

# Atoms and Molecules

MITCHEL WEISSBLUTH

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Mitchel Weissbluth

*Department of Applied Physics  
Stanford University  
Stanford, California*



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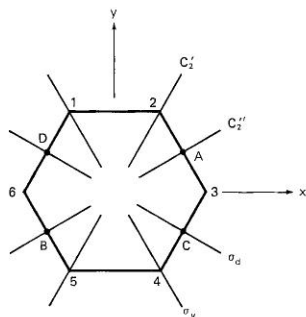
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FIG. 5.2 Coordinate system and symmetry axes for the group  $D_{6h}$ 

### 5.4 Permutation Groups $S_n$ —Young Diagrams

A permutation (also called symmetric) group  $S_n$  consists of the  $n!$  permutations on a set of  $n$  symbols. We devote this section to a summary of selected properties of permutation groups that have relevance to quantum mechanical applications.

Let

$$P = \begin{pmatrix} a_1 & a_2 & a_3 \\ a_2 & a_3 & a_1 \end{pmatrix} \equiv \begin{pmatrix} 1 & 2 & 3 \\ 2 & 3 & 1 \end{pmatrix} \equiv (1 \ 2 \ 3) \quad (5.4-1)$$

represent a permutation in which the sequence  $a_1 a_2 a_3$  is permuted into the sequence  $a_2 a_3 a_1$ . Specifically we interpret the symbol in (5.4-1) to mean

$$\begin{aligned} 1 &\text{ is replaced by } 2 \text{ or } 1 \rightarrow 2, \\ 2 &\text{ is replaced by } 3 \text{ or } 2 \rightarrow 3, \\ 3 &\text{ is replaced by } 1 \text{ or } 3 \rightarrow 1. \end{aligned}$$

It is also useful to think of  $(1 \ 2 \ 3)$  as an operator:

$$(1 \ 2 \ 3)1 = 2, \quad (1 \ 2 \ 3)2 = 3, \quad (1 \ 2 \ 3)3 = 1. \quad (5.4-2)$$

In the form  $(1 \ 2 \ 3)$ ,  $P$  is represented by a *cycle* which may also be written as  $(2 \ 3 \ 1)$  or  $(3 \ 1 \ 2)$ . Hence the order in which the columns are written in the double-rowed parentheses is immaterial. Thus

$$\begin{pmatrix} 1 & 2 & 3 \\ 2 & 3 & 1 \end{pmatrix} = \begin{pmatrix} 2 & 3 & 1 \\ 3 & 1 & 2 \end{pmatrix} = \begin{pmatrix} 3 & 1 & 2 \\ 1 & 2 & 3 \end{pmatrix}.$$

Every permutation of a finite set of elements can be written as a product of cycles with no common elements. For example,

$$\begin{pmatrix} 1 & 2 & 3 & 4 \\ 2 & 3 & 1 & 4 \end{pmatrix} = (1 \ 2 \ 3)(4) = (4)(1 \ 2 \ 3) = (1 \ 2 \ 3),$$

$$\begin{pmatrix} 1 & 2 & 3 & 4 & 5 \\ 2 & 4 & 5 & 1 & 3 \end{pmatrix} = (1 \ 2 \ 4)(3 \ 5) = (3 \ 5)(1 \ 2 \ 4),$$

where a product like  $(1 \ 2 \ 4)(3 \ 5)$  has the meaning

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

Let

$$P_a = \begin{pmatrix} 1 & 2 & 3 & 4 \\ 2 & 4 & 3 & 1 \end{pmatrix}, \quad P_b = \begin{pmatrix} 1 & 2 & 3 & 4 \\ 1 & 4 & 3 & 2 \end{pmatrix}.$$

The product  $P_a P_b = P_c$  is given by

$$\begin{aligned} P_c &= \begin{pmatrix} 1 & 2 & 3 & 4 \\ 2 & 4 & 3 & 1 \end{pmatrix} \begin{pmatrix} 1 & 2 & 3 & 4 \\ 1 & 4 & 3 & 2 \end{pmatrix} \\ &= \begin{pmatrix} 1 & 4 & 3 & 2 \\ 2 & 1 & 3 & 4 \end{pmatrix} \begin{pmatrix} 1 & 2 & 3 & 4 \\ 1 & 4 & 3 & 2 \end{pmatrix} = \begin{pmatrix} 1 & 2 & 3 & 4 \\ 2 & 1 & 3 & 4 \end{pmatrix}. \end{aligned} \quad (5.4-3)$$

It is important to note that  $P_a P_b$  means that the permutation  $P_a$  is performed *after*  $P_b$  in agreement with the standard convention for operator products. This means that the permutations proceed from right to left as, for example, in (5.4-3), where 2 is replaced by 4 (in  $P_b$ ) and 4 is replaced by 1 (in  $P_a$ ) giving a net change whereby 2 is replaced by 1 as in  $P_c$ .

A cycle containing two symbols is called a *transposition*. Any cycle can be written as a product of transpositions

$$(1 \ 2 \ \cdots \ n) = (1 \ n) \cdots (1 \ 3)(1 \ 2) \quad (5.4-4a)$$

or, alternatively,

$$(1 \ 2 \ \cdots \ n) = (1 \ 2)(2 \ 3) \cdots (n-1 \ n). \quad (5.4-4b)$$

Thus

$$\begin{aligned} (1 \ 2 \ 3) &= (1 \ 3)(1 \ 2), \\ &= (1 \ 2)(2 \ 3), \end{aligned}$$

which means (remembering to go from right to left) that

$$\begin{pmatrix} 1 & 2 & 3 \\ 2 & 3 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 3 \\ 3 & 1 \end{pmatrix} \begin{pmatrix} 1 & 2 \\ 2 & 1 \end{pmatrix}.$$

Cycles without common elements commute; if they have an element in common, they generally do not commute as is evident from (5.4-4).

Since permutations can be decomposed into cycles and the latter into transpositions, any permutation can be written as a product of transpositions. If the number of transpositions is even (odd), the *parity*  $p$  of the permutation  $P$  is said to be even (odd).

Consider the group  $S_3$  with six elements labeled as:

$$\begin{aligned} E &= \begin{pmatrix} 1 & 2 & 3 \\ 1 & 2 & 3 \end{pmatrix}, & A &= \begin{pmatrix} 1 & 2 & 3 \\ 1 & 3 & 2 \end{pmatrix}, & B &= \begin{pmatrix} 1 & 2 & 3 \\ 3 & 2 & 1 \end{pmatrix}, \\ C &= \begin{pmatrix} 1 & 2 & 3 \\ 2 & 1 & 3 \end{pmatrix}, & D &= \begin{pmatrix} 1 & 2 & 3 \\ 2 & 3 & 1 \end{pmatrix}, & F &= \begin{pmatrix} 1 & 2 & 3 \\ 3 & 1 & 2 \end{pmatrix}. \end{aligned} \quad (5.4-5)$$

The product  $BC$ , for example, is given by

$$BC = \begin{pmatrix} 1 & 2 & 3 \\ 3 & 2 & 1 \end{pmatrix} \begin{pmatrix} 1 & 2 & 3 \\ 2 & 1 & 3 \end{pmatrix} = \begin{pmatrix} 1 & 2 & 3 \\ 2 & 3 & 1 \end{pmatrix} = D. \quad (5.4-6)$$

If we take all possible pairs of permutations and organize them into a table, the result is just Table 3.1 which, we saw in Section 3.1, was the multiplication table for the group  $D_3$ . The set of permutations (5.4-5) therefore constitutes a group—specifically, the group  $S_3$  which is isomorphic to  $D_3$ . In the same fashion it may be shown that  $S_2$  is isomorphic to  $C_i$  and  $S_4$  to  $O$ , etc. These are just a few examples of *Cayley's Theorem* which states that every finite group of order  $n$  is isomorphic with a subgroup of  $S_n$ .

If an integer  $n$  is split up into a sum of integers according to the scheme

$$\lambda_1 + \lambda_2 + \cdots + \lambda_h = n, \quad \lambda_1 \geq \lambda_2 \geq \cdots \geq \lambda_h, \quad (5.4-7)$$

we call this a *partition*  $[\lambda_1, \lambda_2, \dots, \lambda_h]$ . The partitions of  $n = 2, 3, 4$  are

$$\begin{aligned} n = 2: & [2], [1, 1] \equiv [1^2], \\ n = 3: & [3], [2, 1], [1, 1, 1] \equiv [1^3], \\ n = 4: & [4], [3, 1], [2, 2] \equiv [2^2], [2, 1, 1] \equiv [2, 1^2], [1, 1, 1, 1] \equiv [1^4]. \end{aligned} \quad (5.4-8)$$

Every partition may be represented by a *Young diagram* which consists of an arrangement of  $n$  cells in  $h$  rows; each row begins with the same vertical line and the number of cells in successive rows is  $\lambda_1, \lambda_2, \dots, \lambda_h$ . For  $n = 2, 3$ , and 4 the Young diagrams are:

$n = 2$ :

$$[2] \begin{array}{|c|c|} \hline \square & \square \\ \hline \end{array} \quad [1^2] \begin{array}{|c|} \hline \square \\ \hline \square \\ \hline \end{array} \quad (5.4-9)$$

$n = 3$ :

$$\begin{array}{ccc}
 [3] \begin{array}{|c|c|c|} \hline & & \\ \hline \end{array} &
 [21] \begin{array}{|c|c|} \hline & \\ \hline \square & \\ \hline \end{array} &
 [1^3] \begin{array}{|c|} \hline \\ \hline \square \\ \hline \square \\ \hline \end{array}
 \end{array} \quad (5.4-10)$$

 $n = 4$ :

$$\begin{array}{ccc}
 [4] \begin{array}{|c|c|c|c|} \hline & & & \\ \hline \end{array} &
 [31] \begin{array}{|c|c|c|} \hline & & \\ \hline \square & & \\ \hline \end{array} &
 [22] \begin{array}{|c|c|} \hline & \\ \hline \square & \square \\ \hline \end{array} \\
 & & \\
 [21^2] \begin{array}{|c|c|} \hline & \\ \hline \square & \\ \hline \square & \\ \hline \end{array} &
 [1^4] \begin{array}{|c|} \hline \\ \hline \square \\ \hline \square \\ \hline \square \\ \hline \square \\ \hline \end{array}
 \end{array} \quad (5.4-11)$$

Each partition defines a class of  $S_n$ . Therefore the number of irreducible representations of  $S_n$  is equal to the number of partitions (or Young diagrams). Thus  $S_2$ ,  $S_3$ , and  $S_4$  have 2, 3, and 5 irreducible representations, respectively.

We may also obtain the dimensions of the irreducible representations by the following method: When the squares are numbered with the  $n$  integers we call the resulting pattern a *Young tableau*. If the numbers increase on going down a column and also from left to right along rows, the tableau is called a standard tableau. For  $S_2$ ,  $S_3$ , and  $S_4$  the standard tableaux are

 $S_2$ :

$$\begin{array}{c}
 [2] \begin{array}{|c|c|} \hline 1 & 2 \\ \hline \end{array} \\
 [1^2] \begin{array}{|c|} \hline 1 \\ \hline 2 \\ \hline \end{array}
 \end{array} \quad (5.4-12)$$

 $S_3$ :

$$\begin{array}{c}
 [3] \begin{array}{|c|c|c|} \hline 1 & 2 & 3 \\ \hline \end{array} \\
 [21] \begin{array}{|c|c|} \hline 1 & 2 \\ \hline 3 & \end{array} \quad \begin{array}{|c|} \hline 1 \\ \hline 3 \\ \hline 2 \\ \hline \end{array} \\
 [1^3] \begin{array}{|c|} \hline 1 \\ \hline 2 \\ \hline 3 \\ \hline \end{array}
 \end{array} \quad (5.4-13)$$

$S_4$ :

$$\begin{array}{l}
 [4] \begin{array}{|c|c|c|c|} \hline 1 & 2 & 3 & 4 \\ \hline \end{array} \\
 [31] \begin{array}{|c|c|c|} \hline 1 & 2 & 3 \\ \hline 4 \\ \hline \end{array} \quad \begin{array}{|c|c|c|} \hline 1 & 3 & 4 \\ \hline 2 \\ \hline \end{array} \quad \begin{array}{|c|c|c|} \hline 1 & 2 & 4 \\ \hline 3 \\ \hline \end{array} \\
 [2^2] \begin{array}{|c|c|} \hline 1 & 2 \\ \hline 3 & 4 \\ \hline \end{array} \quad \begin{array}{|c|c|} \hline 1 & 3 \\ \hline 2 & 4 \\ \hline \end{array} \\
 [21^2] \begin{array}{|c|c|} \hline 1 & 2 \\ \hline 3 & 4 \\ \hline \end{array} \quad \begin{array}{|c|c|} \hline 1 & 3 \\ \hline 2 & 4 \\ \hline \end{array} \quad \begin{array}{|c|c|} \hline 1 & 4 \\ \hline 2 & 3 \\ \hline \end{array} \\
 [1^4] \begin{array}{|c|} \hline 1 \\ \hline 2 \\ \hline 3 \\ \hline 4 \\ \hline \end{array}
 \end{array} \tag{5.4-14}$$

Tableaux that are related to one another by an interchange of rows and columns are said to be *adjoint* as, for example, the pair

$$\begin{array}{|c|c|} \hline 1 & 2 \\ \hline 3 \\ \hline \end{array} \quad \begin{array}{|c|c|} \hline 1 & 3 \\ \hline 2 \\ \hline \end{array}$$

or

$$\begin{array}{|c|c|c|} \hline 1 & 2 & 3 \\ \hline 4 \\ \hline \end{array} \quad \begin{array}{|c|c|} \hline 1 & 4 \\ \hline 2 \\ \hline 3 \\ \hline \end{array}$$

(5.4-15)

The importance of the standard tableaux lies in the fact that the dimension of an irreducible representation of  $S_n$  is equal to the number of standard tableaux that can be constructed from the corresponding partition. Hence we may now draw the following conclusions concerning the dimensions of the irreducible representations in  $S_2$ ,  $S_3$ , and  $S_4$ :

- $S_2$  two one-dimensional representations associated with  $[2]$  and  $[1^2]$ , respectively,
- $S_3$  two one-dimensional representations associated with  $[3]$  and  $[1^3]$ , respectively,  
one two-dimensional representation associated with  $[21]$ ,
- $S_4$  two one-dimensional representations associated with  $[4]$  and  $[1^4]$ , respectively,  
one two-dimensional representation associated with  $[2^2]$ ,  
two three-dimensional representations associated with  $[31]$  and  $[21^2]$ , respectively.



Each of these groups has two one-dimensional representations. This is a general property of the groups  $S_n$  in which the partitions  $[n]$  and  $[1^n]$  are associated with one-dimensional representations. All other irreducible representations of  $S_n$  are of dimension greater than one.

Basis functions for the irreducible representations of  $S_n$  can be constructed with the help of certain operators which we now define. Corresponding to any standard tableau let  $P$  be a permutation which interchanges numbers in one row. Such a permutation will be called a *horizontal permutation*. Similarly, a *vertical permutation*  $Q$  interchanges numbers in one column. Also, let

$$S = \sum_P P, \quad (5.4-16)$$

$$A = \sum_Q (-1)^q Q. \quad (5.4-17)$$

The sum in (5.4-16) is over all horizontal permutations;  $S$  is then the *symmetrizing* operator with respect to the rows of a Young tableau. With  $q$  the parity of the permutation  $Q$ ,  $A$  is the *antisymmetrizing* operator with respect to the columns. The product

$$Y = AS \quad (5.4-18)$$

is known as a *Young operator*.

To construct basis functions for an irreducible representation with which a particular partition is associated it is first necessary to construct Young operators corresponding to all the standard tableaux for that partition. Each Young operator acting on a function  $f(\chi_1, \chi_2, \dots, \chi_n)$  projects a basis function for the irreducible representation associated with that particular tableau. For the partitions  $[n]$  and  $[1^n]$  corresponding to one-dimensional representations the Young operator  $Y$  reduces to  $S$  and  $A$ , respectively. Therefore, in the former case, the basis function is totally symmetric (remains unaltered on interchange of any two indices) and the representation is said to be totally symmetric; in the latter case the basis function is totally antisymmetric (changes sign upon an interchange of any two indices) and the representation is said to be antisymmetric.

A few examples will help to clarify the method. Let  $n = 2$  and let

$$f(\chi_1, \chi_2) = a(\chi_1)b(\chi_2) \equiv a_1b_2.$$

For the tableau  $\begin{smallmatrix} 1 & 2 \end{smallmatrix}$  there is only one row; we therefore expect to find a symmetric basis function

$$f_S^{(2)} = Ya_1b_2 = ASa_1b_2 = Sa_1b_2 = \sum_P Pa_1b_2 = a_1b_2 + a_2b_1 \quad (5.4-19)$$

and for the tableau  $\begin{smallmatrix} 1 \\ 2 \end{smallmatrix}$  with just one column there is an antisymmetric basis function

$$f_A^{(2)} = Ya_1b_2 = ASa_1b_2 = Aa_1b_2 = \sum_Q (-1)^q Qa_1b_2 = a_1b_2 - a_2b_1 = \begin{vmatrix} a_1 & b_1 \\ a_2 & b_2 \end{vmatrix}. \quad (5.4-20)$$

Now let  $n = 3$  and let

$$f(\chi_1, \chi_2, \chi_3) = a(\chi_1)b(\chi_2)c(\chi_3) \equiv a_1b_2c_3. \quad (5.4-21)$$

For the one-dimensional representations we have

$$\begin{aligned} [1 \ 2 \ 3]: \quad f_S^{(3)} &= Ya_1b_2c_3 = Sa_1b_2c_3 = \sum_P Pa_1b_2c_3 \\ &= a_1b_2c_3 + a_1b_3c_2 + a_2b_1c_3 + a_2b_3c_1 + a_3b_1c_2 + a_3b_2c_1. \end{aligned} \quad (5.4-22)$$

$$\begin{aligned} \begin{smallmatrix} 1 \\ 2 \\ 3 \end{smallmatrix}: \quad f_A^{(3)} &= Ya_1b_2c_3 = Aa_1b_2c_3 = \sum_Q (-1)^q Qa_1b_2c_3 \\ &= a_1b_2c_3 - a_1b_3c_2 - a_2b_1c_3 + a_2b_3c_1 \\ &\quad + a_3b_1c_2 - a_3b_2c_1 \\ &= \begin{vmatrix} a_1 & b_1 & c_1 \\ a_2 & b_2 & c_2 \\ a_3 & b_3 & c_3 \end{vmatrix}. \end{aligned} \quad (5.4-23)$$

Proceeding to the two-dimensional representation we consider the tableau

$$\begin{smallmatrix} 1 & 2 \\ 3 \end{smallmatrix}$$

In this case

$$Ya_1b_2c_3 = ASa_1b_2c_3$$

where  $S$  is the symmetrization operator with respect to indices 1, 2 and  $A$  the antisymmetrization operator with respect to indices 1, 3. This gives

$$\begin{aligned} Sa_1b_2c_3 &= a_1b_2c_3 + a_2b_1c_3, \\ ASa_1b_2c_3 &= A(a_1b_2c_3 + a_2b_1c_3) \\ &= a_1b_2c_3 - a_3b_2c_1 + a_2b_1c_3 - a_2b_3c_1 \equiv f_1^{(3)}. \end{aligned} \quad (5.4-24)$$

Finally we have the tableau

1	3
2	

for which

$$\begin{aligned}
 Ya_1b_2c_3 &= ASa_1b_2c_3 = A(a_1b_2c_3 + a_3b_2c_1) \\
 &= a_1b_2c_3 - a_2b_1c_3 + a_3b_2c_1 - a_3b_1c_2 \equiv f_2^{(3)}. \quad (5.4-25)
 \end{aligned}$$

The two functions  $f_1^{(3)}$  and  $f_2^{(3)}$  are basis functions for the two-dimensional irreducible representation of  $S_3$ .

are indistinguishable, they may be permuted without affecting the distribution; thus  $(1^+ 0^+ 1^-)$ ,  $(0^+ 1^- 1^+)$ ,  $(1^+ 1^- 0^+)$ , etc., correspond to the same distribution. Also since

$$M_L = \sum_i m_i; \quad M_S = \sum_i m_{s_i} \quad (20.2-4)$$

a distribution like  $(1^+ 0^+ 1^-)$  has associated with it the values  $M_L = 2$ ,  $M_S = \frac{1}{2}$ .

The number of independent distributions of three (indistinguishable) electrons in six orbitals is

$$\frac{6 \times 5 \times 4}{3!} = 20.$$

These may be identified and grouped according to their respective values of  $M_L$  and  $M_S$  as is done in Table 20.4. In fact, the distributions per se are not needed—all that is needed is the number of distributions for each set of values  $(M_L, M_S)$ . Moreover, the number of distributions is the same for  $M_L$  and  $-M_L$  as well as for  $M_S$  and  $-M_S$ . The tabulation may therefore be simplified as shown in the upper part of Table 20.5. Starting with the highest value of  $M_L$ , it is apparent that the entry for  $M_L = 2$ ,  $M_S = \frac{1}{2}$  in Table 20.5—which corresponds to the four entries for  $M_L = \pm 2$ ,  $M_S = \pm \frac{1}{2}$  in Table 20.4—belongs to a  ${}^2D$  term. But  ${}^2D$  also includes  $M_S = \frac{1}{2}$  for  $M_L = 1, 0$  (corresponding to  $M_S = \pm \frac{1}{2}$  for  $M_L = \pm 1, 0$  in Table 20.4). One then removes the entries belonging to  ${}^2D$  and the remaining tabulation is shown in the middle part of Table 20.5. Repetition of the process yields  ${}^2P$  and finally  ${}^4S$ .

TABLE 20.4

Orbital Distributions for  $p^3$

$M_S \backslash M_L$	2	1	0	-1	-2
$\frac{3}{2}$			$(1^+ 0^+ -1^+)$		
$\frac{1}{2}$	$(1^+ 0^+ 1^-)$	$(1^+ 0^+ 0^-)$ $(1^+ -1^+ 1^-)$	$(1^+ 0^+ -1^-)$ $(1^+ -1^+ 0^-)$ $(0^+ -1^+ 1^-)$	$(1^+ -1^+ -1^-)$ $(0^+ -1^+ 0^-)$	$(0^+ -1^- -1^-)$
$-\frac{1}{2}$	$(1^+ 1^- 0^-)$	$(1^+ 1^- -1^-)$ $(0^+ 1^- 0^-)$	$(1^+ 0^- -1^-)$ $(0^+ 1^- -1^-)$ $(-1^+ 1^- 0^-)$	$(0^+ 0^- -1^-)$ $(-1^+ 1^- -1^-)$	$(-1^+ 0^- -1^-)$
$-\frac{3}{2}$			$(1^- 0^- -1^-)$		

3. The relation between the cfp for shells that are more than half-filled to the cfp for shells that are less than half-filled is

$$\begin{aligned} & \langle l^{4l+1-n}(\alpha' L' S') | L S | \rangle l^{4l+2-n} \alpha L S \rangle \\ &= (-1)^{L+L'+S+S'-l-(1/2)} \sqrt{\frac{(n+1)(2L'+1)(2S'+1)}{(4l+2-n)(2L+1)(2S+1)}} \\ & \times \langle l^n(\alpha L S) | L' S' \rangle l^{n+1} \alpha' L' S' \rangle. \end{aligned} \quad (20.3-18)$$

In the example given previously we coupled a  $p'$  electron to the configuration  $p^2$ . In principle we could have proceeded by coupling a  $p$  electron to the configuration  $pp'$ . But on physical grounds the latter would be less preferable simply because we expect the interaction  $p-p'$  to be weaker than  $p-p$ . However, there are numerous situations where no *a priori* decision as to relative strengths of interaction can be made. The question may then be asked as to the consequences of following one or another coupling scheme. We shall take the configuration  $spd$  (20.2-1) as an example. Altogether there are nine terms:  $^4F$ ,  $^4D$ ,  $^4P$ ,  $^2F(2)$ ,  $^2D(2)$ ,  $^2P(2)$ . Regardless of the order in which the electrons are coupled we will obtain the same set of terms. Thus  $^2F$  comes about from the coupling

$$dp(^3F)s \ ^2F, \quad dp(^1F)s \ ^2F \quad (20.3-19a)$$

or

$$sp(^3P)d \ ^2F, \quad sp(^1P)d \ ^2F \quad (20.3-19b)$$

or

$$sd(^3D)p \ ^2F, \quad sd(^1D)p \ ^2F. \quad (20.3-19c)$$

It is possible to work out the combination of Slater determinants for these six functions and they will all be different. However, it is found that

$$\begin{aligned} |sd(^3D)p \ ^2F\rangle &= -\frac{1}{2}|dp(^3F)s \ ^2F\rangle + \frac{1}{2}\sqrt{3}|dp(^1F)s \ ^2F\rangle, \\ |sd(^1D)p \ ^2F\rangle &= -\frac{1}{2}\sqrt{3}|dp(^3F)s \ ^2F\rangle - \frac{1}{2}|dp(^1F)s \ ^2F\rangle, \end{aligned} \quad (20.3-20)$$

that is, the pair (20.3-19a) and the pair (20.3-19c) are connected by a unitary transformation with similar relations connecting other pairs. The Hamiltonian matrix can be constructed using any pair from among the three. Although the specific matrix elements will depend on which pair is chosen, the eigenvalues will be the same for all three as they must be when different sets of basis functions are related by a unitary transformation.

## 20.4 Symmetry Properties

When the spins of two electrons are coupled, the resulting spin functions are either symmetric ( $S = 1$ ) or antisymmetric ( $S = 0$ ) with respect to an

interchange of the coordinates of the two electrons (Table 20.1). From the standpoint of the permutation group  $S_2$  (Section 5.4), the symmetric functions are associated with the Young tableau

$$\begin{array}{|c|c|} \hline 1 & 2 \\ \hline \end{array}$$

and the antisymmetric functions with the tableau

$$\begin{array}{|c|} \hline 1 \\ \hline 2 \\ \hline \end{array}.$$

To generalize this property we shall suppose that  $\mathbf{J}_1$  and  $\mathbf{J}_2$  are two operators that operate on electrons 1 and 2, respectively, and that

$$J_1^2 \psi_m^j(1) = j(j+1) \psi_m^j(1), \quad J_{1z} \psi_m^j(1) = m \psi_m^j(1), \quad (20.4-1a)$$

$$J_2^2 \psi_m^j(2) = j(j+1) \psi_m^j(2), \quad J_{2z} \psi_m^j(2) = m \psi_m^j(2). \quad (20.4-1b)$$

We shall now couple the angular momenta  $\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2$  and construct the two-electron eigenfunctions as linear combinations of the  $\psi_m^j$  using appropriate coupling coefficients. The resulting functions, regardless of the value of  $j$ , will be either symmetric or antisymmetric as long as only two electrons are being coupled. In other words, the coupled eigenfunctions will be associated with either one of the two tableaux

$$\begin{array}{|c|c|} \hline 1 & 2 \\ \hline \end{array} \quad \begin{array}{|c|} \hline 1 \\ \hline 2 \\ \hline \end{array}.$$

This property has already been illustrated in the case of the spin functions where  $j = s = \frac{1}{2}$ . To give another example, let  $j = 1$ . In that case  $J = 0, 1, 2$  and, with the aid of a table of coupling coefficients, all the eigenfunctions  $|JM\rangle$  may be constructed. For example,

$$|JM\rangle = |00\rangle = \frac{1}{\sqrt{3}} [\psi_1^1(1)\psi_{-1}^1(2) - \psi_0^1(1)\psi_0^1(2) + \psi_{-1}^1(1)\psi_1^1(2)], \quad (20.4-2a)$$

$$|11\rangle = \frac{1}{\sqrt{2}} [\psi_1^1(1)\psi_0^1(2) - \psi_0^1(1)\psi_1^1(2)], \quad (20.4-2b)$$

$$|22\rangle = \psi_1^1(1)\psi_1^1(2). \quad (20.4-2c)$$

It is seen that  $|00\rangle$  and  $|22\rangle$  are symmetric while  $|11\rangle$  is antisymmetric. All the eigenfunctions  $|JM\rangle$  may be classified in this fashion with the result that those belonging to  $J = 0$  and  $2$  are symmetric while those belonging to  $J = 1$  are antisymmetric.

In summary, for two electrons, each with angular momentum  $j$  coupled to form a state with angular momentum  $J$  (which belongs to the irreducible

TABLE 20.9

Permutation Symmetries for Two Electrons

	$j$	$J$
$\square \square$	$\frac{1}{2}, \frac{3}{2}, \dots$ $0, 1, \dots$	$1, 3, 5, \dots, 2j$ $0, 2, 4, \dots, 2j$
$\begin{smallmatrix} \square \\ \square \end{smallmatrix}$	$\frac{1}{2}, \frac{3}{2}, \dots$ $0, 1, \dots$	$0, 2, 4, \dots, 2j-1$ $1, 3, 5, \dots, 2j-1$

representation  $D^{(j)}$  of  $O^+(3)$ , the correspondence between  $J$  and the permutation symmetry (Young tableaux) is shown in Table 20.9.

We call attention to the special case  $|JM\rangle = |00\rangle$  in (20.4-2a) which, for all values of  $j$ , has the form

$$|JM\rangle = |00\rangle = \frac{1}{\sqrt{2j+1}} \sum_{m=-j}^j (-1)^{j-m} \psi_m^j(1) \psi_{-m}^j(2). \quad (20.4-3)$$

This function is symmetric for integral values of  $j$  and antisymmetric for half-integral values.

The Pauli principle requires the total wave function to be antisymmetric. Therefore, the total wave function for two electrons is a product of a symmetric (antisymmetric) spin function and an antisymmetric (symmetric) function of the space coordinates. In terms of the Young tableaux this means that spin functions belonging to one tableau are to be multiplied by spatial functions that belong to the adjoint tableau (with rows and columns interchanged). For more than two electrons the total wave function must also be antisymmetric with respect to an interchange of any two sets of space and spin coordinates. However, the total wave function is generally not factorable into a product of two terms one of which depends only on the space coordinates and the other on the spin coordinates. Instead, as we shall see, there is a more complicated decomposition into functions of spatial and spin coordinates.

In Section 6.5 we saw that product functions of the type

$$\psi_{m_1}^j(1) \psi_{m_2}^j(2) \cdots \psi_{m_r}^j(r) \quad (20.4-4)$$

were components of a Cartesian tensor of rank  $r$  with respect to  $SU(2j+1)$ . Such tensors are bases for representations of  $SU(2j+1)$  but the representations are reducible. It must therefore be possible to find linear combinations of the product functions (20.4-4) that will transform irreducibly under the operations of  $SU(2j+1)$ . To construct such irreducible sets one may use the Young operator for each Young tableau. Since  $O^+(3)$  is a subgroup of

$SU(2j+1)$ , it is expected that functions that transform irreducibly under  $O^+(3)$  will also belong to some irreducible representation of  $SU(2j+1)$ . What this means for a multielectron system is that when the one-electron functions  $\psi_m^j$  are coupled to produce basis functions for  $D^{(j)}$ —the irreducible representations of  $O^+(3)$ —it is possible to subject these functions to the Young operator to produce basis functions for the irreducible representations of  $SU(2j+1)$ . Moreover, since rotations and permutations commute, the functions produced by the Young operator will still be basis functions for  $D^{(j)}$ . Therefore, with each tableau it is possible to associate certain values of  $J$  which arise from the coupling of the one-electron angular momenta.

For  $r=2$  (two particles) these features are already evident in Table 20.9. Let us now consider the case of three particles ( $r=3$ ) with  $j=\frac{1}{2}$ . The possible values of  $J$  are  $\frac{1}{2}$  and  $\frac{3}{2}$ . Using the notation

$$|jm\rangle = |\tfrac{1}{2}\tfrac{1}{2}\rangle = \alpha, \quad |jm\rangle = |\tfrac{1}{2}-\tfrac{1}{2}\rangle = \beta$$

and the abbreviation

$$(\alpha\beta\alpha) = \alpha(1)\beta(2)\alpha(3)$$

we have the following angular momentum eigenfunctions as basis functions for the irreducible representations of  $S_3$ , the permutation group for three particles:

$$\begin{aligned} \boxed{1\ 2\ 3} \quad |JM\rangle &= \left| \begin{smallmatrix} 3 & 3 \\ 2 & 2 \end{smallmatrix} \right\rangle = (\alpha\alpha\alpha), \\ &\left| \begin{smallmatrix} 3 & 1 \\ 2 & 2 \end{smallmatrix} \right\rangle = \frac{1}{\sqrt{3}} [(\alpha\alpha\beta) + (\beta\alpha\alpha) + (\alpha\beta\alpha)], \\ &\left| \begin{smallmatrix} 3 & -1 \\ 2 & -2 \end{smallmatrix} \right\rangle = \frac{1}{\sqrt{3}} [(\beta\beta\alpha) + (\alpha\beta\beta) + (\beta\alpha\beta)], \\ &\left| \begin{smallmatrix} 3 & -3 \\ 2 & -2 \end{smallmatrix} \right\rangle = (\beta\beta\beta); \end{aligned} \quad (20.4-5)$$

$$\begin{aligned} \boxed{1\ 2} \\ \boxed{3} \quad |JM\rangle &= \left| \begin{smallmatrix} 1 & 1 \\ 2 & 2 \end{smallmatrix} \right\rangle = \frac{1}{\sqrt{2}} [(\alpha\alpha\beta) - (\beta\alpha\alpha)], \\ &\left| \begin{smallmatrix} 1 & -1 \\ 2 & -2 \end{smallmatrix} \right\rangle = \frac{1}{\sqrt{2}} [(\alpha\beta\beta) - (\beta\beta\alpha)]; \end{aligned} \quad (20.4-6)$$

$$\begin{aligned} \boxed{1\ 3} \\ \boxed{2} \quad |JM\rangle &= \left| \begin{smallmatrix} 1 & 1 \\ 2 & 2 \end{smallmatrix} \right\rangle = \frac{1}{\sqrt{2}} [(\alpha\beta\alpha) - (\beta\alpha\alpha)], \\ &\left| \begin{smallmatrix} 1 & -1 \\ 2 & -2 \end{smallmatrix} \right\rangle = \frac{1}{\sqrt{2}} [(\alpha\beta\beta) - (\beta\alpha\beta)]. \end{aligned} \quad (20.4-7)$$



Finally, for the tableau

$$\begin{array}{|c|} \hline 1 \\ \hline 2 \\ \hline 3 \\ \hline \end{array}$$

we require a basis function which is antisymmetric in all three indices. With only two spin functions,  $\alpha$  and  $\beta$ , all such antisymmetric functions vanish identically.

For  $j = \frac{1}{2}$ , the situation may be summarized as follows: it is *not* possible to construct a wave function which is antisymmetric with respect to more than two particles. For electrons this means that spin functions are limited to basis functions for Young diagrams having no more than two rows:

$$\begin{array}{|c|c|c|c|c|c|c|c|c|c|} \hline & & & & & & & & & \\ \hline & & & & & & & & & \\ \hline \end{array} [\lambda_1, \lambda_2].$$

The spin  $S$  for the system is given by

$$S = \frac{1}{2}(\lambda_1 - \lambda_2) \quad (20.4-8)$$

and

$$\lambda_1 + \lambda_2 = r \quad (20.4-9)$$

where  $r$  is the number of electrons. In other words, a basis function for any of the standard tableaux associated with  $[\lambda_1, \lambda_2]$  is an eigenfunction of  $S^2$  with the eigenvalue  $S(S+1)$ . The number of independent spin functions for a given  $S$  and  $M_S$  is equal to the number of standard tableaux associated with the Young diagram.

The application of these ideas to the construction of totally antisymmetric wave functions is based on the rule that spatial functions that belong to a specific Young tableau are to be multiplied by spin functions that belong to the adjoint tableau. The complete antisymmetric wave function consists of linear combinations of such products. For two electrons, we have seen that the rule is automatically satisfied; for three electrons, this rule may be illustrated by constructing the wave function  $|p^3 \ ^2D_{\frac{1}{2}}\rangle$ . This particular example was chosen for its simplicity since there is only one possible distribution of electrons resulting in a single Slater determinant:

$$|p^3 \ ^2D_{\frac{1}{2}}\rangle = |1^+ 0^+ 1^-\rangle. \quad (20.4-10)$$

To see how this can be written in terms of separate spatial and spin functions we first pick out the proper spin functions corresponding to  $J = S = \frac{1}{2}$  and  $M = M_S = \frac{1}{2}$ . For three electrons we have, from (20.4-6) and (20.4-7),

$$\begin{array}{|c|c|} \hline 1 & 2 \\ \hline 3 & \\ \hline \end{array} \quad \left| \begin{array}{c} 1 \\ 2 \\ 2 \end{array} \right\rangle_I = \frac{1}{\sqrt{2}} [(\alpha\alpha\beta) - (\beta\alpha\alpha)],$$

$$\begin{array}{|c|c|} \hline 1 & 3 \\ \hline 2 & \\ \hline \end{array} \quad \left| \begin{array}{c} 1 \\ 2 \\ 2 \end{array} \right\rangle_{II} = \frac{1}{\sqrt{2}} [(\alpha\beta\alpha) - (\beta\alpha\alpha)]. \quad (20.4-11)$$

Next we construct spatial functions that are basis functions for the adjoint tableaux; in the present case, the latter are simply the same two tableaux as in (20.4-11). It may be readily verified that these functions are

$$\begin{aligned} \left[ \begin{array}{|c|c|} \hline 1 & 2 \\ \hline 3 & \\ \hline \end{array} \right] |2\ 2\rangle_I &= \frac{1}{\sqrt{2}} [(1\ 1\ 0) - (0\ 1\ 1)], \\ \left[ \begin{array}{|c|c|} \hline 1 & 3 \\ \hline 2 & \\ \hline \end{array} \right] |2\ 2\rangle_{II} &= \frac{1}{\sqrt{2}} [(1\ 0\ 1) - (0\ 1\ 1)], \end{aligned} \quad (20.4-12)$$

in which (110), for example, is an abbreviation for the product

$$p_{+1}(1)p_{+1}(2)p_0(3),$$

etc. Finally, let

$$\Psi = \sqrt{\frac{2}{3}} [|2\ 2\rangle_{II} |\frac{1}{2}\frac{1}{2}\rangle_I - |2\ 2\rangle_I |\frac{1}{2}\frac{1}{2}\rangle_{II}],$$

which, on substituting in (20.4-11) and (20.4-12) becomes

$$\begin{aligned} \Psi &= \sqrt{\frac{1}{6}} \{ [(1\ 0\ 1) - (0\ 1\ 1)] [\alpha\alpha\beta] - (\beta\alpha\alpha) \} - [(1\ 1\ 0) - (0\ 1\ 1)] [(\alpha\beta\alpha) - (\beta\alpha\alpha)] \} \\ &= \sqrt{\frac{1}{6}} \begin{vmatrix} p_{+1}(1)\alpha(1) & p_0(1)\alpha(1) & p_{+1}(1)\beta(1) \\ p_{+1}(2)\alpha(2) & p_0(2)\alpha(2) & p_{+1}(2)\beta(2) \\ p_{+1}(3)\alpha(3) & p_0(3)\alpha(3) & p_{+1}(3)\beta(3) \end{vmatrix} \\ &= |1^+ 0^+ 1^-\rangle \end{aligned} \quad (20.4-13)$$

or

$$\begin{aligned} |p^3\ ^2D\frac{3}{2}\rangle &= |1^+ 0^+ 1^-\rangle = \Psi \\ &= \sqrt{\frac{2}{3}} [|2\ 2\rangle_{II} |\frac{1}{2}\frac{1}{2}\rangle_I - |2\ 2\rangle_I |\frac{1}{2}\frac{1}{2}\rangle_{II}]. \end{aligned} \quad (20.4-14)$$

The consequences of this development for atomic wave functions may be summarized.

(1) For a given value of  $j$ , basis functions for Young diagrams with more than  $2j + 1$  rows are identically zero. Thus, for  $j = s = \frac{1}{2}$ , it was shown that it is impossible to construct spin functions for diagrams with more than two rows.

(2) Because of the antisymmetry requirement on the total electronic wave function it is necessary to multiply spin functions belonging to a particular diagram with spatial functions belonging to adjoint diagrams. Since the former are limited to two rows, the latter are limited to two columns. In other words, diagrams for spatial functions are limited to at most, two columns and  $2l + 1$  rows with  $l = 0, 1, 2, \dots$ .

We shall now illustrate how this information, together with a group theoretical analysis, may be used to establish which terms, including their

seniority assignments, arise from a configuration of equivalent electrons. In Section 6.5 it was shown that irreducible representations of  $SU(2l+1)$  can be decomposed into irreducible representations of  $O^+(2l+1)$  and, in turn, the latter can be decomposed into irreducible representations of  $O^+(3)$ . The results for p and d electrons are given in Table 6.1.

Consider the  $d^3$  configuration. For a three-electron system, the spin functions, according to (20.4-5, 6, and 7) belong to the Young diagrams

$$[21] \begin{array}{|c|c|} \hline \square & \square \\ \hline \square & \\ \hline \end{array} \quad S = \frac{1}{2}$$

$$[2] \begin{array}{|c|c|c|} \hline \square & \square & \square \\ \hline \end{array} \quad S = \frac{3}{2}.$$

Since the total wave function must be antisymmetric, the spatial functions must belong to the adjoint diagrams. The adjoint to  $[21]$  is  $[21]$  and the adjoint to  $[3]$  is  $[1^3] \equiv [111]$ . In other words, the only possible spatial functions are those that belong to the irreducible representations  $[21]$  or  $[1^3]$  of  $SU(2l+1)$ . Those that belong to  $[21]$  will have  $S = \frac{1}{2}$ , and those that belong to  $[1^3]$  will have  $S = \frac{3}{2}$ . Turning now to Table 6.1 for the decomposition  $S(2l+1) \rightarrow O^+(2l+1) \rightarrow O^+(3)$ , we find for  $d^3$  ( $l=2, r=3$ )

$SU(2l+1)$	$O^+(2l+1)$	$L$	$S$	Term
$[21]$	(10)	2	$\frac{1}{2}$	${}^2D$
	(21)	1, 2, 3, 4, 5	$\frac{1}{2}$	${}^2P, {}^2D, {}^2F, {}^2G, {}^2H$
$[1^3]$	(11)	1, 3	$\frac{3}{2}$	${}^4P, {}^4F$

$L$  is the label for the irreducible representations of  $O^+(3)$ . We note that the two  ${}^2D$  terms are distinguishable on the basis of the irreducible representations of  $O^+(2l+1)$ , since one  ${}^2D$  belongs to (10) and the other to (21). Hence, it is possible to devise a label which reflects this difference. Such a label is called the *seniority number*,  $v$ , defined as the smallest number of electrons for which a particular irreducible representation  $(\mu_1, \mu_2)$  of  $O^+(2l+1)$  and the same value of  $S$  can occur. Consulting Table 6.1 again for  $l=2$ , it is seen that (10) occurs for the configuration  $d^1$  ( $S = \frac{1}{2}$ ); hence  $v=1$ . The representation (21) appears for the first time in  $d^3$ ; hence all the terms belonging to (21) will have  $v=3$ . The representation (11) with  $S = \frac{3}{2}$  occurs for the first time in  $d^3$ ; hence, here too,  $v = \frac{3}{2}$ . These relations are summarized in Table 20.7.

## 20.5 *jj* Coupling

When angular momenta are combined as in (19.1-14), namely

$$\mathbf{j}_i = \mathbf{l}_i + \mathbf{s}_i, \quad \mathbf{J} = \sum_i \mathbf{j}_i, \quad (20.5-1)$$

we have the  $jj$  coupling scheme. One electron states are designated by  $l_j$  as, for example,  $s_{1/2}$ ,  $p_{1/2}$ ,  $p_{3/2}$ ,  $d_{3/2}$ ,  $d_{5/2}$ ,  $\dots$ , and each state has a degeneracy of  $2j + 1$ . A two-electron state is symbolized by  $(j_1 j_2)_J$  and the possible values of  $J$  range from  $j_1 + j_2$  to  $|j_1 - j_2|$ . Thus, for the  $pd$  configuration, the possible  $jj$  coupling states are

$$(\frac{1}{2} \frac{3}{2})_{1,2}, (\frac{1}{2} \frac{5}{2})_{2,3}, (\frac{3}{2} \frac{3}{2})_{0,1,2,3}, (\frac{3}{2} \frac{5}{2})_{1,2,3,4}.$$

For equivalent electrons the Pauli principle eliminates certain states which would otherwise be possible by angular momentum coupling. The rules for finding the states for two equivalent electrons are given:

(1) When  $j_1 \neq j_2$ , the value of  $J$  in  $(j_1 j_2)_J$  is found by the rules for the coupling of angular momenta.

(2) When  $j_1 = j_2$ , the allowed values of  $J$  in  $(j_1 j_2)_J$  are given by  $J = 2j - 1, 2j - 3, \dots$ .

Thus, for  $p^2$ , the possible states in  $jj$  coupling are

$$(\frac{1}{2} \frac{1}{2})_0, (\frac{1}{2} \frac{3}{2})_{1,2}, (\frac{3}{2} \frac{3}{2})_{0,2},$$

whereas in  $LS$  coupling the states are

$$^1S_0, ^3P_{0,1,2}, ^1D_2.$$

The two sets of states may be uniquely correlated so that even in extreme cases of  $jj$  coupling it is still possible to employ an  $LS$  designation.

Since equivalent electrons reside in orbitals with the same values of  $n$  and  $l$ , the electrostatic interaction is expected to be large in which case  $LS$  coupling would be favored. Hence it is for nonequivalent electrons that  $jj$  coupling holds the greatest interest. There are many situations for which neither  $LS$  nor  $jj$  coupling are valid approximations; in such cases it is necessary to diagonalize the Coulomb repulsion and the spin-orbit interaction for each value of  $J$ . The coupling is then said to be *intermediate*.