

## 9.2: Antisymmetric Wavefunctions

### General Concepts

The total electronic Hamiltonian

$$\hat{H} = \sum_i \left( \frac{-\hbar^2}{2m_e} \nabla_i^2 - \sum_a \frac{Z_a e^2}{r_{ia}} \right) + \sum_{i>j} \frac{e^2}{r_{ij}} + \sum_{a>b} \frac{Z_a Z_b e^2}{r_{ab}}$$

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  $\hat{H}$  to be eigenfunctions of  $\hat{P}_{ij}$ . In fact, the set of such permutation operators form a group called [the symmetric group](#). 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  $\hat{P}_{ij}$  operator.

Because  $\hat{P}_{ij}$  obeys

$$\hat{P}_{ij}^* \hat{P}_{ij} = 1$$

the eigenvalues of the  $\hat{P}_{ij}$  operators must be +1 or -1. Electrons are Fermions (i.e., they have half-integral spin) and they must have wavefunctions which are **odd** under permutation of any pair:

$$\hat{P}_{ij} \Psi = -\Psi$$

Bosons such as photons or deuterium nuclei (i.e., species with integral spin quantum numbers) have wavefunctions, which are **even** under permutation and obey

$$\hat{P}_{ij} \Psi = +\Psi$$

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 (discussed in [Section 6](#)), one can not construct trial wavefunctions which are simple spin-orbital products (i.e., an orbital multiplied by an  $\alpha$  or  $\beta$  spin function for each electron) such as

$$1s\alpha 1s\beta 2s\alpha 2s\beta 2p1\alpha 2p0\alpha.$$

Such spin-orbital product functions must 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 antisymmetrizer operator:

$$A = \frac{1}{\sqrt{N!}} \sum p s p P$$

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:

$$123 \rightarrow 213 \rightarrow 231$$

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,

$$A\varphi_1\varphi_2\varphi_3 = \frac{1}{\sqrt{6}} [\varphi_1\varphi_2\varphi_3 - \varphi_1\varphi_3\varphi_2 - \varphi_3\varphi_2\varphi_1 - \varphi_2\varphi_1\varphi_3 + \varphi_3\varphi_1\varphi_2 + \varphi_2\varphi_3\varphi_1]$$

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  $\varphi_3 \varphi_2 \varphi_1$  represents  $\varphi_3(r_1) \varphi_2(r_2) \varphi_1(r_3)$ ).

It turns out that the permutations  $\hat{P}$  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.

*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  $A\varphi_1\varphi_2\varphi_3$  is represented by the short hand  $|\varphi_1\varphi_2\varphi_3|$  and is referred to as a **Slater determinant**. The origin of this notation can be made clear by noting that  $(1/\sqrt{N!})$  times the determinant of a matrix whose rows are labeled by the index  $i$  of the spin-orbital  $\varphi_i$  and whose columns are labeled by the index  $j$  of the electron at  $r_j$  is equal to the above function:

$$A\varphi_1\varphi_2\varphi_3 = (1/\sqrt{3!})\det(\varphi_i(r_j)).$$

The general structure of such Slater determinants is illustrated below:

$$\frac{1}{\sqrt{N!}}\det\varphi_j(r_i) = \frac{1}{\sqrt{N!}}\varphi_1(1)\varphi_2(1)\varphi_3(1)\dots\varphi_k(1)\dots\dots\varphi_N(1)\varphi_1(2)\varphi_2(2)\varphi_3(2)\dots\varphi_k(2)\dots\dots\varphi_N(2)\dots\dots\varphi_1(N)\varphi_2(N)\varphi_3(N)\dots\varphi_k(N)\dots\varphi_N(N)$$

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  $|1s\alpha 1s\alpha|$  vanish (thereby enforcing the **Pauli exclusion principle**) while  $|1s\alpha 2s\alpha|$  does not vanish, except at points  $r_1$  and  $r_2$  where  $1s(r_1) = 2s(r_2)$ , 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

$$|1s\alpha 1s\beta 2s\alpha 2s\beta| = -|1s\alpha 1s\beta 2s\beta 2s\alpha|.$$

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  $\Psi^* \Psi$ , which appears in any expectation value expression.

*The antisymmetry of many-electron spin-orbital products places constraints on any acceptable model wavefunction.*

### Physical Consequences of Antisymmetry

Once the rules for evaluating energies of determinantal 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  $\pi^1\pi^{*1}$  configuration 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 (e.g.,  $S = 1$ ) of this configuration are:

$$|S = 1, M_S = 1\rangle = |\pi\alpha\pi^*\alpha|$$

$$|S = 1, M_S = -1\rangle = |\pi\beta\pi^*\beta|,$$

and

$$|S = 1, M_S = 0\rangle = \frac{1}{\sqrt{2}}[|\pi\alpha\pi^*\beta| + |\pi\beta\pi^*\alpha|].$$

The singlet spin state is:

$$|S = 0, M_S = 0\rangle = \frac{1}{\sqrt{2}}[|\pi\alpha\pi^*\beta| - |\pi\beta\pi^*\alpha|].$$

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:

- Step 1. We express the bonding  $\pi$  and antibonding  $\pi^*$  orbitals in terms of the atomic p-orbitals from which they are formed:

$$\pi = \frac{1}{\sqrt{2}}[L + R]$$

and

$$\pi^* = \frac{1}{\sqrt{2}}[L - R],$$

where R and L denote the p-orbitals on the left and right carbon atoms, respectively.

- Step 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.
- Step 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:

$$|\pi\alpha\pi^*\alpha\rangle = \frac{1}{2}[|L\alpha L\alpha\rangle - |R\alpha R\alpha\rangle + |R\alpha L\alpha\rangle - |L\alpha R\alpha\rangle] \quad (9.2.1)$$

$$= |R\alpha L\alpha\rangle; \quad (9.2.2)$$

$$\frac{1}{\sqrt{2}}[|\pi\alpha\pi^*\beta\rangle + |\pi\beta\pi^*\alpha\rangle] = \frac{1}{\sqrt{2}}\frac{1}{2}[|L\alpha L\beta\rangle - |R\alpha R\beta\rangle + |R\alpha L\beta\rangle - |L\alpha R\beta\rangle + |L\beta L\alpha\rangle - |R\beta R\alpha\rangle + |R\beta L\alpha\rangle - |L\beta R\alpha\rangle] \quad (9.2.3)$$

$$= \frac{1}{\sqrt{2}}[|R\alpha L\beta\rangle + |R\beta L\alpha\rangle]; \quad (9.2.4)$$

$$|\pi\beta\pi^*\beta\rangle = \frac{1}{2}[|L\beta L\beta\rangle - |R\beta R\beta\rangle + |R\beta L\beta\rangle - |L\beta R\beta\rangle] \quad (9.2.5)$$

$$= |R\beta L\beta\rangle. \quad (9.2.6)$$

The singlet state can be reduced in like fashion:

$$\frac{1}{\sqrt{2}}[|\pi\alpha\pi^*\beta\rangle - |\pi\beta\pi^*\alpha\rangle] = \frac{1}{\sqrt{2}}\frac{1}{2}[|L\alpha L\beta\rangle - |R\alpha R\beta\rangle + |R\alpha L\beta\rangle - |L\alpha R\beta\rangle - |L\beta L\alpha\rangle - |R\beta L\alpha\rangle + |L\beta R\alpha\rangle] \quad (9.2.7)$$

$$= \frac{1}{\sqrt{2}}[|L\alpha L\beta\rangle - |R\beta R\alpha\rangle]. \quad (9.2.8)$$

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  $\pi^1\pi^{*1}$  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  $C^+C^-$  and  $C^-C^+$ , 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.

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