1D
d^2	$L = 3$	Γ_1^a	^3F
d^2	$L = 4$	Γ_1^s	^1G
f^2	$L = 0$	Γ_1^s	^1S
f^2	$L = 1$	Γ_1^a	^3P
f^2	$L = 2$	Γ_1^s	^1D
f^2	$L = 3$	Γ_1^a	^3F
f^2	$L = 4$	Γ_1^s	^1G
f^2	$L = 5$	Γ_1^a	^3H
f^2	$L = 6$	Γ_1^s	^1I

The symmetries of the irreducible representations of the permutation group $P(2)$ label the various spin and orbital angular momentum states. To obtain states allowed by the Pauli Principle, the direct product of the symmetries between the orbital and spin states must contain Γ_1^a

For the antisymmetric combination $(S = 0)$ as in (17.22), we can have only $M_S = 0$ and the corresponding linear combination of spin states is given in Table 17.2. For the symmetric spin combination $(S = 1)$, we can have three linear combinations. Only the $M_S = 1$ combination $(\alpha_1\alpha_2 + \alpha_2\alpha_1)/\sqrt{2}$ is listed explicitly in Table 17.2. The $M_S = 0$ combination $(\alpha_1\beta_2 + \beta_1\alpha_2)/\sqrt{2}$ and the $M_S = -1$ combination $(\beta_1\beta_2 + \beta_2\beta_1)/\sqrt{2}$ do not appear in the table.

We also make entries in Table 17.2 for the symmetries of the orbital angular momentum states. If the two electrons are in the same symmetric orbital s

state ($L = 0$), then the spin functions must transform as an antisymmetric linear combination Γ_1^a in Table 17.2 and corresponding to the spectroscopic notation ^1S as in (17.22). However, if the two s electrons have different principal quantum numbers, then we can make both a symmetric and an antisymmetric combination of orbital states, as is illustrated here for the two electrons occupying $1s$ and $2s$ states, where the symmetric and antisymmetric combinations are

$$(\psi_{1s}(\boldsymbol{r}_1)\psi_{2s}(\boldsymbol{r}_2) + \psi_{1s}(\boldsymbol{r}_2)\psi_{2s}(\boldsymbol{r}_1))/\sqrt{2},$$

which transforms as Γ_1^s and

$$(\psi_{1s}(\boldsymbol{r}_1)\psi_{2s}(\boldsymbol{r}_2) - \psi_{1s}(\boldsymbol{r}_2)\psi_{2s}(\boldsymbol{r}_1))/\sqrt{2},$$

which transforms as Γ_1^a. Because of the Pauli principle, the orbital Γ_1^s combination goes with the Γ_1^a spin state leading to an ^1S level, while the Γ_1^a orbital state goes with the Γ_1^s spin state leading to an ^3S level (see Table 17.2). The state with Γ_{n-1} symmetry will be a one-dimensional representation also, but we already have two one-dimensional representations and there can be no more than two irreducible representations for $P(2)$ because we have only two classes.

We now consider the next category of entries in Table 17.2. If one electron is in an s state and the second is in a p state (configuration labeled sp), the total L value must be $L = 1$. We however have two choices for the orbital states: a symmetric Γ_1^s state or an antisymmetric Γ_1^a state. The symmetric combination of orbital wave functions (Γ_1^s) must then correspond to the $S = 0$ antisymmetric spin state (Γ_1^a), resulting in the ^1P level, whereas the antisymmetric orbital combination (transforming as Γ_1^a) goes with the symmetric triplet Γ_1^s spin state and yields the ^3P level (see Table 17.2).

Placing two electrons in p states with the same principal quantum number (configuration p^2 in Table 17.2) allows for a total angular momentum of $L = 0$ (which must have Γ_1^s symmetry), of $L = 1$ (with Γ_1^a symmetry) and of $L = 2$ (again with Γ_1^s symmetry). Each p electron can be in one of the three orbital states (p^+, p^0, p^-), corresponding to $m_l = 1, 0, -1$, respectively, for each one-electron state. Combining the p^+p^+ product yields an $M_L = 2$ state which belongs exclusively to the $L = 2$ multiplet, whereas combining the p^+p^0 states symmetrically yields the $M_L = 1$ state of the $L = 2$ multiplet. We use the notation p^+p^0 to denote $\psi_{p^+}(\boldsymbol{r}_1)\psi_{p^0}(\boldsymbol{r}_2)$. However, combining p^+p^0 antisymmetrically yields the $M_L = 1$ state of the $L = 1$ multiplet. The formation of the two-electron states for the various L and M_L values occurring for the p^2 configuration is given below. Since the orbital functions for the $L = 1$ state transform as Γ_1^a the spin functions transform as Γ_1^s and the $L = 1$ multiplet is a triplet spin state ^3P. The $L = 0$ and $L = 2$ states both transform as Γ_1^s and thus the allowed spin states must be the singlet spin state $S = 0$ (see Table 17.2).

The wave functions for the p^2 configuration sketched above can be found in many standard quantum mechanics text books and are:

$L = 2$ symmetry (Γ_1^s) going with Γ_1^a for the spins to yield a ^1D state.

$$\Psi(L = 2, M_L = 2) = (p^+p^+)$$
$$\Psi(L = 2, M_L = 1) = (p^0p^+ + p^+p^0)/\sqrt{2}$$
$$\Psi(L = 2, M_L = 0) = [(p^0p^0) + (p^+p^- + p^-p^+)/\sqrt{2}]/\sqrt{2}$$
$$\Psi(L = 2, M_L = -1) = (p^0p^- + p^-p^0)/\sqrt{2}$$
$$\Psi(L = 2, M_L = -2) = (p^-p^-). \tag{17.23}$$

$L = 1$ symmetry (Γ_1^a) going with a symmetric spin state (Γ_1^s) to yield a ^3P state.

$$\Psi(L = 1, M_L = 1) = (p^0p^+ - p^+p^0)/\sqrt{2}$$
$$\Psi(L = 1, M_L = 0) = (p^+p^- - p^-p^+)/\sqrt{2}$$
$$\Psi(L = 1, M_L = -1) = (p^0p^- - p^-p^0)/\sqrt{2}. \tag{17.24}$$

$L = 0$ symmetry (Γ_1^s) going with an antisymmetric spin state (Γ_1^a) to yield a ^1S state.

$$\Psi(L = 0, M_L = 0) = [(p^0p^0) - (p^+p^- + p^-p^+)/\sqrt{2}]/\sqrt{2}. \tag{17.25}$$

Following this explanation for the p^2 configuration, the reader can now fill in the corresponding explanations for the states formed from two-electron states derived from the pd, d^2 or f^2 configurations listed in Table 17.2.

17.4.2 Three-Electron States

For the case of three electrons, the use of group theory becomes more important. In this case we have the permutation group of three objects $P(3)$ which has six elements, three classes and three irreducible representations (see Table 17.3). In the extended character table above, we label the class

Table 17.3. Extended character table for permutation group $P(3)$

	$\chi(E)$	$\chi(A,B,C)$	$\chi(D,F)$	
$P(3)$	(1^3)	$3(2,1)$	$2(3)$	
Γ_1^s	1	1	1	
Γ_1^a	1	-1	1	
Γ_2	2	0	-1	
$\Gamma_{\text{perm.}}(\psi_1\psi_1\psi_1)$	1	1	1	$\Rightarrow \Gamma_1^s$
$\Gamma_{\text{perm.}}(\psi_1\psi_1\psi_2)$	3	1	0	$\Rightarrow \Gamma_1^s + \Gamma_2$
$\Gamma_{\text{perm.}}(\psi_1\psi_2\psi_3)$	6	0	0	$\Rightarrow \Gamma_1^s + \Gamma_1^a + 2\Gamma_2$

(1^3) to denote the cyclic structure $(1)(2)(3)$ and class $(2,1)$ to denote the cyclic structures $(1\,2)(3), (2)(1\,3), (1)(2\,3)$, and class (3) to denote the cyclic structure $(1\,2\,3)$. The correspondence between the six symmetry elements E, A, B, C, D, F and these three classes is immediate and is given in the table explicitly. Also given below the character table are all the possible symmetries of the permutations for three-electron wave functions. Because of these additional listings, we call this an extended character table. The first permutation representation $\Gamma_{\text{perm.}}$ for the three-electron state would correspond to having all the same one-electron states $(\psi_1\psi_1\psi_1)$. This function is invariant under any of the six permutations of the group, so that all characters are one and the function $(\psi_1\psi_1\psi_1)$ transforms as Γ_1^s. In the second possible case, one of the electrons is in a different state $(\psi_1\psi_1\psi_2)$, and since there are three possible combinations that can be formed with the ψ_2 one-electron wave function, we have three distinct functions that can be obtained from permutation of the electrons. Hence $(\psi_1\psi_1\psi_2)$ transforms as a three-dimensional reducible representation of the permutation group $P(3)$ with three partners for this state. The identity operation leaves the three partners invariant so we get a character three. Each of the permutation operations $[3(2,1)]$ leaves one of the partners invariant, so we get a character of one, while the cyclic permutations change all partners yielding a character of zero. The reduction of this reducible representation to its irreducible components yields $\Gamma_1^s + \Gamma_2$ as indicated on the table. Finally, we consider the case when all three electrons are in different states $(\psi_1\psi_2\psi_3)$. This choice gives rise to six partners, and it is only the identity operation which leaves the partners $(\psi_1\psi_2\psi_3)$ invariant. This reducible representation [like the regular representation can be expressed in terms of its irreducible constituents using the relation $h = \sum_i(\ell_i^2)$] contains $\Gamma_1^s + \Gamma_1^a + 2\Gamma_2$ as is expected for the regular representation. The equivalence principle is thus used to form reducible representations such as those for $P(3)$ given in Table 17.3. This table is also given in Appendix F as Table F.1.

Let us now look at the spin states that can be made from three electrons. Referring to Sect. 17.3 we can make a symmetric state

$$(\alpha_1\alpha_2\alpha_3)$$

with symmetry Γ_1^s that corresponds to the $S = 3/2$ and $M_S = 3/2$ spin state. To obtain the linear combination of spin states for the three other M_S values $(M_S = 1/2, -1/2, -3/2)$, we must apply lowering operators to the $M_S = 3/2$ state $(\alpha_1\alpha_2\alpha_3)$. With regard to the $S = 1/2$ state, (17.17) tells us that this state is a two-dimensional representation with partners:

$$\Psi'_{\Gamma_2} = \begin{cases} (g_1 + \omega g_2 + \omega^2 g_3) \\ (g_1 + \omega^2 g_2 + \omega g_3) , \end{cases} \tag{17.26}$$

where $\omega = \exp(2\pi i/3)$ and where the functions g_i are assembled by sequentially selecting the spin down state β at each of the sites 1, 2 or 3. This explains the first two entries in Table 17.4. The state Ψ'_{Γ_2} corresponds to the

Table 17.4. Transformation properties of three-electron states under permutations[a]

configuration	state	irreducible representation	allowed state
$(\uparrow\uparrow\downarrow)$	$S = 1/2$	Γ_2	
$(\uparrow\uparrow\uparrow)$	$S = 3/2$	Γ_1^s	
s^3	$L = 0$	Γ_1^s	$-$
$1s^2 2s$	$L = 0$	$\Gamma_1^s + \Gamma_2$	^2S
$s^2 p$	$L = 1$	$\Gamma_1^s + \Gamma_2$	^2P
sp^2	$L = 0$	$\Gamma_1^s + \Gamma_2$	^2S
sp^2	$L = 1$	$\Gamma_1^a + \Gamma_2$	$^2P, \, ^4P$
sp^2	$L = 2$	$\Gamma_1^s + \Gamma_2$	^2D
$(2p)^2(3p)$	$L = 0$	$\Gamma_1^a + \Gamma_2$	$^2S, \, ^4S$
$(2p)^2(3p)$	$L = 1$	$2\Gamma_1^s + \Gamma_1^a + 3\Gamma_2$	$^2P, \, ^2P, \, ^2P, \, ^4P$
$(2p)^2(3p)$	$L = 2$	$\Gamma_1^s + \Gamma_1^a + 2\Gamma_2$	$^2D, \, ^2D, \, ^4D$
$(2p)^2(3p)$	$L = 3$	$\Gamma_1^s + \Gamma_2$	^2F
p^3	$L = 0$	Γ_1^a	^4S
p^3	$L = 1$	$\Gamma_1^s + \Gamma_2$	^2P
p^3	$L = 2$	Γ_2	^2D
p^3	$L = 3$	Γ_1^s	$-$
d^3	$L = 0$	Γ_1^s	$-$
d^3	$L = 1$	$\Gamma_1^a + \Gamma_2$	$^2P, \, ^4P$
d^3	$L = 2$	$\Gamma_1^s + 2\Gamma_2$	$^2D, \, ^2D$
d^3	$L = 3$	$\Gamma_1^s + \Gamma_1^a + \Gamma_2$	$^2F, \, ^4F$
d^3	$L = 4$	$\Gamma_1^s + \Gamma_2$	^2G
d^3	$L = 5$	Γ_2	^2H
d^3	$L = 6$	Γ_1^s	$-$
f^3	$L = 0$	Γ_1^a	^4S
f^3	$L = 1$	$\Gamma_1^s + \Gamma_2$	^2P
f^3	$L = 2$	$\Gamma_1^a + 2\Gamma_2$	$^2D, \, ^2D, \, ^4D$
f^3	$L = 3$	$2\Gamma_1^s + \Gamma_1^a + 2\Gamma_2$	$^2F, \, ^2F, \, ^4F$
f^3	$L = 4$	$\Gamma_1^s + \Gamma_1^a + 2\Gamma_2$	$^2G, \, ^2G, \, ^4G$
f^3	$L = 5$	$\Gamma_1^s + 2\Gamma_2$	$^2H, \, ^2H$
f^3	$L = 6$	$\Gamma_1^s + \Gamma_1^a + \Gamma_2$	$^2I, \, ^4I$
f^3	$L = 7$	$\Gamma_1^s + \Gamma_2$	^2J
f^3	$L = 8$	Γ_2	^2K
f^3	$L = 9$	Γ_1^s	$-$

[a] The symmetries of the irreducible representations of the permutation group $P(3)$ label the various spin and orbital angular momentum states. To obtain the states allowed by the Pauli Principle, the direct product of the symmetries between the orbital and spin states must contain Γ_1^a

state with Γ_{n-1} symmetry in Table 17.4. Using the g_1, g_2, and g_3 functions we can write the state with Γ_1^s symmetry as

$$\Psi'_{\Gamma_1^s} = \frac{1}{\sqrt{3}}(g_1 + g_2 + g_3) \tag{17.27}$$

and the state with Γ_1^a symmetry as the Slater determinant

$$\Psi'_{\Gamma_1^a} = \frac{1}{\sqrt{3}} \begin{vmatrix} g_1(x_1) & g_1(x_2) & g_1(x_3) \\ g_2(x_1) & g_2(x_2) & g_2(x_3) \\ g_3(x_1) & g_3(x_2) & g_3(x_3) \end{vmatrix} . \tag{17.28}$$

Now let us examine the spatial states. Putting all three electrons in the same s state would yield a state with $L = 0$, $M_L = 0$ and having Γ_1^s symmetry. Taking the direct product between Γ_1^s for the orbital $L = 0$ state and either of the spin states $\Gamma_1^s \otimes (\Gamma_1^s + \Gamma_2)$ does not yield a state with Γ_1^a symmetry, and therefore the s^3 configuration is not allowed because of the Pauli principle. This is a group theoretical statement of the fact that a particular s level can only accommodate one spin up and one spin down electron. If now one of the electrons is promoted to a $2s$ state, then we can make an Γ_1^s state and a Γ_2 state in accordance with Sect. 17.3 and with the character table for $P(3)$ in Table 17.3, taking $g_1 = \psi_{2s}(\boldsymbol{r}_1)\psi_{1s}(\boldsymbol{r}_2)\psi_{1s}(\boldsymbol{r}_3)$, etc. and forming states such as given in (17.18) and (17.19). The direct product

$$\Gamma_2 \otimes \Gamma_2 = \Gamma_1^s + \Gamma_1^a + \Gamma_2$$

then ensures that a state with Γ_1^a symmetry can be assembled to satisfy the Pauli principle. Since the spin state with Γ_2 symmetry corresponds to a Pauli-allowed component $S = 1/2$, the allowed $1s^2 2s$ state will be a doublet ^2S state as shown in Table 17.4. Similar arguments apply to the formation of $s^2 p$ states with $L = 1$.

For the sp^2 configuration the orbital angular momentum can be $L = 0$, $L = 1$ and $L = 2$. This corresponds to $(2 \times 6 \times 6 = 72)$ possible states in the multiplet. We show below using the Pauli principle and group theory arguments that the number of allowed states is 30. The spatial states for the sp^2 configuration with $L = 2$ are formed from products of the type $sp^+ p^+$ for the $M_L = 2$ state (see (17.23)–(17.25)). Once again from the character table (Table 17.3) for $P(3)$, the symmetries which are contained in the three-electron wave function $sp^+ p^+$ (denoting $\psi_s(\boldsymbol{r}_1)\psi_{p+}(\boldsymbol{r}_2)\psi_{p+}(\boldsymbol{r}_3)$) are Γ_1^s and Γ_2 just as was obtained for the $1s^2 2s$ configuration. The only possible allowed state for $L = 2$ has $S = 1/2$ which results in the ^2D state listed in the table. The $M_L = 1$ states are linear combinations of the $sp^+ p^0$ functions which have the symmetries $\Gamma_1^s + \Gamma_1^a + 2\Gamma_2$, since this case corresponds to $(\psi_1 \psi_2 \psi_3)$ in the character table. Of these symmetry types, the $\Gamma_1^s + \Gamma_2$ states are associated with the $M_L = 1$ state of the $L = 2$ multiplet, since the irreducible representation is specified by the quantum number L and the M_L only specify the partners

of that irreducible representation. After this subtraction has been performed the symmetry types $\Gamma_1^a + \Gamma_2$ for the $L = 1$, $M_L = 1$ level are obtained.

Referring to Table 17.4, the symmetry for the $L = 0$ state of the sp^2 configuration could arise from a sp^0p^0 state which is of the $(\psi_1\psi_1\psi_2)$ form and therefore transforms according to $\Gamma_1^s + \Gamma_2$ symmetry (see the character table (Table 17.3) for $P(3)$). These orbital states go with the spin states Γ_1^a.

For the $L = 1$ state, the orbital Γ_1^a irreducible representation goes with the Γ_1^s spin 3/2 state to give rise to a quartet ^4P state while the Γ_2 orbital state can only go with the Γ_2 spin state to give a Γ_1^a state when taking the direct product of the symmetries of the orbital and spin states $(\Gamma_2 \otimes \Gamma_2)$. The case of the p^3 configuration is an instructive example where we can see how group theory can be used to simplify the analysis of the symmetries of multi-electron states. As the number of electrons increases, the use of group theory becomes essential to keep track of the symmetries that are possible by the addition of angular momentum and the symmetries that are allowed by the Pauli principle. For the p^3 configuration, we can have a total of $6 \times 6 \times 6 = 216$ states. We will show below that if all electrons have the same principal quantum number, only 20 of these states are allowed by the Pauli principle and we will here classify their symmetry types.

For the p^3 configuration we can have $L = 3$, 2, 1 and 0 total orbital angular momentum states. In the discussion that follows we will assume that all electrons have the same principal quantum number (e.g., $2p^3$). For the $L = 3$ state to be allowed, we must be able to put all three electrons into a $(p^+p^+p^+)$ state to make the $M_L = 3$ state. From the extended character table (Table 17.3) for $P(3)$, we see that $L = 3$ must transform as Γ_1^s. Since the direct product of the orbital and spin states $\Gamma_1^s \otimes (\Gamma_1^s + \Gamma_2)$ does not contain Γ_1^a this state is not allowed. The $L = 2$ multiplet is constructed from an $M_L = 2$ state having $p^+p^+p^0$ combinations which from the character table (Table 17.3) for $P(3)$ transform as $\Gamma_1^s + \Gamma_2$. Since $M_L = 2$ also contributes to the $L = 3$ state with symmetry Γ_1^s, we must subtract Γ_1^s from $\Gamma_1^s + \Gamma_2$ to get the symmetry Γ_2 for the $L = 2$ state. If we take a direct product of the orbital and spin states for this case, we obtain

$$\Gamma_2 \otimes (\Gamma_1^s + \Gamma_2) = \Gamma_1^s + \Gamma_1^a + 2\Gamma_2\,,$$

but it is only the direct product $\Gamma_2 \otimes \Gamma_2$ which contributes a state with Γ_1^a symmetry that is allowed by the Pauli principle. Thus only the ^2D state is symmetry-allowed as indicated in Table 17.4. To get the symmetry of the $L = 1$ state, consider the combinations $p^+p^0p^0$ and $p^+p^+p^-$ which contribute to the $M_L = 1$ state. In this case the $M_L = 1$ state contains irreducible representations $2(\Gamma_1^s + \Gamma_2)$. Since $M_L = 1$ also appears for $L = 2$ and $L = 3$, we need to subtract $(\Gamma_1^s + \Gamma_2)$ to obtain $(\Gamma_1^s + \Gamma_2)$ for the symmetries of the orbital $L = 1$ state (see Table 17.4). For the $M_L = 0$ levels we have the combinations $p^0p^0p^0$ and $p^+p^-p^0$, the first transforming as Γ_1^s and the second as $\Gamma_1^s + \Gamma_1^a + 2\Gamma_2$ to give a total of $2\Gamma_1^s + \Gamma_1^a + 2\Gamma_2$. However $M_L = 0$ is also present in the $L = 3$, 2 and 1 multiplets, so we must subtract the irreducible

representations $(\Gamma_1^s) + (\Gamma_2) + (\Gamma_1^s + \Gamma_2)$ to obtain Γ_1^a for the $L = 0$ state. For an orbital angular momentum with symmetry Γ_1^a, it is only the $S = 3/2\ \Gamma_1^s$ spin state that is allowed by the Pauli principle (see Table 17.4).

The same procedure can be used to obtain all the other entries in Table 17.4, as well as the many three-electron states not listed. As the angular momentum increases (e.g., for the case of d^3 or f^3 configurations), group theoretical concepts become increasingly important.

17.4.3 Four-Electron States

In consideration of the four-electron problem we must consider the permutation group $P(4)$. The character table for the group $P(4)$ is given in Table 17.5 and also in Table F.2. The irreducible representations are denoted by subscripts referring to their dimensionality. Also shown in Table 17.5 are the transformation properties for the various products of functions. These transformation properties are obtained in the same way as for the case of the group $P(3)$ discussed in Sect. 17.4.2. The various four-electron states of a free ion or atom that are consistent with the Pauli principle are formed with the help of this extended character table.

We first consider the possible spin states for the four-electron configuration. The transformation of the spin states under the operations of the permutation group are shown in Table 17.6. The four spins can be arranged to give a total spin of $S = 2$, $S = 1$ and $S = 0$. The representation for the fully symmetric $(\alpha_1\alpha_2\alpha_3\alpha_4)$ state, which appears in Table 17.5 as $\Gamma_{\text{perm.}}(\psi_1\psi_1\psi_1\psi_1)$, has $S = 2$ and clearly transforms as Γ_1^s. The $S = 1$ state is formed from a combination $(\alpha_1\alpha_2\alpha_3\beta_4)$ with $M_S = 1$ and the product wave-function is of the form $(\psi_1\psi_1\psi_1\psi_2)$, which from the extended character table in Table 17.5 transforms as $\Gamma_1^s + \Gamma_3$. But $M_S = 1$ also contributes to the $S = 2$ state which transforms as Γ_1^s. Thus by subtraction, $S = 1$ transforms as Γ_3. Likewise, the $S = 0$

Table 17.5. Extended character table for group $P(4)$

$P(4)$	(1^4)	$8(3,1)$	$3(2^2)$	$6(2,1^2)$	$6(4)$	
Γ_1^s	1	1	1	1	1	
Γ_1^a	1	1	1	-1	-1	
Γ_2	2	-1	2	0	0	
Γ_3	3	0	-1	1	-1	
$\Gamma_{3'}$	3	0	-1	-1	1	
$\Gamma_{\text{perm.}}(\psi_1\psi_1\psi_1\psi_1)$	1	1	1	1	1	$\Rightarrow \Gamma_1^s$
$\Gamma_{\text{perm.}}(\psi_1\psi_1\psi_1\psi_2)$	4	1	0	2	0	$\Rightarrow \Gamma_1^s + \Gamma_3$
$\Gamma_{\text{perm.}}(\psi_1\psi_1\psi_2\psi_2)$	6	0	2	2	0	$\Rightarrow \Gamma_1^s + \Gamma_2 + \Gamma_3$
$\Gamma_{\text{perm.}}(\psi_1\psi_1\psi_2\psi_3)$	12	0	0	2	0	$\Rightarrow \Gamma_1^s + \Gamma_2 + 2\Gamma_3 + \Gamma_{3'}$
$\Gamma_{\text{perm.}}(\psi_1\psi_2\psi_3\psi_4)$	24	0	0	0	0	$\Rightarrow \Gamma_1^s + \Gamma_1^a + 2\Gamma_2 + 3\Gamma_3 + 3\Gamma_{3'}$

Table 17.6. Transformation properties of four-electron states under permutations[a]

configuration	state	irreducible representation	allowed state
$(\uparrow\uparrow\downarrow\downarrow)$	$S=0$	Γ_2	
$(\uparrow\uparrow\uparrow\downarrow)$	$S=1$	Γ_3	
$(\uparrow\uparrow\uparrow\uparrow)$	$S=2$	Γ_1^s	
s^4	$L=0$	Γ_1^s	$-$
$1s^3 2s$	$L=0$	$\Gamma_1^s + \Gamma_3$	$-$
$1s^2 2s^2$	$L=0$	$\Gamma_1^s + \Gamma_2 + \Gamma_3$	^1S
sp^3	$L=0$	$\Gamma_1^a + \Gamma_{3'}$	$^3S,\ ^5S$
sp^3	$L=1$	$\Gamma_1^s + \Gamma_2 + 2\Gamma_3 + \Gamma_{3'}$	$^1P,\ ^3P$
sp^3	$L=2$	$\Gamma_2 + \Gamma_3 + \Gamma_{3'}$	$^1D,\ ^3D$
sp^3	$L=3$	$\Gamma_1^s + \Gamma_3$	$-$
$(2p)^3(3p)$	$L=0$	$\Gamma_1^s + \Gamma_2 + 2\Gamma_3 + \Gamma_{3'}$	$^1S,\ ^3S$
$(2p)^3(3p)$	$L=1$	$\Gamma_1^s + \Gamma_1^a + 2\Gamma_2 + 3\Gamma_3 + 3\Gamma_{3'}$	$^1P,\ ^1P,\ ^3P,\ ^3P,\ ^3P,\ ^5P$
$(2p)^3(3p)$	$L=2$	$2\Gamma_1^s + 2\Gamma_2 + 4\Gamma_3 + 2\Gamma_{3'}$	$^1D,\ ^1D,\ ^3D,\ ^3D$
$(2p)^3(3p)$	$L=3$	$\Gamma_1^s + \Gamma_2 + 2\Gamma_3 + \Gamma_{3'}$	$^1F,\ ^3F$
$(2p)^3(3p)$	$L=4$	$\Gamma_1^s + \Gamma_3$	$-$
p^4	$L=0$	$\Gamma_1^s + \Gamma_2$	^1S
p^4	$L=1$	$\Gamma_3 + \Gamma_{3'}$	^3P
p^4	$L=2$	$\Gamma_1^s + \Gamma_2 + \Gamma_3$	^1D
p^4	$L=3$	Γ_3	$-$
p^4	$L=4$	Γ_1^s	$-$
d^4	$L=0$	$\Gamma_1^s + 2\Gamma_2$	$^1S,\ ^1S$
d^4	$L=1$	$2\Gamma_3 + 2\Gamma_{3'}$	$^3P,\ ^3P$
d^4	$L=2$	$2\Gamma_1^s + \Gamma_1^a + 2\Gamma_2 + 2\Gamma_3 + \Gamma_{3'}$	$^1D,\ ^1D,\ ^3D,\ ^5D$
d^4	$L=3$	$\Gamma_2 + 3\Gamma_3 + 2\Gamma_{3'}$	$^1F,\ ^3F,\ ^3F$
d^4	$L=4$	$2\Gamma_1^s + 2\Gamma_2 + 2\Gamma_3 + \Gamma_{3'}$	$^1G,\ ^1G,\ ^3G$
d^4	$L=5$	$\Gamma_1^s + 2\Gamma_3 + \Gamma_{3'}$	^3H
d^4	$L=6$	$\Gamma_1^s + \Gamma_2 + \Gamma_3$	^1I
d^4	$L=7$	Γ_3	$-$
d^4	$L=8$	Γ_1^s	$-$
f^4	$L=0$	$2\Gamma_1^s + \Gamma_1^a + 3\Gamma_3$	^5S
f^4	$L=1$	$2\Gamma_2 + 3\Gamma_3 + 3\Gamma_{3'}$	$^1P,\ ^1P,\ ^3P,\ ^3P,\ ^3P$
f^4	$L=2$	$2\Gamma_1^s + \Gamma_1^a + 4\Gamma_2 + 3\Gamma_3 + 2\Gamma_{3'}$	$^1D,\ ^1D,\ ^1D,\ ^1D,\ ^3D,\ ^3D,\ ^5D$
f^4	$L=3$	$\Gamma_1^s + \Gamma_1^a + \Gamma_2 + 5\Gamma_3 + 4\Gamma_{3'}$	$^1F,\ ^3F,\ ^3F,\ ^3F,\ ^3F,\ ^5F$
f^4	$L=4$	$3\Gamma_1^s + \Gamma_1^a + 4\Gamma_2 + 4\Gamma_3 + 3\Gamma_{3'}$	$^1G,\ ^1G,\ ^1G,\ ^1G,\ ^3G,\ ^3G,\ ^3G,\ ^5G$
f^4	$L=5$	$\Gamma_1^s + 2\Gamma_2 + 5\Gamma_3 + 4\Gamma_{3'}$	$^1H,\ ^1H,\ ^3H,\ ^3H,\ ^3H$
f^4	$L=6$	$3\Gamma_1^s + \Gamma_1^a + 3\Gamma_2 + 4\Gamma_3 + 2\Gamma_{3'}$	$^1I,\ ^1I,\ ^1I,\ ^3I,\ ^3I,\ ^5I$
f^4	$L=7$	$\Gamma_1^s + \Gamma_2 + 4\Gamma_3 + 2\Gamma_{3'}$	$^1J,\ ^3J,\ ^3J$
f^4	$L=8$	$2\Gamma_1^s + 2\Gamma_2 + 2\Gamma_3 + \Gamma_{3'}$	$^1K,\ ^1K,\ ^3K$
f^4	$L=9$	$\Gamma_1^s + 2\Gamma_3 + \Gamma_{3'}$	^3L
f^4	$L=10$	$\Gamma_1^s + \Gamma_2 + \Gamma_3$	^1M
f^4	$L=11$	Γ_3	$-$
f^4	$L=12$	Γ_1^s	$-$

[a] The symmetries of the irreducible representations of the permutation group $P(4)$ label the various spin and orbital angular momentum states. To obtain the states allowed by the Pauli Principle the direct product of the symmetries between the orbital and spin states must contain Γ_1^a

state is formed from a configuration $(\alpha_1\alpha_2\beta_3\beta_4)$ with $M_S = 0$ which from the extended character Table 17.5 is of the form $(\psi_1\psi_1\psi_2\psi_2)$ and transforms as $\Gamma_1^s + \Gamma_2 + \Gamma_3$. Upon subtraction of the symmetry types for the $S = 1$ and $S = 2$ states $(\Gamma_3 + \Gamma_1^s)$, we obtain the symmetry Γ_2 for the $S = 0$ state, as shown in Table 17.6. This completes the discussion for the spin entries to Table 17.6.

The allowed states resulting from the s^4, $1s^32s$ and $1s^22s^2$ orbital states follow from the discussion in Sect. 17.4.2. Some similarity is also found for the sp^3 states in Table 17.6. We now illustrate the four-electron problem with the p^4 electron configuration, assuming the same principal quantum number for all four electrons as for example in a $(2p^4)$ state. Here we can have $L = 4, 3, 2, 1$ and 0 (see Table 17.6). Starting with the $L = 4$ multiplet, the $M_L = 4$ state $p^+p^+p^+p^+$ would have Γ_1^s symmetry. This state is forbidden by the Pauli principle since the direct product of the orbital and spin states $\Gamma_1^s \otimes (\Gamma_1^s + \Gamma_2 + \Gamma_3)$ does not contain Γ_1^a symmetry. To find the symmetry for the $L = 3$ multiplet, we consider the $M_L = 3$ states which arise from a $p^+p^+p^+p^0$ configuration and from Table 17.5 (giving the character table for $P(4)$), we see that $(\psi_1\psi_1\psi_1\psi_2)$ contains the irreducible representations $\Gamma_1^s + \Gamma_3$. Thus subtracting Γ_1^s for the $L = 4$ state gives the symmetry Γ_3 for the $L = 3$ multiplet. The direct product of the orbital and spin states

$$\Gamma_3 \otimes (\Gamma_1^s + \Gamma_2 + \Gamma_3) = \Gamma_1^s + \Gamma_2 + 3\Gamma_3 + 2\Gamma_{3'}$$

again does not contain Γ_1^a and therefore is not allowed by the Pauli principle. However the $L = 2$ state is allowed and gives rise to a ^1D level since $M_L = 2$ arises from $p^+p^+p^0p^0$ or $p^+p^+p^+p^-$ which, respectively, correspond to the symmetries

$$(\Gamma_1^s + \Gamma_2 + \Gamma_3) + (\Gamma_1^s + \Gamma_3).$$

Thus subtracting the contributions of $M_L = 2$ to the $L = 3$ and $L = 4$ states gives $(\Gamma_1^a + \Gamma_2 + \Gamma_3)$. Now taking the direct product between the orbital and spin states

$$(\Gamma_1^s + \Gamma_2 + \Gamma_3) \otimes (\Gamma_1^s + \Gamma_2 + \Gamma_3) = 3\Gamma_1^s + \Gamma_1^a + 4\Gamma_2 + 5\Gamma_3 + 3\Gamma_{3'}$$

does contain the Γ_1^a symmetry arising from the direct product of $\Gamma_2 \otimes \Gamma_2$ and corresponding to the $S = 0$ spin state which is a singlet state. Likewise the symmetries of the ^3P and ^1S states for $L = 1$ and $L = 0$, respectively, can be found, and the results are given in Table 17.6. Since a p^4 electron configuration is equivalent to a p^2 hole configuration the allowed states for p^4 should be the same as for p^2. This can be verified by comparing the allowed states for p^2 in Table 17.2 with those $(^1S, \, ^3P, \, ^1D)$ for p^4 in Table 17.6.

It is left to the reader to verify the other entries in Table 17.6 and to explore the symmetries of other four-electron combinations not listed. In finding these entries it should be noted that

$$\Gamma_2 \otimes \Gamma_2 = \Gamma_1^s + \Gamma_1^a + \Gamma_2$$

and

$$\Gamma_3 \otimes \Gamma_{3'} = \Gamma_1^a + \Gamma_2 + \Gamma_3 + \Gamma_{3'}$$

so that the spatial functions with Γ_1^a, Γ_2 and $\Gamma_{3'}$ all can give rise to states allowed by the Pauli principle.

17.4.4 Five-Electron States

The character table for the permutation group of five electrons is shown in Table F.3 of Appendix F. Note that there are no 2D or 3D irreducible representations, but rather there are four, five and six-dimensional irreducible representations, yielding $h = \sum l_i^2 = 120 = 5!$, as required. Also listed in Table F.3 of Appendix F are the characters for all possible distinct products of five functions considered within the equivalence representation. The irreducible representations of $P(5)$ contained in the decomposition of the reducible equivalence representation $\Gamma_{\mathrm{perm.}}$ are listed below the character table for $P(5)$ (Table F.3 of Appendix F). With the help of these tables, the entries in Table 17.7 can be obtained for the spin and orbital symmetries for a number of the five-electron states that are listed in this table. The possible spin states are $S = 1/2$ which occurs ten times, the $S = 3/2$ which occurs five times and the $S = 5/2$ which occurs once. In making the antisymmetric combinations it should be noted that

$$\Gamma_4 \otimes \Gamma_{4'} = \Gamma_1^a + \Gamma_{4'} + \Gamma_{5'} + \Gamma_6 \quad \text{and}$$

$$\Gamma_5 \otimes \Gamma_{5'} = \Gamma_1^a + \Gamma_4 + \Gamma_{4'} + \Gamma_5 + \Gamma_{5'} + \Gamma_6 \,,$$

so that the spatial functions with Γ_1^a, $\Gamma_{4'}$ and $\Gamma_{5'}$ may all give rise to states that are allowed by the Pauli Principle. Five-electron states occur in a half-filled d level. Such half-filled d levels are important in describing the magnetic ions in magnetic semiconductors formed by the substitution of Mn^{2+} for Cd in CdTe or CdSe.

17.4.5 General Comments on Many-Electron States

The Pauli-allowed states for n electrons in a more than half filled p shell and for $6 - n$ holes are the same. For example, referring to Table 17.7, the only Pauli-allowed state for p^5 is an $L = 1$, ^2P state. But this state corresponds to a single hole in a p-shell, which has the same allowed angular momentum states as a single p electron ($S = 1/2$) in a p-shell. We can denote both of these states by p^1 corresponding to the level designation ^2P. Using the same arguments, we find that p^2 and p^4 have the same allowed states. Similarly, the states for the d^6 electron configuration are identical to those for the d^4 hole configuration which are worked out in the

Table 17.7. Transformation properties of five-electron states under permutations[a]

configuration	state	irreducible representation	allowed state
$(\uparrow\uparrow\uparrow\downarrow\downarrow)$	$S = 1/2$	Γ_5	
$(\uparrow\uparrow\uparrow\uparrow\downarrow)$	$S = 3/2$	Γ_4	
$(\uparrow\uparrow\uparrow\uparrow\uparrow)$	$S = 5/2$	Γ_1^s	
s^5	$L = 0$	Γ_1^s	$-$
$1s^42s$	$L = 0$	$\Gamma_1^s + \Gamma_4$	$-$
$1s^22s^23s$	$L = 0$	$\Gamma_1^s + 2\Gamma_4 + 2\Gamma_5 + \Gamma_{5'} + \Gamma_6$	^2S
p^5	$L = 0$	Γ_6	$-$
p^5	$L = 1$	$\Gamma_1^s + \Gamma_4 + \Gamma_5 + \Gamma_{5'}$	^2P
p^5	$L = 2$	$\Gamma_4 + \Gamma_5 + \Gamma_6$	$-$
p^5	$L = 3$	$\Gamma_1^s + \Gamma_4 + \Gamma_5$	$-$
p^5	$L = 4$	Γ_4	$-$
p^5	$L = 5$	Γ_1^s	$-$
d^5	$L = 0$	$\Gamma_1^a + \Gamma_4 + \Gamma_{5'} + \Gamma_6$	$^2S, {}^6S$
d^5	$L = 1$	$\Gamma_1^s + 2\Gamma_4 + \Gamma_{4'} + 3\Gamma_5 + \Gamma_{5'} + 2\Gamma_6$	$^2P, {}^4P$
d^5	$L = 2$	$2\Gamma_1^s + 3\Gamma_4 + \Gamma_{4'} + 4\Gamma_5 + 3\Gamma_{5'} + 2\Gamma_6$	$^2D, {}^2D, {}^2D, {}^4D$
d^5	$L = 3$	$\Gamma_1^s + 4\Gamma_4 + \Gamma_{4'} + 3\Gamma_5 + 2\Gamma_{5'} + 4\Gamma_6$	$^2F, {}^2F, {}^4F$
d^5	$L = 4$	$2\Gamma_1^s + 4\Gamma_4 + \Gamma_{4'} + 4\Gamma_5 + 2\Gamma_{5'} + 2\Gamma_6$	$^2G, {}^2G, {}^4G$
d^5	$L = 5$	$\Gamma_1^s + 3\Gamma_4 + 3\Gamma_5 + \Gamma_{5'} + 3\Gamma_6$	^2H
d^5	$L = 6$	$2\Gamma_1^s + 3\Gamma_4 + 2\Gamma_5 + \Gamma_{5'} + \Gamma_6$	^2I
d^5	$L = 7$	$\Gamma_1^s + 2\Gamma_4 + \Gamma_5 + \Gamma_6$	$-$
d^5	$L = 8$	$\Gamma_1^s + \Gamma_4 + \Gamma_5$	$-$
d^5	$L = 9$	Γ_4	$-$
d^5	$L = 10$	Γ_1^s	$-$

[a] The symmetries of the irreducible representations of the permutation group $P(5)$ label the various spin and orbital angular momentum states. To obtain the states allowed by the Pauli Principle the direct product of the symmetries between the orbital and spin states must contain Γ_1^a

Table 17.6, etc. In this sense, the tables that are provided in this chapter are sufficient to handle all atomic s, p and d levels. To treat the f levels completely we would need to construct tables for the permutation groups $P(6)$ and $P(7)$, and the character tables for $P(6)$ and $P(7)$ are found in Appendix F.

In solids and molecules where point group symmetry rather than full rotational symmetry applies, the application of permutation groups to the many-electron states is identical. Thus the $3d$ levels of a transition metal ion in a crystal field of cubic symmetry are split into a E_g and a T_{2g} level (see Sect. 5.3) and the allowed d^2 levels would be either a ^1E_g or a $^1T_{2g}$,

$^3T_{2g}$ level. In general, crystal field splittings are applied to the many-electron states whose symmetries are given in Tables 17.2, 17.4, 17.6 and 17.7. The d states in icosahedral symmetry do not experience any crystal field splitting and all the arguments of this chapter apply directly. Character tables for the groups $P(3)$, $P(4)$, $P(5)$, $P(6)$ and $P(7)$ are found in Appendix F.

Selected Problems

17.1. Use the following character table for the permutation group $P(5)$ given in Table F.3.

(a) Using (17.10) find the number of symmetry elements in each of the classes for the permutation group $P(5)$, and check the entries to Table F.3.
(b) What are the characters for the equivalence transformation for a state where three of the five electrons are in one state (e.g., a d-state) and two electrons are in another state (e.g., a p-state)? Explain how you obtained your result. What irreducible representations are contained in this equivalence transformation (see Table F.3)?
(c) Multiply element

$$P_i = \begin{pmatrix} 1\ 2\ 3\ 4\ 5 \\ 3\ 2\ 1\ 4\ 5 \end{pmatrix}$$

by element

$$P_j = \begin{pmatrix} 1\ 2\ 3\ 4\ 5 \\ 4\ 2\ 5\ 1\ 3 \end{pmatrix}$$

to form P_iP_j and P_jP_i. Are your results consistent with the character table?
(c) Referring to Table 17.7, what are the irreducible representations for the spin configuration ($\uparrow\uparrow\downarrow\downarrow$)? How did you obtain this result?
(e) What are the Pauli allowed states (as would be given in Table 17.7) with the largest L value for the p^3d^2 configuration? Note that this calculation would make a new entry to Table 17.7.

17.2. (a) Consider the addition of Mn^{2+} as a substitutional magnetic impurity for CdTe. Since Mn^{2+} has five $3d$ electrons, use the permutation group $P(5)$ to find the Pauli-allowed states for the Mn^{2+} ion in CdTe (Table F.3 in Appendix F). Of these Pauli-allowed d^5 states, which is the ground state based on Hund's rule?
(b) Using the electric dipole selection rule for optical transitions, find the allowed transitions from the ground state in (a) to Pauli-allowed states in the $3d^34p^2$ configuration (see Problem 17.1(e)).

17.3. Use the character table for the permutation group $P(6)$ (Table F.4 in Appendix F).

(a) Starting with $q = 6$ objects, show that there are 11 classes of the form given in the character table for $P(6)$ (see Sect. 17.2). Show that all 6! symmetry elements are contained in these classes.

(b) Show that there are 45 symmetry elements in the class $(2^2, 1^2)$ and 40 symmetry elements in class $(3, 1^3)$.

(c) Show that the irreducible representations Γ_5''' and Γ_9 as given in the character table are orthogonal. (This is a check that the entries in the character table in Table F.4 are correct.) Which of the four five-dimensional irreducible representations correspond to the basis functions $\Psi_{\Gamma_{n-1}}'$ in (17.19)?

(d) What are the irreducible representations in $P(6)$ that represent the spin angular momentum states $S = 3, 2, 1, 0$? To solve this problem, you will have to find the equivalence transformations corresponding to selected permutations of spin configurations that are needed to construct the various spin angular momentum states (see Tables F.3 and F.4 for the permutation group $P(5)$ to provide guidance for solving this problem for $P(6)$).

(e) According to Hund's rule, what are the S, L and J values for placing six electrons in a d^6 electronic configuration. To which irreducible representations of $P(6)$ do the spin and spatial parts of this Hund's rule ground state correspond?

17.4. In this chapter, we considered multielectron occupation of atomic states. Consider both the case of no spin–orbit interaction and of including the spin–orbit interaction for the following cases.

(a) What is the effect of time inversion on two $1s$ electrons in an atomic state? What is the effect of time inversion symmetry on two $2p$ electrons?

(b) What is the effect of time inversion symmetry on three $2p$ electrons?