# Chapter 9

*Electronic Wavefunctions Must be Constructed to Have Permutational Antisymmetry Because the N Electrons are Indistinguishable Fermions* 

## I. Electronic Configurations

Atoms, linear molecules, and non-linear molecules have orbitals which can be labeled either according to the symmetry appropriate for that isolated species or for the species in an environment which produces lower symmetry. These orbitals should be viewed as regions of space in which electrons can move, with, of course, at most two electrons (of opposite spin) in each orbital. Specification of a particular occupancy of the set of orbitals available to the system gives an <u>electronic configuration</u>. For example,  $1s^22s^22p^4$  is an electronic configuration for the Oxygen atom (and for the F<sup>+1</sup> ion and the N<sup>-1</sup> ion);  $1s^22s^22p^33p^1$  is another configuration for O, F<sup>+1</sup>, or N<sup>-1</sup>. These configurations represent situations in which the electrons occupy low-energy orbitals of the system and, as such, are likely to contribute strongly to the true ground and low-lying excited states and to the low-energy states of molecules formed from these atoms or ions.

Specification of an electronic configuration does not, however, specify a particular electronic state of the system. In the above  $1s^22s^22p^4$  example, there are many ways (fifteen, to be precise) in which the 2p orbitals can be occupied by the four electrons. As a result, there are a total of fifteen states which cluster into three energetically distinct <u>levels</u>, lying within this single configuration. The  $1s^22s^22p^33p^1$  configuration contains thirty-six states which group into six distinct energy levels (the word <u>level</u> is used to denote one or more state with the same energy). Not all states which arise from a given electronic configuration have the same energy because various states occupy the degenerate (e.g., 2p and 3p in the above examples) orbitals differently. That is, some states have orbital occupancies of the form  $2p^2_12p^{1}_02p^{1}_{-1}$  while others have  $2p^2_12p^2_02p^0_{-1}$ ; as a result, the states can have quite different coulombic repulsions among the electrons (the state with two doubly occupied orbitals would lie higher in energy than that with two singly occupied orbitals). Later in this Section and in Appendix G techniques for constructing wavefunctions for each state contained within a particular configuration are given in detail. Mastering these tools is an important aspect of learning the material in this text.

In summary, an atom or molecule has many orbitals (core, bonding, non-bonding, Rydberg, and antibonding) available to it; occupancy of these orbitals in a particular manner gives rise to a configuration. If some orbitals are partially occupied in this configuration,

more than one state will arise; these states can differ in energy due to differences in how the orbitals are occupied. In particular, if degenerate orbitals are partially occupied, many states can arise and have energies which differ substantially because of differences in electron repulsions arising in these states. Systematic procedures for extracting all states from a given configuration, for labeling the states according to the appropriate symmetry group, for writing the wavefunctions corresponding to each state and for evaluating the energies corresponding to these wavefunctions are needed. Much of Chapters 10 and 11 are devoted to developing and illustrating these tools.

#### II. Antisymmetric Wavefunctions

## A. General Concepts

The total electronic Hamiltonian

$$H = -i (-h^2/2m_e - i^2 - a Z_a e^2/r_{ia}) + -i \ge i e^2/r_{ij} + a \ge b Z_a Z_b e^2/r_{ab},$$

where i and j label electrons and a and b label the nuclei (whose charges are denoted  $Z_a$ ), commutes with the operators  $P_{ij}$  which permute the names of the electrons i and j. This, in turn, requires eigenfunctions of H to be eigenfunctions of  $P_{ij}$ . In fact, the set of such permutation operators form a group called the symmetric group (a good reference to this subject is contained in Chapter 7 of <u>Group Theory</u>, M. Hamermesh, Addison-Wesley, Reading, Mass. (1962)). In the present text, we will not exploit the full group theoretical nature of these operators; we will focus on the simple fact that all wavefunctions must be eigenfunctions of the  $P_{ij}$  (additional material on this subject is contained in Chapter XIV of Kemble).

Because  $P_{ij}$  obeys  $P_{ij} * P_{ij} = 1$ , the eigenvalues of the  $P_{ij}$  operators must be +1 or -1. Electrons are Fermions (i.e., they have half-integral spin), and they have wavefunctions which are odd under permutation of any pair:  $P_{ij} = -$ . Bosons such as photons or deuterium nuclei (i.e., species with integral spin quantum numbers) have wavefunctions which obey  $P_{ij} = +$ .

These permutational symmetries are not only characteristics of the exact eigenfunctions of H belonging to any atom or molecule containing more than a single electron but they are also conditions which must be placed on any acceptable model or trial wavefunction (e.g., in a variational sense) which one constructs. In particular, within the orbital model of electronic structure (which is developed more systematically in Section 6), one can not construct trial wavefunctions which are simple spin-orbital products (i.e., an orbital multiplied by an or spin function for each electron) such as 1s 1s 2s 2s  $2p_1 2p_0$ . Such spin-orbital product functions <u>must</u> be made permutationally antisymmetric if the N-electron trial function is to be properly antisymmetric. This can be accomplished for any such product wavefunction by applying the following <u>antisymmetrizer operator</u>:

$$A = (1/N!) p s_p P,$$

where N is the number of electrons, P runs over all N! permutations, and  $s_p$  is +1 or -1 depending on whether the permutation P contains an even or odd number of pairwise permutations (e.g., 231 can be reached from 123 by two pairwise permutations-123==>213==>231, so 231 would have  $s_p$ =1). The permutation operator P in A acts on a product wavefunction and permutes the ordering of the spin-orbitals. For example, A 1 2 3= (1/ 6) [1 2 3- 1 3 2- 3 2 1- 2 1 3+ 3 1 2+ 2 3 1], where the convention is that electronic coordinates  $r_1$ ,  $r_2$ , and  $r_3$  correspond to the orbitals as they appear in the product (e.g., the term 3 2 1 represents 3(r\_1) 2(r\_2) 1(r\_3)).

It turns out that the permutations P can be allowed either to act on the "names" or labels of the electrons, keeping the order of the spin-orbitals fixed, or to act on the spin-orbitals, keeping the order and identity of the electrons' labels fixed. The resultant wavefunction, which contains N! terms, is exactly the same regardless of how one allows the permutations to act. Because we wish to use the above convention in which the order of the electronic labels remains fixed as 1, 2, 3, ... N, we choose to think of the permutations acting on the names of the spin-orbitals.

It should be noted that the effect of A on any spin-orbital product is to produce a function that is a sum of N! terms. In each of these terms the same spin-orbitals appear, but the order in which they appear differs from term to term. Thus antisymmetrization does not alter the overall orbital occupancy; it simply "scrambles" any knowledge of which electron is in which spin-orbital.

The antisymmetrized orbital product  $A_{1,2,3}$  is represented by the short hand  $|_{1,2,3}|$  and is referred to as a <u>Slater determinant</u>. The origin of this notation can be made clear by noting that (1/ N!) times the determinant of a matrix whose rows are labeled by the index i of the spin-orbital  $_{i}$  and whose columns are labeled by the index j of the electron at  $\mathbf{r}_{j}$  is equal to the above function:  $A_{1,2,3} = (1/3!) \det(_{i}(\mathbf{r}_{j}))$ . The general structure of such Slater determinants is illustrated below:

$$(1/N!)^{1/2} \det\{ j(\mathbf{r}_{i})\} = (1/N!)^{1/2} \begin{bmatrix} 1(1) 2(1) 3(1) \cdots k(1) \cdots N(1) \\ 1(2) 2(2) 3(2) \cdots k(2) \cdots N(2) \\ \cdots \\ 1(1) 2(1) 3(1) \cdots k(1) \cdots N(1) \end{bmatrix}$$

The antisymmetry of many-electron spin-orbital products places constraints on any acceptable model wavefunction, which give rise to important physical consequences. For example, it is antisymmetry that makes a function of the form | 1s 1s | vanish (thereby enforcing the Pauli exclusion principle) while | 1s 2s | does not vanish, except at points  $\mathbf{r}_1$  and  $\mathbf{r}_2$  where  $1s(\mathbf{r}_1) = 2s(\mathbf{r}_2)$ , and hence is acceptable. The Pauli principle is embodied in the fact that if any two or more columns (or rows) of a determinant are identical, the determinant vanishes. Antisymmetry also enforces indistinguishability of the electrons in that |1s 1s 2s 2s | =

- |1s| 1s| 2s| 2s| |. That is, two wavefunctions which differ simply by the ordering of their spin-orbitals are equal to within a sign (+/- 1); such an overall sign difference in a wavefunction has no physical consequence because all physical properties depend on the product \*, which appears in any expectation value expression.

### **B.** Physical Consequences of Antisymmetry

Once the rules for evaluating energies of determinental wavefunctions and for forming functions which have proper spin and spatial symmetries have been put forth (in Chapter 11), it will be clear that antisymmetry and electron spin considerations, in addition to orbital occupancies, play substantial roles in determining energies and that it is precisely these aspects that are responsible for energy splittings among states arising from one configuration. A single example may help illustrate this point. Consider the 1 \*1configuration of ethylene (ignore the other orbitals and focus on the properties of these two). As will be shown below when spin angular momentum is treated in full, the triplet spin states of this configuration are:

$$|S=1, M_S=1>=|$$
 \* |,

$$|S=1, M_S=-1>=|$$
 \* |,

and

$$|S=1, M_S=0>=2^{-1/2}[| * |+| * |].$$

The singlet spin state is:

$$|S=0, M_S=0> = 2^{-1/2}[| * |-| * |].$$

To understand how the three triplet states have the same energy and why the singlet state has a different energy, and an energy different than the  $M_S=0$  triplet even though these two states are composed of the same two determinants, we proceed as follows:

1. We express the bonding and antibonding \* orbitals in terms of the atomic p-orbitals from which they are formed:  $= 2^{-1/2} [L + R]$  and  $* = 2^{-1/2} [L - R]$ , where R and L denote the p-orbitals on the left and right carbon atoms, respectively.

2. We substitute these expressions into the Slater determinants that form the singlet and triplet states and collect terms and throw out terms for which the determinants vanish.

3. This then gives the singlet and triplet states in terms of atomic-orbital occupancies where it is easier to see the energy equivalences and differences.

Let us begin with the triplet states:

$$| * |= 1/2 [ |L L | - |R R | + |R L | - |L R | ]$$
  
= |R L |;  
$$2^{-1/2}[ | * | + | * |] = 2^{-1/2} 1/2[ |L L | - |R R | + |R L | - |L R | ]$$
  
|L R | + |L L | - |R R | + |R L | - |L R | ]  
= 2^{-1/2} [ |R L | + |R L | ];  
| \* | = 1/2 [ |L L | - |R R | + |R L | - |L R | ]

= |R L|.

The singlet state can be reduced in like fashion:

$$2^{-1/2}[| * |-| * |] = 2^{-1/2} \frac{1}{2}[|L L |-|R R |+|R L |-|R R |+|R L |-|R R |-|L L |+|R R |-|R L |+|L R |]$$
$$= 2^{-1/2}[|L L |-|R R |].$$

Notice that all three triplet states involve atomic orbital occupancy in which one electron is on one atom while the other is on the second carbon atom. In contrast, the singlet state places both electrons on one carbon (it contains two terms; one with the two electrons on the left carbon and the other with both electrons on the right carbon).

In a "valence bond" analysis of the physical content of the singlet and triplet <sup>1</sup> \*1 states, it is clear that the energy of the triplet states will lie below that of the singlet because the singlet contains "zwitterion" components that can be denoted C<sup>+</sup>C<sup>-</sup> and C<sup>-</sup>C<sup>+</sup>, while the three triplet states are purely "covalent". This case provides an excellent example of how the spin and permutational symmetries of a state "conspire" to qualitatively affect its energy and even electronic character as represented in its atomic orbital occupancies. Understanding this should provide ample motivation for learning how to form proper antisymmetric spin (and orbital) angular momentum eigenfunctions for atoms and molecules.