10.8: The Self-Consistent Field and the Hartree-Fock Limit

In a modern *ab initio* electronic structure calculation on a closed shell molecule, the electronic Hamiltonian is used with a single determinant wavefunction. This wavefunction, ψ, is constructed from molecular orbitals, ψ that are written as linear combinations of contracted Gaussian basis functions, φ

$$\varphi_j = \sum_k c_{jk} \psi_k \tag{10.8.1}$$

The contracted Gaussian functions are composed from primitive Gaussian functions to match Slater-type orbitals (STOs). The exponential parameters in the STOs are optimized by calculations on small molecules using the nonlinear variational method and then those values are used with other molecules. The problem is to calculate the electronic energy from

$$E = \frac{\displaystyle\int \psi^* \hat{H} \psi d\tau}{\displaystyle\int \psi^* \psi d\tau} \tag{10.8.2}$$

and find the optimum coefficients c_{jk} for each molecular orbital in Equation 10.8.1 by using the Self Consistent Field Method and the Linear Variational Method to minimize the energy as was described in the previous chapter for the case of atoms.

To obtain the total energy of the molecule, we need to add the internuclear repulsion to the electronic energy calculated by this procedure. The total energy of the molecule can be calculated for different geometries (i.e. bond lengths and angles) to find the minimum energy configuration. Also, the total energies of possible transition states can be calculated to find the lowest energy pathway to products in chemical reactions.

$$V_{rs} = \sum_{r=1}^{N-1} \sum_{s=r+1}^{N} \frac{Z_r Z_s}{r_{rs}} \tag{10.8.3}$$

> ### Exercise 10.8.1
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> For a molecule with three nuclei, show that the sums in Equation 10.8.3 correctly include all the pairwise potential energy terms without including any twice.

As we improve the basis set used in calculations by adding more and better functions, we expect to get better and better energies. The variational principle says an approximate energy is an upper bound to the exact energy, so the lowest energy that we calculate is the most accurate. At some point, the improvements in the energy will be very slight. This limiting energy is the lowest that can be obtained with a single determinant wavefunction. This limit is called the *Hartree-Fock limit*, the energy is the *Hartree-Fock energy*, the molecular orbitals producing this limit are called *Hartree-Fock orbitals*, and the determinant is the *Hartree-Fock wavefunction*.

> ### Exercise 10.8.2
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> Write a one-sentence definition of the Hartree-Fock wavefunction that captures all the essential features of this function.

> ### Restricted vs. Unrestricted Hartree-Fock
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> You may encounter the terms *restricted* and *unrestricted* Hartree-Fock. The above discussion pertains to a restricted HF calculation. In a restricted HF calculation, electrons with α spin are restricted or constrained to occupy the same spatial orbitals as electrons with β spin. This constraint is removed in an unrestricted calculation. For example, the spin orbital for electron 1 could be $\psi_A(r_1)\alpha(1)$, and the spin orbital for electron 2 in a molecule could be $\psi_B(r_2)\beta(2)$, where both the spatial molecular orbital and the spin function differ for the two electrons. Such spin orbitals are called *unrestricted*. If both electrons are constrained to have the same spatial orbital, e.g. $\psi_A(r_1)\alpha(1)$ and $\psi_A(r_2)\beta(2)$, then the spin orbital is said to be *restricted*. While unrestricted spin orbitals can provide a better description of the electrons, twice as many spatial orbitals are needed, so the demands of the calculation are much higher. Using unrestricted orbitals is particular beneficial when a molecule contains an odd number of electrons because there are more electrons in one spin state than in the other.

Carbon Dioxide

Now consider the results of a self-consistent field calculation for carbon monoxide, CO. It is well known that carbon monoxide is a poison that acts by binding to the iron in hemoglobin and preventing oxygen from binding. As a result, oxygen is not transported by the blood to cells. Which end of carbon monoxide, carbon or oxygen, do you think binds to iron by donating electrons? We all know that oxygen is more electron-rich than carbon (8 vs 6 electrons) and more electronegative. A reasonable answer to this question therefore is *oxygen*, but experimentally it is carbon that binds to iron.

A quantum mechanical calculation done by Winifred M. Huo, published in J. Chem. Phys. 43, 624 (1965), provides an explanation for this counter-intuitive result. The basis set used in the calculation consisted of 10 functions: the ls, 2s, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals of C and O. Ten molecular orbitals (mo's) were defined as linear combinations of the ten atomic orbitals, which are written as

$$\psi_k = \sum_{j=1}^{10} C_{kj}\varphi_j \tag{10.8.4}$$

where k identifies the mo and j identifies the atomic orbital basis function. The ground state wavefunction ψ is written as the Slater Determinant of the five lowest energy molecular orbitals ψ_k. Equation 10.8.5 gives the energy of the ground state,

$$E = \frac{\left\langle \psi | \hat{H} | \psi \right\rangle}{\langle \psi | \psi \rangle} \tag{10.8.5}$$

where the denominator accounts for the normalization requirement. The coefficients C_{kj} in the linear combination are determined by the variational method to minimize the energy. The solution of this problem gives the following equations for the molecular orbitals. Only the largest terms have been retained here. These functions are listed and discussed in order of increasing energy.

- $1s \approx 0.941 s_o$. The 1 says this is the first σ orbital. The σ says it is symmetric with respect to reflection in the plane of the molecule. The large coefficient, 0.94, means this is essentially the 1s atomic orbital of oxygen. The oxygen 1s orbital should have a lower energy than that of carbon because the positive charge on the oxygen nucleus is greater.
- $2s \approx 0.921 s_c$. This orbital is essentially the 1s atomic orbital of carbon. Both the 1σ and 2σ are "nonbonding" orbitals since they are localized on a particular atom and do not directly determine the charge density between atoms.
- $3s \approx (0.722 s_o + 0.182 p_{zo}) + (0.282 s_c + 0.162 p_{zc})$. This orbital is a "bonding" molecular orbital because the electrons are delocalized over C and O in a way that enhances the charge density between the atoms. The 3 means this is the third σ orbital. This orbital also illustrates the concept of hybridization. One can say the 2s and 2p orbitals on each atom are hybridized and the molecular orbital is formed from these hybrids although the calculation just obtains the linear combination of the four orbitals directly without the *à priori* introduction of hybridization. In other words, hybridization just falls out of the calculation. The hybridization in this bonding LCAO increases the amplitude of the function in the region of space between the two atoms and decreases it in the region of space outside of the bonding region of the atoms.
- $4s \approx (0.372 s_c + 0.12 p_{zc}) + (0.542 p_{zo} - 0.432 s_0)$. This molecular orbital also can be thought of as being a hybrid formed from atomic orbitals. The hybridization of oxygen atomic orbitals, because of the negative coefficient with $2s_O$, decreases the electron density between the nuclei and enhances electron density on the side of oxygen facing away from the carbon atom. If we follow how this function varies along the internuclear axis, we see that near carbon the function is positive whereas near oxygen it is negative or possibly small and positive. This change means there must be a node between the two nuclei or at the oxygen nucleus. Because of the node, the electron density between the two nuclei is low so the electrons in this orbital do not serve to shield the two positive nuclei from each other. This orbital therefore is called an "antibonding" mo and the electrons assigned to it are called antibonding electrons. This orbital is the antibonding partner to the 3σ orbital.
- $1\pi \approx 0.322 p_{xc} + 0.442 p_{xo}$ and $2\pi \approx 0.322 p_{yc} + 0.442 p_{yo}$. These two orbitals are degenerate and correspond to bonding orbitals made up from the p_x and p_y atomic orbitals from each atom. These orbitals are degenerate because the x and y directions are equivalent in this molecule. π tells us that these orbitals are antisymmetric with respect to reflection in a plane containing the nuclei.
- $5\sigma \approx 0.382 s_C - 0.382 p_C - 0.292 p_{zO}$. This orbital is the sp hybrid of the carbon atomic orbitals. The negative coefficient for $2p_C$ puts the largest amplitude on the side of carbon away from oxygen. There is no node between the atoms. We conclude this is a nonbonding orbital with the nonbonding electrons on carbon. This is not a "bonding" orbital because the electron density between the nuclei is lowered by hybridization. It also is not an antibonding orbital because there is no node between the nuclei. When carbon monoxide binds to Fe in hemoglobin, the bond is made between the C and the Fe. This bond involves the

donation of the 5σ nonbonding electrons on C to empty d orbitals on Fe. Thus mo theory allows us to understand why the C end of the molecule is involved in this electron donation when we might naively expect O to be more electron-rich and capable of donating electrons to iron.

Exercise 10.8.3

Summarize how Quantum Mechanics is used to describe bonding and the electronic structure of molecules.

Exercise 10.8.4

Construct an energy level diagram for CO that shows both the atomic orbitals and the molecular orbitals. Show which atomic orbitals contribute to each molecular orbital by drawing lines to connect the mo's to the ao's. Label the molecular orbitals in a way that reveals their symmetry. Use this energy level diagram to explain why it is the carbon end of the molecule that binds to hemoglobin rather than the oxygen end.