Chapter 10   Theories of Electronic Molecular Structure

Solving the Schrödinger equation for a molecule first requires specifying the Hamiltonian and then finding the wavefunctions that satisfy the equation. The wavefunctions involve the coordinates of all the nuclei and electrons that comprise the molecule. The complete molecular Hamiltonian consists of several terms. The nuclear and electronic kinetic energy operators account for the motion of all of the nuclei and electrons. The Coulomb potential energy terms account for the interactions between the nuclei, the electrons, and the nuclei and electrons. Other terms account for the interactions between all the magnetic dipole moments and the interactions with any external electric or magnetic fields. The charge distribution of an atomic nucleus is not always spherical and, when appropriate, this asymmetry must be taken into account as well as the relativistic effect that a moving electron experiences as a change in mass.

This complete Hamiltonian is too complicated and is not needed for many situations. In practice, only the terms that are essential for the purpose at hand are included. Consequently in the absence of external fields, interest in spin-spin and spin-orbit interactions, and in electron and nuclear magnetic resonance spectroscopy (ESR and NMR), the molecular Hamiltonian usually is considered to consist only of the kinetic and potential energy terms, and the Born-Oppenheimer approximation is made in order to separate the nuclear and electronic motion.

In general, electronic wavefunctions for molecules are constructed from approximate one-electron wavefunctions. These one-electron functions are called molecular orbitals. The expectation value expression for the energy is used to optimize these functions, i.e. make them as good as possible. The

criterion for quality is the energy of the ground state. According to the Variational Principle, an approximate ground state energy always is higher than the exact energy, so the best energy in a series of approximations is the lowest energy. In this chapter we describe how the variational method, perturbation theory, the self-consistent field method, and configuration interaction all are used to describe the electronic states of molecules. The ultimate goal is a mathematical description of electrons in molecules that enables chemists and other scientists to develop a deep understanding of chemical bonding, to calculate properties of molecules, and to make predictions based on these calculations. For example, an active area of research in industry involves calculating changes in chemical properties of pharmaceutical drugs as a result of changes in their chemical structure.

10.1   The Born-Oppenheimer Approximation

The Born-Oppenheimer approximation is one of the basic concepts underlying the description of the quantum states of molecules. This approximation makes it possible to separate the motion of the nuclei and the motion of the electrons. This is not a new idea for us. We already made use of this approximation in the particle-in-a-box model when we explained the electronic absorption spectra of cyanine dyes without considering the motion of the nuclei. Then we discussed the translational, rotational and vibrational motion of the nuclei without including the motion of the electrons. In this chapter we will examine more closely the significance and consequences of this important approximation. Note, in this discussion nuclear refers to the atomic nuclei as parts of molecules not to the internal structure of the nucleus.

The Born-Oppenheimer approximation neglects the motion of the atomic nuclei when describing the electrons in a molecule. The physical basis for the Born-Oppenheimer approximation is the fact that the mass of an atomic nucleus in a molecule is much larger than the mass of an electron (more than 1000

times). Because of this difference, the nuclei move much more slowly than the electrons. In addition, due to their opposite charges, there is a mutual attractive force of Ze^2/r^2 acting on an atomic nucleus and an electron. This force causes both particles to be accelerated. Since the magnitude of the acceleration is inversely proportional to the mass, $a = f/m$, the acceleration of the electrons is large and the acceleration of the atomic nuclei is small; the difference is a factor of more than 1000. Consequently, the electrons are moving and responding to forces very quickly, and the nuclei are not. You can imagine running a 100-yard dash against someone whose acceleration is a 1000 times greater than yours. That person could literally run circles around you. So a good approximation is to describe the electronic states of a molecule by thinking that the nuclei aren't moving, i.e. that they are stationary. The nuclei, however, can be stationary at different positions so the electronic wavefunction can depend on the positions of the nuclei even though their motion is neglected.

Now we look at the mathematics to see what is done in solving the Schrödinger equation after making the Born-Oppenheimer approximation. For a diatomic molecule as an example, the Hamiltonian operator is grouped into three terms

$$\hat{H}(\mathbf{r},\mathbf{R}) \;=\; \hat{T}_{nuc}(\mathbf{R}) + \frac{e^2}{4\pi\varepsilon_0}\frac{Z_A\,Z_B}{R} + \hat{H}_{elec}(\mathbf{r},\mathbf{R}) \qquad \{10\text{-}1\}$$

where

$$T_{nuc}(\mathbf{R}) \;=\; -\frac{\hbar^2}{2m_A}\nabla_A^2 - \frac{\hbar^2}{2m_B}\nabla_B^2 \qquad \{10\text{-}2\}$$

and

$$\hat{H}_{elec}(\mathbf{r},\mathbf{R}) \;=\; \frac{-\hbar^2}{2m}\sum_i \nabla_i^2 + \frac{e^2}{4\pi\varepsilon_0}\left(-\sum_i\frac{Z_A}{r_{Ai}} - \sum_i\frac{Z_B}{r_{Bi}} + \frac{1}{2}\sum_i\sum_{j\neq i}\frac{1}{r_{ij}} \right) \quad \{10\text{-}3\}$$

In Equation {10-1}, the first term represents the kinetic energy of the nuclei, the second term represents the Coulomb repulsion of the two nuclei, and the third term represents the contribution to the energy from the electrons, which consists of their kinetic energy, mutual repulsion for each other, and attraction for the nuclei. Bold-face type is used to represent that **r** and **R** are vectors specifying the positions of <u>all</u> the electrons and <u>all</u> the nuclei, respectively.

Exercise 10.1 Define all the symbols in Equations {10-1} through {10-3}.

Exercise 10.2 Explain why the factor of 1/2 appears in the last term in Equation {10-3}.

The Born-Oppenheimer approximation says that the nuclear kinetic energy terms in the complete Hamiltonian, Equation {10-1}, can be neglected in solving for the electronic wavefunctions and energies. Consequently, the electronic wavefunction $\phi_e(\mathbf{r},\mathbf{R})$ is found as a solution to the electronic Schrödinger equation, ▲

$$\hat{H}_{elec}(\mathbf{r},\mathbf{R})\,\varphi_e(\mathbf{r},\mathbf{R}) \;=\; E_e(\mathbf{R})\,\varphi_e(\mathbf{r},\mathbf{R}) \qquad \{10\text{-}4\}$$

Even though the nuclear kinetic energy terms are neglected, the Born-Oppenheimer approximation still takes into account the variation in the positions of the nuclei in determining the electronic energy and the resulting electronic wavefunction depends upon the nuclear positions, **R**.

As a result of the Born-Oppenheimer approximation, the molecular wavefunction can be written as a product ▲

$$\psi_{ne}(\mathbf{r},\mathbf{R}) \;=\; \chi_{ne}(\mathbf{R})\,\varphi_e(\mathbf{r},\mathbf{R}) \qquad \{10\text{-}5\}$$

This product wavefunction is called the Born-Oppenheimer wavefunction. The function $\chi_{ne}(\mathbf{R})$ is the vibrational wavefunction, which is a function of the nuclear coordinates **R** and depends upon both the vibrational and electronic quantum numbers or states, n and e, respectively. The electronic function,

$\phi_e(\mathbf{r,R})$, is a function of both the nuclear and electronic coordinates, but only depends upon the electronic quantum number or electronic state, e. Translational and rotational motion is not included here. The translational and rotational wavefunctions simply multiply the vibrational and electronic functions in Equation {10-5} to give he complete molecular wavefunction when the translational and rotational motions are not coupled to the vibrational and electronic motion.

In the *Crude Born-Oppenheimer Approximation*, $\mathbf{R}$ is set equal to $\mathbf{R_0}$, the equilibrium separation of the nuclei, and the electronic wavefunctions are taken to be the same for all positions of the nuclei.

The electronic energy, $E_e(\mathbf{R})$, in Equation {10-4} combines with the repulsive Coulomb energy of the two nuclei, to form the potential energy function that controls the nuclear motion as shown in Figure 10.1.

$$V_e(\mathbf{R}) \quad = \quad E_e(\mathbf{R}) + \frac{e^2}{4\pi\varepsilon_0} \frac{Z_A Z_B}{R} \qquad \{10\text{-}6\}$$

Consequently the Schrödinger equation for the vibrational motion is

$$\left[\hat{T}_{nuc}(R) + V(\mathbf{R}) \right] \chi_{ne}(\mathbf{R}) \quad = \quad E_{ne} \, \chi_{ne}(\mathbf{R}) \qquad \{10\text{-}7\}$$

In Chapter 6, the potential energy was approximated as a harmonic potential depending on the displacement, Q, of the nuclei from their equilibrium positions.
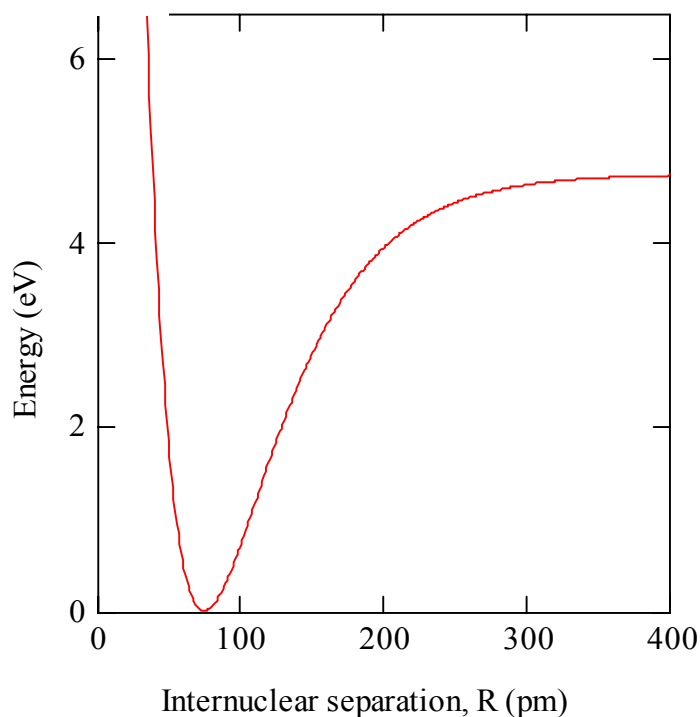
Figure 10.1   The potential energy function for a diatomic molecule.

In practice the electronic Schrödinger equation is solved using approximations at particular values of $\mathbf{R}$ to obtain the wavefunctions $\phi_e(\mathbf{r},\mathbf{R})$ and potential energies $V_e(\mathbf{R})$. The potential energies can be graphed as illustrated in Figure 10.1.

The graph in Figure 10.1 is the energy of a diatomic molecule as a function of internuclear separation, which serves as the potential energy function for the nuclei. When R is very large there are two atoms that are weakly interacting. As R becomes smaller, the interaction becomes stronger, the energy becomes a large negative value, and we say a bond is formed between the atoms. At very small values of R, the internuclear repulsion is very large so the energy is large and positive. This energy function controls the motion of the nuclei. Previously, we approximated this function by a harmonic potential to obtain the description of vibrational motion in terms of the harmonic oscillator model. Other approximate functional forms could be used

as well, e.g. the Morse potential. The equilibrium position of the nuclei is where this function is a minimum, i.e. at $R = R_0$. If we obtain the wavefunction at $R = R_0$, and use this function for all values of R, we have employed the *Crude Born-Oppenheimer* approximation.

> **Exercise 10.3** Relate Equation {10-7} to the one previously used in our description of molecular vibrations in terms of the harmonic oscillator model.

In this section we started with the Schrödinger equation for a diatomic molecule and separated it into two equations, an electronic Schrödinger equation and a nuclear Schrödinger equation. In order to make the separation, we had to make an approximation. We had to neglect the effect of the nuclear kinetic energy on the electrons. The fact that this assumption works can be traced to the fact that the nuclear masses are much larger than the electron mass. We then used the solution of the electronic Schrödinger equation to provide the potential energy function for the nuclear motion. The solution to the nuclear Schrödinger equation provides the vibrational wavefunctions and energies.

> **Exercise 10.4** Explain the difference between the Born-Oppenheimer approximation and the Crude Born-Oppenheimer approximation.

10.2 The Orbital Approximation and Orbital Configurations

You should be able to recognize from the form of the electronic Hamiltonian, Equation {10-3}, that the electronic Schrödinger equation, Equation {10-4}, cannot be solved. The problem, as for the case of atoms, is the electron-electron repulsion terms. Approximations must be made, and these approximations are based on the idea of using one-electron wavefunctions to describe multi-electron systems, in this case molecules just as is done for multi-electron atoms. Initially two different approaches were developed. Heitler and London originated one in 1927, called the Valence Bond Method, and Robert

Mulliken and others developed the other somewhat later, called the Molecular Orbital Method. By using configuration interaction, both methods can provide equivalent electronic wavefunctions and descriptions of bonding in molecules, although the basic concepts of the two methods are different. We will develop only the molecular orbital method because this is the method that is predominantly employed now. The wavefunction for a single electron in a molecule is called a molecular orbital in analogy with the one-electron wavefunctions for atoms being called atomic orbitals.

To describe the electronic states of molecules, we construct wavefunctions for the electronic states by using molecular orbitals. These wavefunctions are approximate solutions to the Schrödinger equation. A mathematical function for a molecular orbital is constructed, ψ_i, as a linear combination of other functions, ϕ_j, which are called basis functions because they provide the basis for representing the molecular orbital.

$$\psi_i \;=\; \sum_j c_{ij}\, \phi_j \qquad\qquad \{10\text{-}8\}$$

The variational method is used to find values for parameters in the basis functions and for the constant coefficients in the linear combination that optimize these functions, i.e. make them as good as possible. The criterion for quality in the variational method is making the ground state energy of the molecule as low as possible. ▲ Here and in the rest of this chapter, the following notation is used: σ = a general spin function (can be either α or β), ϕ = basis function (usually represents an atomic orbital), ψ = molecular orbital, Ψ = electronic state wavefunction (representing a single Slater determinant or linear combination of Slater determinants).

The ultimate goal is a mathematical description of electrons in molecules that enables chemists and other scientists to develop a deep understanding of chemical bonding and reactivity, to calculate properties of molecules, and to make predictions based on these calculations. For example, an active area of

research in industry involves calculating changes in chemical properties of pharmaceutical drugs as a result of changes in chemical structure.

Just as for atoms, each electron in a molecule can be described by a product of a spatial orbital and a spin function. These product functions are called spin orbitals. Since electrons are fermions, the electronic wavefunction must be antisymmetric with respect to the permutation of any two electrons. A Slater determinant containing the molecular spin orbitals produces the antisymmetric wavefunction. For example for two electrons,

$$\Psi(\mathbf{r_1},\mathbf{r_2}) = 2^{-\frac{1}{2}} \begin{vmatrix} \psi_A(\mathbf{r_1})\,\alpha(1) & \psi_B(\mathbf{r_1})\,\beta(1) \\ \psi_A(\mathbf{r_2})\,\alpha(2) & \psi_B(\mathbf{r_2})\,\beta(2) \end{vmatrix} \qquad \{10\text{-}9\}$$

Solving the Schrödinger equation in the orbital approximation will produce a set of spatial molecular orbitals, each with a specific energy, ε. Following the Aufbau Principle, 2 electrons with different spins (α and β, consistent with the Pauli Exclusion Principle) are assigned to each spatial molecular orbital in order of increasing energy. For the ground state of the 2n electron molecule, the n lowest energy spatial orbitals will be occupied, and the electron configuration will be given as $\psi_1^2\,\psi_2^2\,\psi_3^2\cdots\psi_n^2$. The electron configuration also can be specified by an orbital energy level diagram as shown in Figure 10.2. Higher energy configurations exist as well, and these configurations produce excited states of molecules. Some examples are shown in Figure 10.2.

a)   b)   c)   d)

ε_5 ———   ———   ———   ———

ε_4 ———   ———   ———   ———

ε_3 ———   ———   ———   ———

ε_2 ———   ———   ———   ———
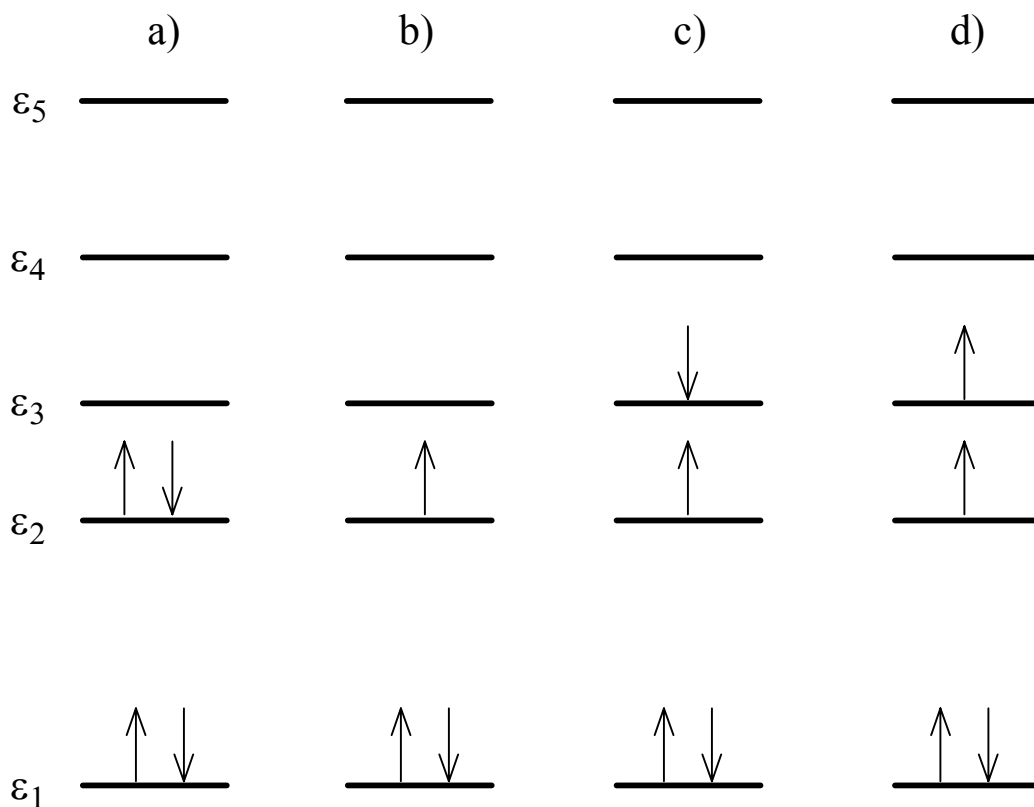
ε_1 ———   ———   ———   ———

Figure 10.2   a) The lowest energy configuration of a closed-shell system. b) The lowest energy configuration of an open-shell radical. c) An excited singlet configuration. d) An excited triplet configuration.

Molecular orbitals usually are identified by their symmetry or angular momentum properties. For example, a typical symbol used to represent an orbital in an electronic configuration of a diatomic molecule is $2\sigma_g^2$. The superscript in symbol means that this orbital is occupied by two electrons; the prefix means that it is the second sigma orbital with *gerade* symmetry.

Diatomic molecules retain a component of angular momentum along the internuclear axis. The molecular orbitals of diatomic molecule therefore can be identified in terms of this angular momentum. A Greek letter, e.g. σ or π, encodes this information, as well as information about the symmetry of the orbital. A σ means the component of angular momentum is 0, and there is no

node in any plane containing the internuclear axis, so the orbital must be symmetric with respect to reflection in such a plane. A π means there is a node and the wavefunction is antisymmetric with respect to reflection in a plane containing the internuclear axis. For homonuclear diatomic molecules, a *g* or a *u* is added as a subscript to designate whether the orbital is symmetric or antisymmetric with respect to the center of inversion of the molecule.

A homonuclear diatomic molecule has a center of inversion in the middle of the bond. This center of inversion means that $\psi(x,y,z) = \pm\psi(-x, -y, -z,)$ with the origin at the inversion center. Inversion takes you from (x,y,z) to (−x,−y,−z). For a heteronuclear diatomic molecule, there is no center of inversion so the symbols g and u are not used. A prefix 1, 2, 3, etc. simply means the first, second, third, etc. orbital of that type. We can specify an electronic configuration of a diatomic molecule by these symbols by using a superscript to denote the number of electrons in that orbital, e.g. the lowest energy configuration of N_2 is

$$1\sigma_g^2 \, 1\sigma_u^2 \, 2\sigma_g^2 \, 2\sigma_u^2 \, 1\pi_u^4 \, 3\sigma_g^2. \hspace{2cm} \{10\text{-}10\}$$

10.3 Basis Functions

The molecular spin-orbitals that are used in the Slater determinant usually are expressed as a linear combination of some chosen functions, which are called *basis functions*. This set of functions is called the *basis set*. The fact that one function can be represented by a linear combination of other functions is a general property. All that is necessary is that the basis functions *span-the-space*, which means that the functions must form a complete set and must be describing the same thing. For example, spherical harmonics cannot be used to describe a hydrogen atom radial function because they do not involve the distance r, but they can be used to describe the angular properties of anything in three-dimensional space.

This span-the-space property of functions is just like the corresponding property of vectors. The unit vectors $(\vec{x}, \vec{y}, \vec{z})$ describe points in space and form a complete set since any position in space can be specified by a linear combination of these three unit vectors. These unit vectors also could be called basis vectors.

Exercise 10.5   Explain why the unit vectors $(\vec{x}, \vec{y})$ do not form a complete set to describe your classroom.

Just as we discussed for atoms, parameters in the basis functions and the coefficients in the linear combination can be optimized in accord with the Variational Principle to produce a self-consistent field (SCF) for the electrons. This optimization means that the ground state energy calculated with the wavefunction is minimized with respect to variation of the parameters and coefficients defining the function. As a result, that ground state energy is larger than the exact energy, but is the best value that can be obtained with that wavefunction.

Intuitively one might select hydrogenic atomic orbitals as the basis set for molecular orbitals. After all, molecules are composed of atoms, and hydrogenic orbitals describe atoms exactly if the electron-electron interactions are neglected. At a better level of approximation, the nuclear charge that appears in these functions can be used as a variational parameter to account for the shielding effects due to the electron-electron interactions. Also, the use of atomic orbitals allows us to interpret molecular properties and charge distributions in terms of atomic properties and charges, which is very appealing since we picture molecules as composed of atoms. As described in the previous chapter, calculations with hydrogenic functions were not very efficient so other basis functions, *Slater-type atomic orbitals* (STOs), were invented.

A minimal basis set of STOs for a molecule includes only those STOs that would be occupied by electrons in the atoms forming the molecule. A larger basis set, however, improves the accuracy of the calculations by providing more

variable parameters to produce a better approximate wavefunction, but at the expense of increased computational time.

For example, one can use more than one STO to represent one atomic orbital, as shown in Equation {10-11}, and rather than doing a nonlinear variational calculation to optimize each zeta, use two STOs with different values for zeta. The linear variation calculation then will produce the coefficients (C_1 and C_2) for these two functions in the linear combination that best describes the charge distribution in the molecule. The function with the large zeta accounts for charge near the nucleus, while the function with the smaller zeta accounts for the charge distribution at larger values of the distance from the nucleus. This expanded basis set is called a *double-zeta basis set*.

$$R_{2s}(r) = C_1\, r\, e^{-\zeta_1 r} + C_2\, r\, e^{-\zeta_2 r} \qquad\qquad \{10\text{-}11\}$$

Exercise 10.6
(a) Plot the normalized radial probability density for a 2s hydrogenic orbital for lithium using an effective nuclear charge of 1.30.
(b) Fit that radial probability density with the radial probability density for 1 STO by varying the zeta parameter in the STO.
(c) Also fit the radial probability density for the hydrogenic orbital with that for the sum of 2 STOs, as in Equation {10-11}, by varying the zeta parameters for each and their coefficients in the sum.
(d) Report your values for the zeta parameters and the coefficients and provide graphs of these functions and the corresponding radial probability densities. What are your conclusions regarding the utility of using STOs with single or double zeta values to describe the charge distributions in atoms and molecules?

The use of double zeta functions in basis sets is especially important because without them orbitals of the same type are constrained to be identical even though in the molecule they may be chemically inequivalent. For example, in acetylene the p_z orbital along the internuclear axis is in a quite different chemical environment and is being used to account for quite different bonding

than the p_x and p_y orbitals. With a double zeta basis set the p_z orbital is not constrained to be the same size as the p_x and p_y orbitals.

Exercise 10.7   Explain why the p_x, p_y, and p_z orbitals in a molecule might be constrained to be the same in a single-zeta basis set calculation, and how the use of a double-zeta basis set would allow the p_x, p_y, and p_z orbitals to differ.

The use of a minimal basis set with fixed zeta parameters severely limits how much the electronic charge can be changed from the atomic charge distribution in order to describe molecules and chemical bonds. This limitation is removed if STOs with larger n values and different spherical harmonic functions, the $Y_\ell^m(\theta, \varphi)$ in the definition of STO's in Chapter 9, are included. Adding such functions is another way to expand the basis set and obtain more accurate results. Such functions are called polarization functions because they allow for charge polarization away form the atomic distribution to occur.

While the STO basis set was an improvement over hydrogenic orbitals in terms of computational efficiency, representing the STOs with Gaussian functions produced further improvements that were needed to accurately describe molecules. A Gaussian basis function has the form shown in Equation {10-12}. Note that in all the basis sets, only the radial part of the orbital changes, and the spherical harmonic functions are used in all of them to describe the angular part of the orbital.

$$G_{n\ell m}(r, \theta, \varphi) \; = \; N_n \, r^{\,n-1} \, e^{-\alpha r^2} \, Y_\ell^m(\theta, \varphi) \qquad \{10\text{-}12\}$$

Unfortunately Gaussian functions do not match the shape of an atomic orbital very well. In particular, they are flat rather than steep near the atomic nucleus at r = 0, and they fall off more rapidly at large values of r.

> **Exercise 10.8**   Make plots of the following two functions
> $$(1.108) \exp(-r^2/3)$$
> $$(2.000) \exp(-r)$$
> to illustrate how Gaussian functions differ from hydrogenic orbitals and Slater-type orbitals. The constants multiplying the exponentials normalize these functions. Describe the differences you observe between a Gaussian and a Slater-type function.

To compensate for this problem, each STO is replaced with a number of Gaussian functions with different values for the exponential parameter α. These Gaussian functions form a *primitive Gaussian basis set*. Linear combinations of the primitive Gaussians are formed to approximate the radial part of a STO. This linear combination is not optimized further in the energy variational calculation but rather is frozen and treated as a single function. The linear combination of *primitive Gaussian functions* is called a *contracted Gaussian function*. Although more functions and more integrals now are part of the calculation, the integrals involving Gaussian functions are quicker to compute than those involving exponentials so there is a net gain in the efficiency of the calculation.

Gaussian basis sets are identified by abbreviations such as N-MPG[*]. N is the number of Gaussian primitives used for each inner-shell orbital. The hyphen indicates a split-basis set where the valence orbitals are double zeta. The M indicates the number of primitives that form the large zeta function (for the inner valence region), and P indicates the number that form the small zeta function (for the outer valence region). G identifies the set a being Gaussian. The addition of an asterisk to this notation means that a single set of Gaussian 3d polarization functions is included. A double asterisk means that a single set of Gaussian 2p functions is included for each hydrogen atom.

For example 3G means each STO is represented by a linear combination of three primitive Gaussian functions. 6-31G means each inner shell (1s orbital) STO is a linear combination of 6 primitives and each valence shell STO

is split into an inner and outer part (double zeta) using 3 and 1 primitive Gaussians, respectively.

Exercise 10.9 The 1s Slater-type orbital
$$S_1(r) = \sqrt{4\zeta_1}\, e^{-\zeta_1 r} \qquad \text{with} \qquad \zeta_1 = 1.24$$
is represented as a sum of three primitive Gaussian functions.
$$S_G(r) = \sum_{j=1}^{3} C_j\, e^{-\alpha_j r^2}$$
This sum is the contracted Gaussian function for the STO.
(a) Make plots of the STO and the contracted Gaussian function on the same graph so they can be compared easily. All distances should be in units of the Bohr radius. Use the following values for the coefficients, C, and the exponential parameters, α.

index j	α_j	C_j
1	0.1688	0.4
2	0.6239	0.7
3	3.425	1.3

(b) Change the values of the coefficients and exponential parameters to see if a better fit can be obtained.
(c) Comment on the ability of a linear combination of Gaussian functions to accurately describe a STO.

10.4   The Case of H_2^+

One can develop an intuitive sense of molecular orbitals and what a chemical bond is by considering the simplest molecule, H_2^+. This ion consists of two protons held together by the electrostatic force of a single electron. Clearly the two protons, two positive charges, repeal each other. The protons must be held together by an attractive Coulomb force that opposes the repulsive Coulomb force. A negative charge density between the two protons would produce the required counter-acting Coulomb force needed to pull the protons together. So intuitively, to create a chemical bond between two protons or two positively charged nuclei, a high density of negative charge between them is needed. We expect the molecular orbitals that we find to reflect this intuitive notion.

The electronic Hamiltonian for H_2^+ is

$$\hat{H}_{elec}(\mathbf{r}, R) = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0\, r_A} - \frac{e^2}{4\pi\varepsilon_0\, r_B} + \frac{e^2}{4\pi\varepsilon_0\, R} \qquad \{10\text{-}13\}$$

where $\mathbf{r}$ gives the coordinates of the electron, and R is the distance between the two protons. Although the Schrödinger equation for H_2^+ can be solved exactly because there is only one electron, we will develop approximate solutions in a manner applicable to other diatomic molecules that have more than one electron.

For the case where the protons in H_2^+ are infinitely far apart, we have a hydrogen atom and an isolated proton when the electron is near one proton or the other. The electronic wavefunction would just be $1s_A(\mathbf{r})$ or $1s_B(\mathbf{r})$ depending upon which proton, labeled A or B, the electron is near. Here $1s_A$ denotes a 1s hydrogen atomic orbital with proton A serving as the origin of the spherical polar coordinate system in which the position $\mathbf{r}$ of the electron is specified. Similarly $1s_B$ has proton B as the origin. A useful approximation for the molecular orbital when the protons are close together therefore is a linear combination of the two atomic orbitals. The general method of using

$$\psi(\mathbf{r}) = C_A\, 1s_A(\mathbf{r}) + C_B\, 1s_B(\mathbf{r}) \qquad \{10\text{-}14\}$$

i.e. of finding molecular orbitals as linear combinations of atomic orbitals is called the *Linear Combination of Atomic Orbitals - Molecular Orbital (LCAO-MO) Method*. In this case we have two basis functions in our basis set, the hydrogenic atomic orbitals $1s_A$ and $1s_B$.

For H_2^+, the simplest molecule, the starting function is given by Equation 10.2.2. We must determine values for the coefficients, C_A and C_B. We could

use the variational method to find a value for these coefficients, but for the case of H_2^+ evaluating these coefficients is easy. Since the two protons are identical, the probability that the electron is near A must equal the probability that the electron is near B. These probabilities are given by $|C_A|^2$ and $|C_B|^2$, respectively. Consider two possibilities that satisfy the condition $|C_A|^2 = |C_B|^2$; namely, $C_A = C_B = C_+$, and $C_A = -C_B = C_-$. These two cases produce two molecular orbitals:

$$
\begin{aligned}
\psi_+ &= C_+ \, (1s_A + 1s_B) \\
\psi_- &= C_- \, (1s_A - 1s_B)
\end{aligned}
\qquad \{10\text{-}15\}
$$

The probability density for finding the electron at any point in space is given by $|\psi|^2$ and the electronic charge density is just $e|\psi|^2$. The important difference between ψ_+ and ψ_- is that the charge density for ψ_+ is enhanced between the two protons, whereas it is diminished for ψ_- as shown in Figures 10.3 and 10.4. ψ_- has a node in the middle while ψ_+ corresponds to our intuitive sense of what a chemical bond must be like. The electronic charge density is enhanced in the region between the two protons. So ψ_+ is called a *bonding molecular orbital*. If the electron were described by ψ_-, the low charge density between the two protons would not balance the Coulomb repulsion of the protons, so ψ_- is called an *antibonding molecular orbital*.

Now we want to evaluate C_+ and C_- and then calculate the energy. The bonding and antibonding character of ψ_+ and ψ_- also should be reflected in the energy. If ψ_+ indeed describes a bonding orbital, then the energy of this state should be less than that of a proton and hydrogen atom that are separated. The calculation of the energy will tell us whether this simple theory predicts H_2^+ to

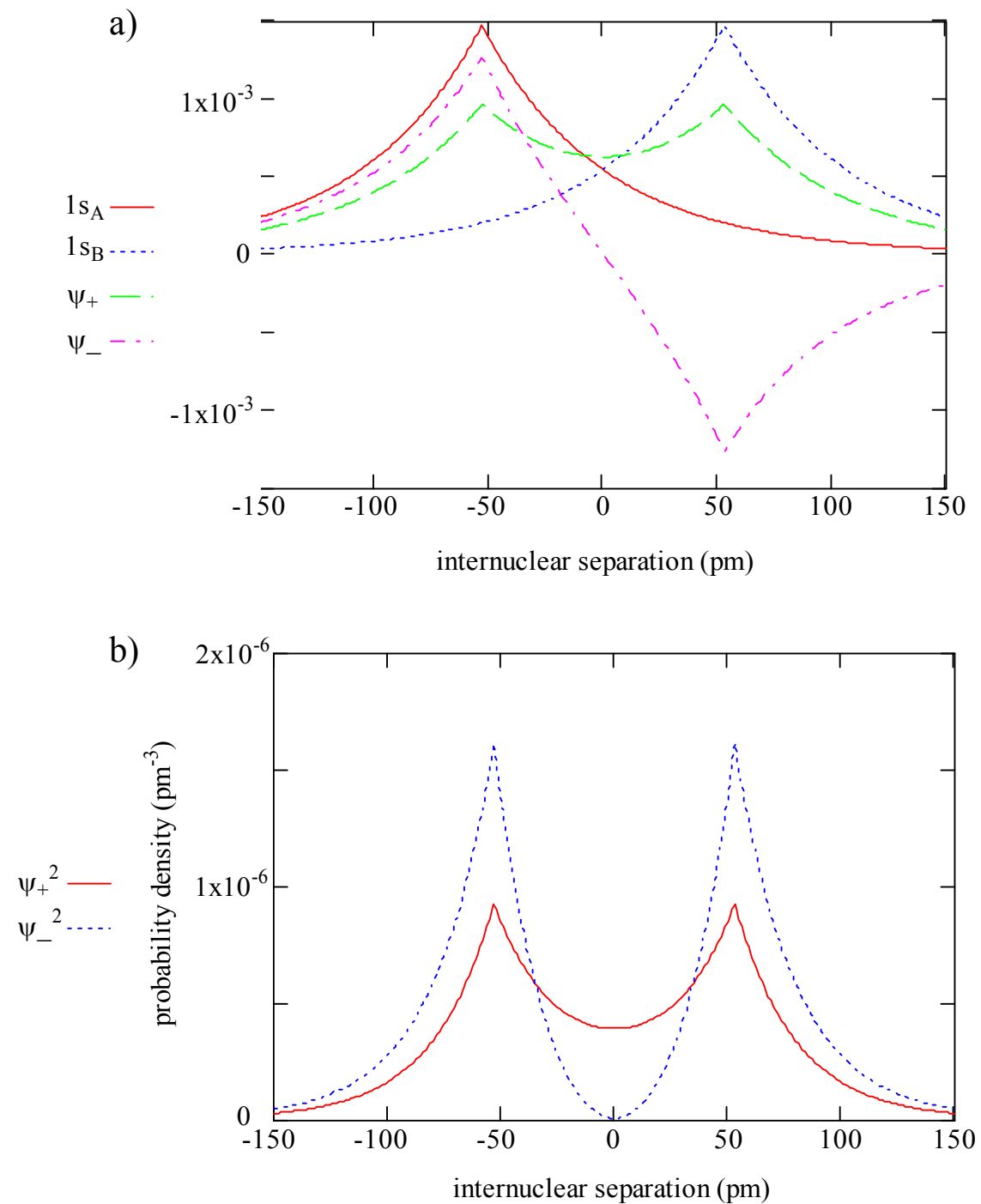be stable or not and also how much energy is required to dissociate this molecule.

Figure 10.3   a) The 1s basis functions and bonding and antibonding molecular orbitals plotted along the internuclear axis, which is defined as the z-axis, for H_2^+. The protons are

located at ± 53 pm, which corresponds to the experimental bond length. b) The electron probability density for the bonding and antibonding molecular orbitals.
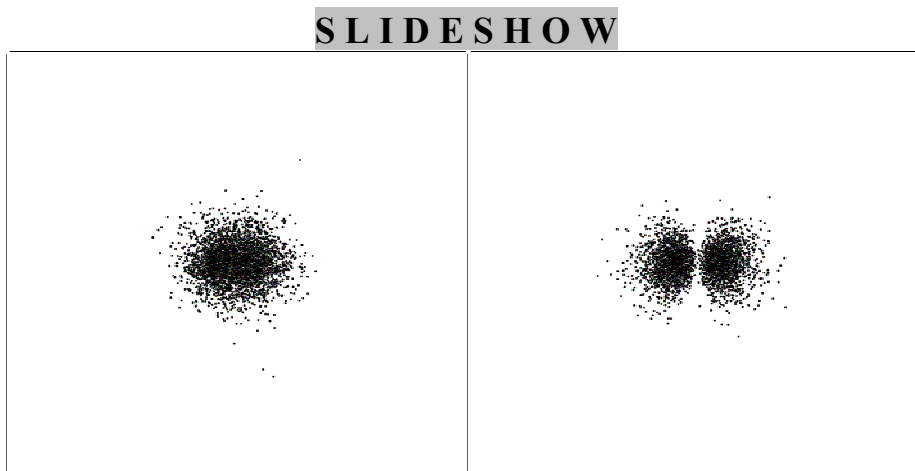
SLIDESHOW

Figure 10.4   Click the images above to open slideshows that demonstrate bonding and antibonding orbitals for H_2 as a function of the internuclear separation.

Exercise 10.10   From the information in Figure 10.1 for H_2^+, calculate the difference in the electronic charge density (C/pm^3) at a point halfway between the two nuclei for an electron in the bonding molecular orbital compared to one in the antibonding molecular orbital.

The constants C_+ and C_- are evaluated from the normalization condition. Bracket notation, $\langle \; | \; \rangle$, is used in Equation {10-16} to represent integration over all the coordinates of the electron for both functions ψ_+ and ψ_-. The right bracket represents a function, the left bracket represents the complex conjugate of the function, and the two together mean integrate over all the coordinates.

$$\int \psi_\pm^* \, \psi_\pm \; d\tau \;\; = \;\; \langle \psi_\pm | \psi_\pm \rangle \;\; = \;\; 1 \qquad\qquad \{10\text{-}16\}$$

$$\langle C_\pm \left[1s_A \pm 1s_B \right] | \; C_\pm \left[1s_A \pm 1s_B \right] \rangle \;\; = \;\; 1 \qquad\qquad \{10\text{-}17\}$$

$$|C_\pm|^2 \left[\left(1s_A | 1s_A \right) + \left(1s_B | 1s_B \right) \pm \left(1s_B | 1s_A \right) \pm \left(1s_A | 1s_B \right) \right] \;\; = \;\; 1 \qquad \{10\text{-}18\}$$

Since the atomic orbitals are normalized, the first two integrals are just 1. The last two integrals are called *overlap integrals* and are symbolized by S and S*, respectively, since one is the complex conjugate of the other.

<div style="border:1px solid blue; padding:10px;">

Exercise 10.11   Show that for two arbitrary functions $\langle \varphi_B | \varphi_A \rangle$ is the complex conjugate of $\langle \varphi_A | \varphi_B \rangle$ and that these two integrals are equal if the functions are real.

</div>

The overlap integrals are telling us to take the value of $1s_B$ at a point multiply by the value of $1s_A$ at that point and sum (integrate) such a product over all of space. If the functions don't overlap, i.e. if one is zero when the other one isn't and vice versa, these integrals then will be zero. It also is possible in general for such integrals to be zero even if the functions overlap because of the cancellation of positive and negative contributions, as was discussed in Section 4.4.

If the overlap integral is zero, for whatever reason, the functions are said to be *orthogonal*. Notice that the overlap integral ranges from 0 to 1 as the separation between the protons varies from $R = \infty$ to $R = 0$. Clearly when the protons are infinite distance apart, there is no overlap, and when $R = 0$ both functions are centered on one nucleus and $\langle 1s_A | 1s_B \rangle$ becomes identical to $\langle 1s_A | 1s_A \rangle$, which is normalized to 1, because then $1s_A = 1s_B$.

With these considerations and using the fact that 1s wavefunctions are real so

$$\langle 1s_A | 1s_B \rangle \;=\; \langle 1s_B | 1s_A \rangle \;=\; S \qquad\qquad \{10\text{-}19\}$$

Equation {10-18} becomes

$$\left| C_\pm \right|^2 \left(2 \pm 2S \right) \;=\; 1 \qquad\qquad \{10\text{-}20\}$$

The solution to Equation {10-20} is given by

$$C_{\pm} = \left[2(1 \pm S)\right]^{-\frac{1}{2}} \qquad \{10\text{-}21\}$$

The energy is calculated from the expectation value integral,

$$E_{\pm} = \left\langle \psi_{\pm} \middle| \hat{H}_{elec} \middle| \psi_{\pm} \right\rangle, \qquad \{10\text{-}22\}$$

which expands to give

$$E_{\pm} = \frac{1}{2(1 \pm S)}\left[\left\langle 1s_A \middle| \hat{H}_{elec} \middle| 1s_A \right\rangle + \left\langle 1s_B \middle| \hat{H}_{elec} \middle| 1s_B \right\rangle \pm \left\langle 1s_A \middle| \hat{H}_{elec} \middle| 1s_B \right\rangle \pm \left\langle 1s_B \middle| \hat{H}_{elec} \middle| 1s_A \right\rangle\right]$$

$$\{10\text{-}23\}$$

Exercise 10.12 Show that Equation {10-22} expands to give Equation {10-23}.

The four integrals in Equation {10-23} can be represented by H_{AA}, H_{BB}, H_{AB}, and H_{BA}, respectively. Notice that A and B appear equivalently in the Hamiltonian operator, Equation {10-13}. This equivalence means that integrals involving $1s_A$ must be the same as corresponding integrals involving $1s_B$, i.e.

$$H_{AA} = H_{BB} \qquad \{10\text{-}24\}$$

and since the wavefunctions are real,

$$H_{AB} = H_{BA} \qquad \{10\text{-}25\}$$

giving

$$E_{\pm} = \frac{1}{1 \pm S} \left(H_{AA} \pm H_{AB} \right). \qquad \{10\text{-}26\}$$

Now examine the details of H_{AA} after inserting Equation {10-13} for the Hamiltonian operator.

$$H_{AA} = \left\langle 1s_A \left| -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0\, r_A} \right| 1s_A \right\rangle + \frac{e^2}{4\pi\varepsilon_0\, R} \left\langle 1s_A \left| 1s_A \right. \right\rangle - \left\langle 1s_A \left| \frac{e^2}{4\pi\varepsilon_0\, r_B} \right| 1s_A \right\rangle$$

$$\{10\text{-}27\}$$

The first term is just the integral for the energy of the hydrogen atom, E_H. The second integral is equal to 1 by normalization; the prefactor is just the Coulomb repulsion of the two protons. The last integral, <u>including the minus sign</u>, is represented by J and is called the Coulomb integral. Physically J is the potential energy of interaction of the electron located around proton A with proton B. It is negative because it is an attractive interaction. It is the average interaction energy of an electron described by the $1s_A$ function with proton B.

Now consider H_{AB}.

$$H_{AB} = \left\langle 1s_A \left| -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0\, r_B} \right| 1s_B \right\rangle + \frac{e^2}{4\pi\varepsilon_0\, R} \left\langle 1s_A \left| 1s_B \right. \right\rangle - \left\langle 1s_A \left| \frac{e^2}{4\pi\varepsilon_0\, r_A} \right| 1s_B \right\rangle$$

$$\{10\text{-}28\}$$

In the first integral we have the hydrogen atom Hamiltonian and the H atom function $1s_B$. The function $1s_B$ is an eigenfunction of the operator with eigenvalue E_H. Since E_H is a constant it factors out of the integral, which then

becomes the overlap integral, S. The first integral therefore reduces to $E_H S$. The second term is just the Coulomb energy of the two protons times the overlap integral. The third term, <u>including the minus sign</u>, is given the symbol K and is called the *exchange integral*. It is called an exchange integral because the electron is described by the $1s_A$ orbital on one side and by the $1s_B$ orbital on the other side of the operator. The electron changes or exchanges position in the molecule. In a Coulomb integral the electron always is in the same orbital; whereas, in an exchange integral, the electron is in one orbital on one side of the operator and in a different orbital on the other side.

Using the expressions for H_{AA} and H_{AB} and substituting into Equation {10-26} produces

$$E_\pm \;=\; \frac{1}{1 \pm S}\left[\left(E_H + \frac{e^2}{4\pi\varepsilon_o R}\right)(1 \pm S) + J \pm K\right] \qquad \{10\text{-}29\}$$

$$E_\pm \;=\; E_H + \frac{e^2}{4\pi\varepsilon_0 R} + \frac{J \pm K}{1 \pm S} \qquad \{10\text{-}30\}$$

$$\Delta E_\pm \;=\; E_\pm - E_H \;=\; \frac{e^2}{4\pi\varepsilon_0 R} + \frac{J \pm K}{1 \pm S} \qquad \{10\text{-}31\}$$

Equation {10-30} tells us that the energy of the H_2^+ molecule is the energy of a hydrogen atom plus the repulsive energy of two protons plus some additional electrostatic interactions of the electron with the protons. These additional interactions are given by $\frac{J \pm K}{1 \pm S}$. If the protons are infinitely far apart then only E_H is nonzero. To get a chemical bond and a stable H_2^+ molecule, $\Delta E_\pm = E_\pm - E_H$

must be less than zero and have a minimum, i.e. $\dfrac{J \pm K}{1 \pm S}$ must be sufficiently

negative to overcome the positive repulsive energy of the two protons $\dfrac{e^2}{4\pi\varepsilon_0\, R}$

for some value of R. For large R these terms are zero, and for small R, the
Coulomb repulsion of the protons rises to infinity.

Exercise 10.13   Show that Equation {10-31} follows from Equation {10-26}.

   We will examine more closely how the Coulomb repulsion term and the
integrals J, K, and S depend on the separation of the protons, but first we want
to discuss the physical significance of J, the Coulomb integral, and K, the
exchange integral. J and K have been defined as

$$J \;=\; \left\langle 1s_A \left| \dfrac{-e^2}{4\pi\varepsilon_0\, r_B} \right| 1s_A \right\rangle \;=\; -\int \varphi^{*}_{1s_A}(\mathbf{r})\, \varphi_{1s_A}(\mathbf{r})\, \dfrac{e^2}{4\pi\varepsilon_0\, r_B}\, d\tau \qquad \{10\text{-}32\}$$

$$K \;=\; \left\langle 1s_A \left| \dfrac{-e^2}{4\pi\varepsilon_0\, r_A} \right| 1s_B \right\rangle \;=\; -\int \varphi^{*}_{1s_A}(\mathbf{r})\, \varphi_{1s_B}(\mathbf{r})\, \dfrac{e^2}{4\pi\varepsilon_0\, r_A}\, d\tau \qquad \{10\text{-}33\}$$

   Note that both integrals are negative since all quantities in the integrand
are positive. In the Coulomb integral, $e\,\varphi^{*}_{1s_A}(\mathbf{r})\, \varphi_{1s_A}(\mathbf{r})$ is the charge density of the
electron around proton A, since $\mathbf{r}$ represents the coordinates of the electron
relative to proton A. Since r_B is the distance of this electron to proton B, the
Coulomb integral gives the potential energy of the charge density around proton
A interacting with proton B. J can be interpreted as an average potential energy
of this interaction because $\varphi^{*}_{1s_A}(\mathbf{r})\, \varphi_{1s_A}(\mathbf{r})$ is the probability density for the
electron at point $\mathbf{r}$, and $\dfrac{e^2}{4\pi\varepsilon_0\, r_B}$ is the potential energy of the electron at that
point due to the interaction with proton B. Essentially, J accounts for the
attraction of proton B to the electron density of hydrogen atom A. As the two

protons get further apart, this integral goes to zero because all values for r_B become very large and all values for $1/r_B$ become very small.

In the exchange integral, K, the product of the two functions is nonzero only in the regions of space where the two functions overlap. If one function is zero or very small at some point then the product will be zero or small. The exchange integral also approaches zero as internuclear distances increase because the both the overlap and the $1/r$ values become zero. The product $e\,\varphi_{1s_A}^{*}(r)\,\varphi_{1s_B}(r)$ is called the *overlap charge density*. Since the overlap charge density is significant in the region of space between the two nuclei, it makes an important contribution to the chemical bond. The exchange integral, K, is the potential energy due to the interaction of the overlap charge density with one of the protons. While J accounts for the attraction of proton B to the electron density of hydrogen atom A, K accounts for the added attraction of the proton due the build-up of electron charge density between the two protons.

Exercise 10.14   Write a paragraph describing in your own words the physical significance of the Coulomb and exchange integrals for H_2^{+}.

Figure 10.5 shows graphs of the terms contributing to the energy of H_2^{+}. In this figure you can see that as the internuclear distance R approaches zero, the Coulomb repulsion of the two protons goes from near zero to a large positive number, the overlap integral goes for zero to one, and J and K become increasingly negative.
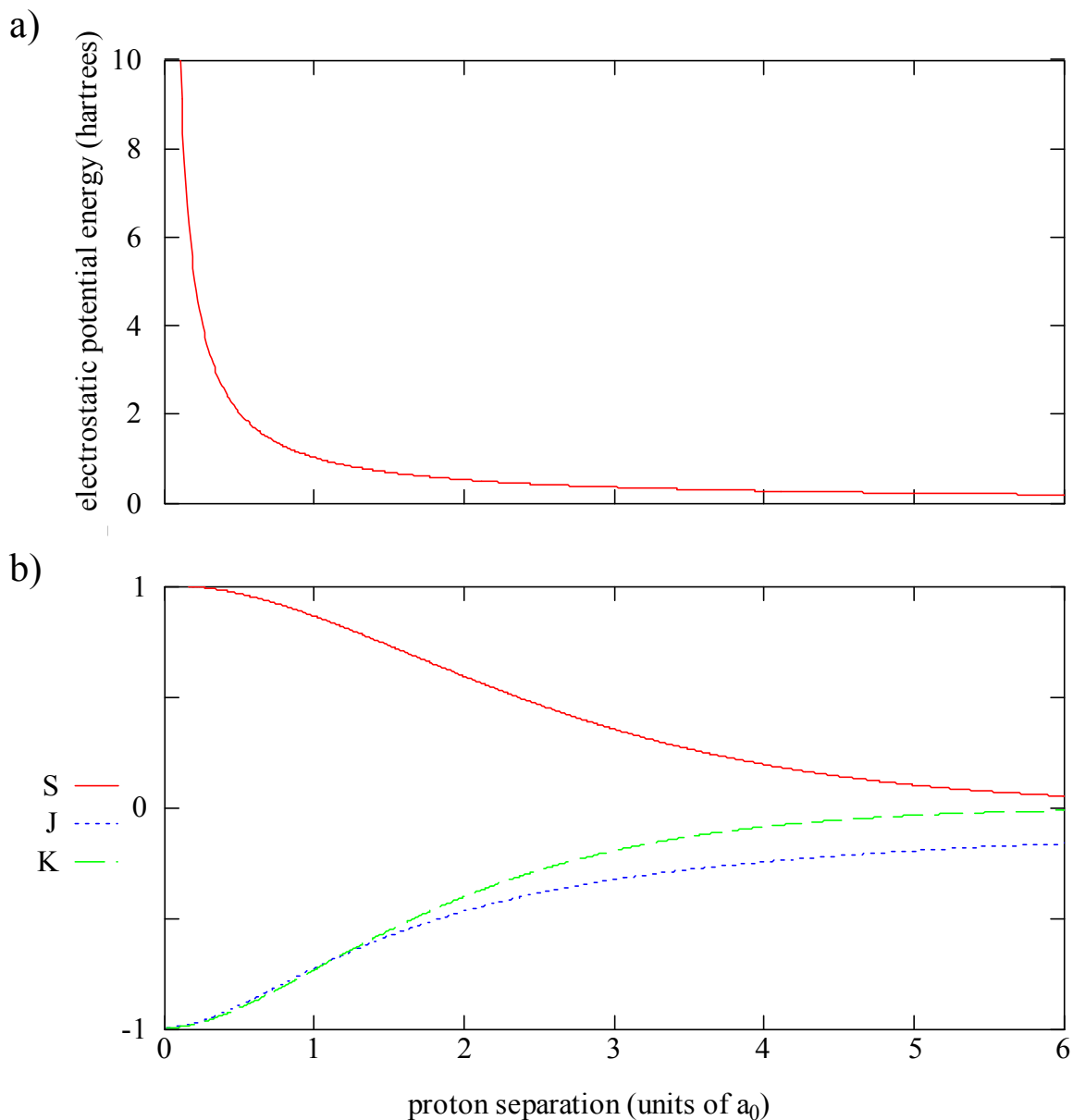
Figure 10.5   a) The electrostatic energy (in hartrees, 27.2 eV) of two protons separated by a distance R in units of the Bohr radius (52.92 pm). b) The overlap, Coulomb, and exchange integrals at different proton separations. The units for J and K are hartrees; S has no units.

Figure 10.6 shows the energy of H_2^+ relative to the energy of a separated hydrogen atom and a proton as given by Equation {10-30}. For the electron in the antibonding orbital, the energy of the molecule, $E_-(R)$, always is greater than the energy of the separated atom and proton.
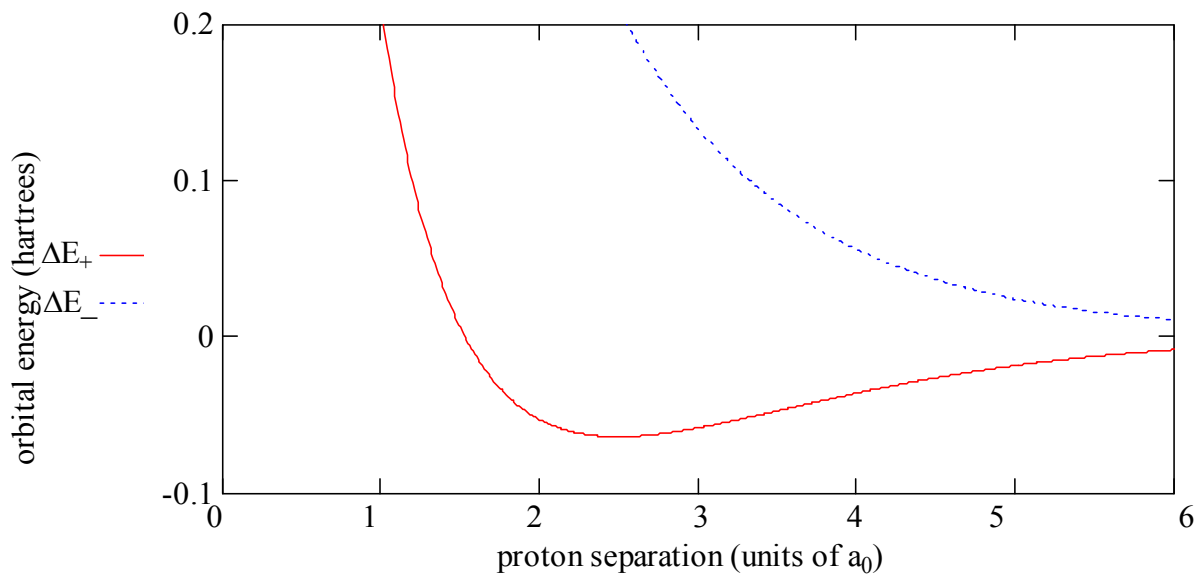
Figure 10.6   Energy of the H_2^+ bonding molecular orbital ΔE_+ and the antibonding molecular orbital ΔE_-, relative to the energy of a separated hydrogen atom and proton.

For the electron in the bonding orbital, you can see that the big effect for the energy of the bonding orbital, $E_+(R)$, is the balance between the repulsion of the two protons $\dfrac{e^2}{4\pi\varepsilon_0 R}$ and J and K, which are both negative. J and K manage to compensate for the repulsion of the two protons until their separation is less than 100 pm (i.e the energy is negative up until this point), and a minimum in the energy is produced at 134 pm. This minimum represents the formation of a chemical bond. The effect of S is small. It only causes the denominator in Equation {10-30} to increase from 1 to 2 as R approaches 0.

For the antibonding orbital, -K is a positive quantity and essentially cancels J so there is not sufficient compensation for the Coulomb repulsion of the protons. The effect of the -K in the expression, Equation {10-30}, for E_- is to account for the absence of overlap charge density and the enhanced repulsion because the charge density between the protons for ψ_- is even lower than that given by the atomic orbitals.

This picture of bonding in H_2^+ is very simple but gives reasonable results when compared to an exact calculation. The equilibrium bond distance is 134 pm compared to 106 pm (exact), and a dissociation energy is 1.8 eV compared to 2.8 eV (exact).

Exercise 10.15 Write the final expressions for the energy of ψ_+ and ψ_-, explain what these expressions mean, and explain why one describes the chemical bond in H_2^+ and the other does not.

Exercise 10.16 Figure 10.5 shows that $S = 1$ and $J = K = 1$ hartree when $R = 0$. Explain why S equals 1 and J and K equal -1 hartree when $R = 0$.

To describe chemical bonding we need to account for the increase in electron density between the two nuclei. The 1s orbitals alone are not particularly good for this purpose because they are spherically symmetric and show no preference for the space between the atomic nuclei. The use of additional atomic orbitals can correct this situation and provide additional parameters, which can be optimized by the variational method, to give a better function with a lower energy and more accurate description of the charge density. Introducing a 2s and 2p orbital provides a hybrid function that points in the direction of the bond and does not decrease as rapidly with distance away from the atomic nucleus as the 1s functions do. The construction of such hybrid functions that point in the direction of the bonds is called *hybridization*, and these functions are known as *hybrid orbitals*.

The result of adding a p_z function to an s function produces a function with a larger amplitude on one side of the nucleus, where both functions are positive, and a smaller amplitude on the other side, where the p function is negative. The shape of the hybrid function resembles that of the p function.

To describe methane, which is tetrahedral, hybrid orbitals are used because the linear combination of an s orbital with three p orbitals provides

four functions that point to the corners of a tetrahedron. Methane is tetrahedral because this geometry is the lowest energy configuration for a C atom and 4 H atoms. Methane is not tetrahedral because of sp^3 hybridization. The sp^3 hybridization scheme only serves to describe the bonding in methane that is determined by the interactions among the nuclei and the electrons. The coefficients in the linear combination required to form the sp^3 hybrid orbitals can be deduced from the constraint that the orbitals point to the corners of a tetrahedron.

Exercise 10.17 Define hybridization and explain why hybrid orbitals are used, why methane is tetrahedral, and why sp^3-hybridized orbitals are used for methane.

10.5 Homonuclear Diatomic Molecules

The LCAO-MO method that we used for H_2^+ can be applied qualitatively to homonuclear diatomic molecules to provide additional insight into chemical bonding. A more quantitative approach also is helpful, especially for more complicated situations, like heteronuclear diatomic molecules and polyatomic molecules. Quantitative theories are described in subsequent sections.

First consider diatomic carbon, C_2. The first question to ask is, "Are the electrons paired or unpaired?" For example, if we start with acetylene and remove 2 hydrogen atoms, we get C_2 with an unpaired electron on each carbon. On the other hand, it might be possible for these electrons to pair up and give C_2 with a quadruple bond. Let's examine the molecular orbital theory of C_2 to see what that theory predicts.

Just as for the hydrogen molecule, we combine the two corresponding atomic orbitals from each atom. We are using the smallest possible basis set for this discussion. From each combination, we get a bonding molecular orbital

and an antibonding molecular orbital. We expect the p_z orbitals on the two atoms to have more overlap than the p_x and p_y orbitals. We therefore expect the exchange integrals to be larger and the resulting molecular orbital $2p_z\sigma_g$ to have a lower energy, i.e. be more bonding, than the $2p_x\pi_u$ and $2p_y\pi_u$, which are degenerate since the x and y directions are equivalent. Using the Aufbau Principle, we assign 2 electrons to each orbital as shown in Figure 10.7, and end up with two electrons to put in two degenerate orbitals. Because of electron-electron repulsion, the lowest energy state will have each electron in a different degenerate orbital where they can be further apart than if they were in the same orbital. This separation reduces the repulsive Coulomb potential energy. Thus in C_2 we have 2 unpaired electrons, each in a bonding molecular orbital. The bond order, which is given by the number of electrons in bonding molecular orbitals minus the number of electrons in antibonding molecular orbitals divided by 2, is however 2, and each unpaired electron is not localized on a single C atom. So we see that the electronic structure of C_2 ($1s\sigma_g^2$, $1s\sigma_u^2$, $2s\sigma_g^2$, $2s\sigma_u^2$, $2p\sigma_g^2$, $2p\pi_u^2$) is quite different from what we would expect by thinking it is acetylene without the two H atoms. The acetylene structure naively predicts a triple bond and two nonbonded electrons on each carbon atom.

The two unpaired electrons in the two $2p\pi_u$ orbitals of C_2 predicted by this simple theory produce a singlet or a triplet ground state. The singlet ground state results if the electron spins are antiparallel ($\alpha\beta$), and the triplet ground state results if the electron spins are parallel (the three triplet spin functions are $\alpha\alpha$, $\alpha\beta+\beta\alpha$, and $\beta\beta$). Hund's rules predict the triplet state to have the lower energy, but the ground state of C_2 is known experimentally to be a singlet state. The singlet state results from a configuration where the $2p\sigma_g$ orbital has a higher energy than the $2p\pi_u$ orbitals, and all electrons are paired ($1s\sigma_g^2$, $1s\sigma_u^2$, $2s\sigma_g^2$, $2s\sigma_u^2$, $2p\pi_u^4$, $2p\sigma_g^0$). The bond order is still 2, but there are no unpaired electrons. All the molecular orbitals are doubly occupied.
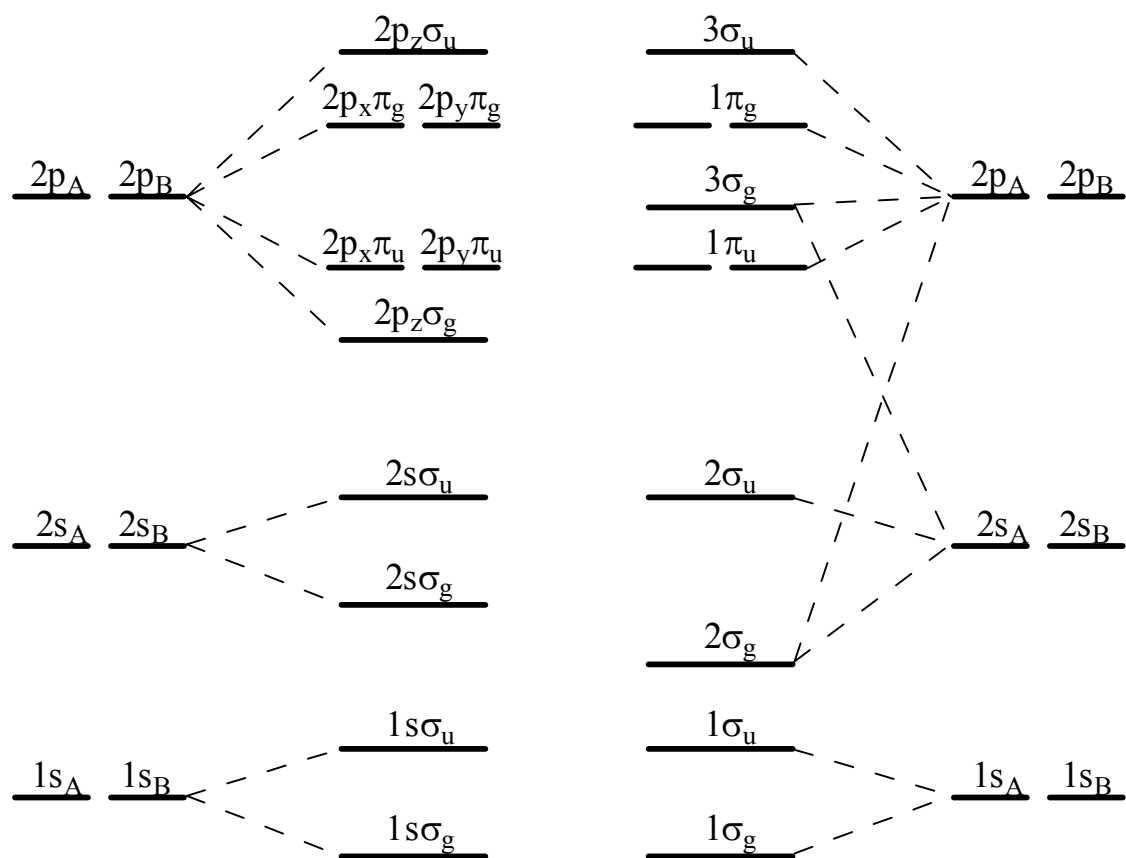
Figure 10.7   Ordering of molecular orbitals by energy for homonuclear diatomic molecules with (right side) and without (left side) significant mixing of molecular orbitals. The vertical energy axis is not to scale.

This configuration is accounted for theoretically by a more complete theory that allows the molecular orbitals to be written as linear combinations of all the valence atomic orbitals not just a pair of them, see Equation {10-8}. The $2\sigma_g$ orbital, which in the simple scheme is $2s_A+2s_B$, is stabilized by mixing with $2p_{zA}+2p_{zB}$, which is the $3\sigma_g$ orbital. As a result of this mixing, the $3\sigma_g$ orbital is destabilized and pushed to higher energy, above the $2p\pi_u$ orbitals. This mixing is just an example of hybridization. Better wavefunctions and better energies are obtained by using hybrid functions, which in this case is a linear combination of 1s and $2p_z$ functions. The relative energies of these hybrid orbitals also are shown on the right hand side of Figure 10.7.

For such mixing to be important, the orbitals must have the same symmetry and be close to each other in energy. Because of these constraints, this mixing is most important for the $2s\sigma_g$ and $2p\sigma_g$ orbitals, both of which have σ_g symmetry.

This ordering is found for all the diatomic molecules of the first row elements except O_2 and F_2. For these two molecules, the energy separation between the 2s and 2p orbitals is larger, and consequently the mixing is not strong enough to alter the energy level structure from that predicted by using the simple two-function basis set.

10.6　　　　Semi-Empirical Methods: Extended Hückel

An electronic structure calculation from first principles (*ab initio*) presents a number of challenges. Many integrals must be evaluated followed by a self-consistent process for assessing the electron-electron interaction and then electron correlation effects must be taken into account. Semi-empirical methods do not proceed analytically in addressing these issues, but rather uses experimental data to facilitate the process. Several such methods are available. These methods are illustrated here by the approaches built on the work of Hückel.

One of the first semi-empirical methods to be developed was [Hückel Molecular Orbital Theory](#) (HMO). HMO was developed to describe molecules containing conjugated double bonds. HMO considered only electrons in pi orbitals and ignored all other electrons in a molecule. It was successful because it could address a number of issues associated with a large group of molecules at a time when calculations were done on mechanical calculators.

The Extended Hückel Molecular Orbital Method (EH) grew out of the need to consider all valence electrons in a molecular orbital calculation. By considering all valence electrons, chemists could determine molecular structure,

compute energy barriers for rotation about bonds, and even determine energies and structures of transition states for reactions. The computed energies could be used to choose between proposed transitions states to clarify reaction mechanisms.

In the EH method, only the n valence electrons are considered. The total valence electron wavefunction is described as a product of the one-electron wavefunctions.

$$\Psi_{valence} \quad = \quad \psi_1(1)\,\psi_2(2)\,\psi_3(3)\,\psi_4(4)\cdots\psi_j(n) \qquad \{10\text{-}34\}$$

where n is the number of electrons and j identifies the molecular orbital. Each molecular orbital is written as an linear combination of atomic orbitals (LCAO).

$$\psi_j \quad = \quad \sum_{r=1}^{N} c_{jr}\,\varphi_r \qquad j \;=\; 1, 2, \dots N \qquad \{10\text{-}35\}$$

where now the ϕ_r are the valance atomic orbitals chosen to include the 2s, $2p_x$, $2p_y$, and $2p_z$ of the carbons and heteroatoms in the molecule and the 1s orbitals of the hydrogen atoms. These orbitals form the *basis set*. Since this basis set contains only the atomic-like orbitals for the valence shell of the atoms in a molecule, it is called a *minimal basis set*.

Each ψ_j, with j = 1...N, represents a molecular orbital, i.e. a wavefunction for one electron moving in the electrostatic field of the nuclei and the other electrons. Two electrons with different spins are placed in each molecular orbital so that the number of occupied molecular orbitals N is half the number of electrons, n, i.e. N = n/2.

The number of molecular orbitals that one obtains by this procedure is equal to the number of atomic orbitals. Consequently, the indices j and r both run from 1 to N. The c_{jr} are the weighting coefficients for the atomic orbitals in the molecular orbital. These coefficients are not necessarily equal, or in

other words, the orbital on each atom is not used to the same extent to form each molecular orbital. Different values for the coefficients give rise to different net charges at different positions in a molecule. This charge distribution is very important when discussing spectroscopy and chemical reactivity.

The energy of the jth molecular orbital is given by a one-electron Schrödinger equation using an effective one electron Hamiltonian, h_{eff}, which expresses the interaction of an electron with the rest of the molecule.

$$h_{eff} \, \psi_j \;\; = \;\; \varepsilon_j \, \psi_j \qquad\qquad \{10\text{-}36\}$$

ε_j is the energy eigenvalue of the jth molecular orbital, corresponding to the eigenfunction ψ_j. The beauty of this method, as we will see later, is that the exact form of h_{eff} is not needed. The total energy of the molecule is the sum of the single electron energies.

$$E_\pi \;\; = \;\; \sum_j n_j \, \varepsilon_j \qquad\qquad \{10\text{-}37\}$$

where n_j is the number of electrons in orbital j.

The expectation value expression for the energy for each molecular orbital is used to find ε_j and then E_π.

$$\varepsilon_j \;\; = \;\; \frac{\int \psi_j * h_{eff} \, \psi_j \, d\tau}{\int \psi_j * \psi_j \, d\tau} \;\; = \;\; \frac{\left\langle \psi_j \left| h_{eff} \right| \psi_j \right\rangle}{\left\langle \psi_j \middle| \psi_j \right\rangle}. \qquad\qquad \{10\text{-}38\}$$

The notation $\left\langle \; || \; \right\rangle$, which is called a bra-ket, just simplifies writing the expression for the integral. Note that the complex conjugate now is identified by the left-side position and the bra notation $\left\langle \; \right|$ and not by an explicit *.

After substituting Equation {10-35} into {10-38}, we obtain for each molecular orbital

$$\varepsilon_j \;=\; \frac{\left\langle \sum\limits_{r=1}^{N} c_{jr}\, \varphi_r \,\middle|\, h_{eff} \,\middle|\, \sum\limits_{s=1}^{N} c_{js}\, \varphi_s \right\rangle}{\left\langle \sum\limits_{r=1}^{N} c_{jr}\, \varphi_r \,\middle|\, \sum\limits_{s=1}^{N} c_{js}\, \varphi_s \right\rangle} \qquad \{10\text{-}39\}$$

which can be rewritten as

$$\varepsilon \;=\; \frac{\sum\limits_{r=1}^{N}\sum\limits_{s=1}^{N} c_r^{*}\, c_s \left\langle \varphi_r \,\middle|\, h_{eff} \,\middle|\, \varphi_s \right\rangle}{\sum\limits_{r=1}^{N}\sum\limits_{s=1}^{N} c_r^{*}\, c_s \left\langle \varphi_r \,\middle|\, \varphi_s \right\rangle} \qquad \{10\text{-}40\}$$

where the index j for the molecular orbital has been dropped because this equation applies to any of the molecular orbitals.

Exercise 10.18   Consider a molecular orbital made up of three atomic orbitals, e.g. the three carbon $2p_z$ orbitals of the allyl radical, where the internuclear axes lie in the xy-plane. Write the LCAO for this MO. Derive the full expression, starting with Equation {10-38} and writing each term explicitly, for the energy expectation value for this LCAO in terms of h_{eff}. Compare your result with Equation {10-40} to verify that Equation {10-40} is the general representation of your result.

Exercise 10.19   Write a paragraph describing how the Variational Method could be used to find values for the coefficients c_{jr} in the linear combination of atomic orbitals.

To simplify the notation we use the following definitions. The integrals in the denominator of Equation {10-40} represent the overlap between two atomic orbitals used in the linear combination. The overlap integral is written as S_{rs}. The integrals in the numerator of Equation {10-40} are called either resonance integrals or coulomb integrals depending on the atomic orbitals on either side of the operator h_{eff} as described below.

$S_{rs} = \langle \varphi_r | \varphi_s \rangle$ is the overlap integral. $S_{rr} = 1$ because we use normalized atomic orbitals. For atomic orbitals r and s on different atoms, S_{rs} has some value between 1 and 0: the further apart the two atoms, the smaller the value of S_{rs}.

$H_{rr} = \langle \varphi_r | h_{eff} | \varphi_r \rangle$ is the *Coulomb Integral*. It is the kinetic and potential energy of an electron in, or described by, an atomic orbital, ϕ_r, experiencing the electrostatic interactions with all the other electrons and all the positive nuclei.

$H_{rs} = \langle \varphi_r | h_{eff} | \varphi_s \rangle$ is the *Resonance Integral or Bond Integral*. This integral gives the energy of an electron in the region of space where the functions ϕ_r and ϕ_s overlap. This energy sometimes is referred to as the energy of the overlap charge. If r and s are on adjacent bonded atoms, this integral has a finite value. If the atoms are not adjacent, the value is smaller, and assumed to be zero in the Hückel model.

In terms of this notation, Equation {10-40} can be written as

$$\varepsilon \;\; = \;\; \frac{\displaystyle\sum_{r=1}^{N} \sum_{s=1}^{N} c_r^* c_s H_{rs}}{\displaystyle\sum_{r=1}^{N} \sum_{s=1}^{N} c_r^* c_s S_{rs}}. \qquad\qquad \{10\text{-}41\}$$

We now must find the coefficients, the c's. One must have a criterion for finding the coefficients. The criterion used is the *Variational Principle*. Since the energy depends linearly on the coefficients in Equation {10-41}, the method we use to find the best set of coefficients is called the Linear Variational Method.

The task is to minimize the energy with respect to all the coefficients by solving the N simultaneous equations produced by differentiating Equation {10-41} with respect to each coefficient.

$$\frac{\partial \varepsilon}{\partial c_t} = 0 \quad \text{for} \quad t = 1, 2, 3, \ldots N \quad \{10\text{-}42\}$$

Actually we also should differentiate Equation $\{10\text{-}41\}$ with respect to the c_t^*, but this second set of N equations is just the complex conjugate of the first and produces no new information or constants.

To carry out this task, rewrite Equation $\{10\text{-}41\}$ to obtain Equation $\{10\text{-}43\}$ and then take the derivative of Equation $\{10\text{-}43\}$ with respect to each of the coefficients.

$$\varepsilon \sum_r \sum_s c_r^* c_s S_{rs} = \sum_r \sum_s c_r^* c_s H_{rs} \quad \{10\text{-}43\}$$

Actually we don't want to do this differentiation N times, so consider the general case where the coefficient is c_t. Here t represents any number between 1 and N.

This differentiation is relatively easy, and the result, which is shown by Equation $\{10\text{-}44\}$, is relatively simple because some terms in Equation $\{10\text{-}43\}$ don't involve c_t and others depend linearly on c_t. The derivative of the terms that don't involve c_t is zero (e.g. $\dfrac{\partial c_3^* c_4 H_{34}}{\partial c_2} = 0$). The derivative of terms that contain c_t is just the constant factor that multiples the c_t, (e.g. $\dfrac{\partial c_3^* c_2 H_{32}}{\partial c_2} = c_3^* H_{32}$). Consequently, only terms in Equation $\{10\text{-}43\}$ that contain c_t contribute to the result, and whenever a term contains c_t, that term appears in Equation $\{10\text{-}44\}$ without the c_t because we are differentiating with respect to c_t. The result after differentiating is

$$\varepsilon \sum_r c_r^* S_{rt} = \sum_r c_r^* H_{rt} . \quad \{10\text{-}44\}$$

If we take the complex conjugate of both sides, we obtain

$$\varepsilon^* \sum_r c_r S_{rt}^* = \sum_r c_r H_{rt}^* . \qquad \{10\text{-}45\}$$

Since $\varepsilon = \varepsilon^*$, $S_{rt}^* = S_{tr}$, and $H_{rt}^* = H_{tr}$, this equation can be reversed and written as

$$\sum_r c_r H_{tr} = \varepsilon \sum_r c_r S_{tr} \qquad \{10\text{-}46\}$$

or upon rearranging as

$$\sum_r c_r (H_{tr} - S_{tr} \varepsilon) = 0 . \qquad \{10\text{-}47\}$$

There are N simultaneous equations that look like this general one; N is the number of coefficients in the LCAO. Each equation is obtained by differentiating Equation {10-43} with respect to one of the coefficients.

Exercise 10.20 Explain why the energy $\varepsilon = \varepsilon^*$, show that $S_{rt}^* = S_{tr}$ (write out the integral expressions and take the complex conjugate of S_{rt}), and show that $H_{rt}^* = H_{tr}$ (write out the integral expressions, take the complex conjugate of H_{rt}, and use the Hermitian property of quantum mechanical operators).

Exercise 10.21 Rewrite your solution to Exercise 10.18 for the 3-carbon pi system found in the allyl radical in the form of Equation {10-43} and then derive the set of three simultaneous equations for the coefficients. Compare your result with Equation {10-47} to verify that Equation {10-47} is a general representation of your result.

This method is called the linear variational method because the variable parameters affect the energy linearly unlike the shielding parameter in the wavefunction that was discussed in Chapter 10. The shielding parameter appears in the exponential part of the wavefunction and the effect on the energy is nonlinear. A nonlinear variational calculation is more laborious than a linear variational calculation.

Equations {10-46} and {10-47} represent a set of homogeneous linear equations. As we discussed for the case of normal mode analysis in Chapter 6, a number of methods can be used for solving these equations to obtain values for the energies, ε's, and the coefficients, the c_r's.

Matrix methods are the most convenient and powerful. First we write more explicitly the set of simultaneous equations that is represented by Equation {10-46}. The first equation has t = 1, the second t = 2, *etc*. N represents the index of the last atomic orbital in the linear combination.

$$
\begin{aligned}
c_1 H_{11} + c_2 H_{12} + \cdots c_n H_{1N} &= c_1 S_{11} \varepsilon + c_2 S_{12} \varepsilon + \cdots c_N S_{1N} \varepsilon \\
c_1 H_{21} + c_2 H_{22} + \cdots c_n H_{2N} &= c_1 S_{21} \varepsilon + c_2 S_{22} \varepsilon + \cdots c_N S_{2N} \varepsilon \\
\vdots \qquad\qquad \vdots &= \vdots \qquad\qquad\qquad \vdots \\
c_1 H_{N1} + c_2 H_{N22} + \cdots c_N H_{NN} &= c_1 S_{N1} \varepsilon + c_2 S_{N2} \varepsilon + \cdots c_N S_{NN} \varepsilon
\end{aligned}
\qquad \text{\{10-48\}}
$$

This set of equations can be represented in matrix notation.

$$
\mathbf{H}\,\mathbf{C}' = \mathbf{S}\,\mathbf{C}'\,\varepsilon \qquad\qquad \text{\{10-49\}}
$$

Here we have square matrix $\mathbf{H}$ and $\mathbf{S}$ multiplying a column vector $\mathbf{C'}$ and a scalar ε. Rearranging produces

$$
\begin{aligned}
\mathbf{H}\,\mathbf{C}' - \mathbf{S}\,\mathbf{C}'\,\varepsilon &= 0 \\
[\mathbf{H} - \mathbf{S}\,\varepsilon]\,\mathbf{C}' &= 0
\end{aligned}
\qquad \text{\{10-50\}}
$$

Exercise 10.22   For the three atomic orbitals you used in Exercises 10.18 and 10.6, write the Hamiltonian matrix **H**, the overlap matrix **S**, and the vector **C'**. Show by matrix multiplication according to Equation {10-49} that you produce the same Equations that you obtained in Exercise 10.21.

The problem is to solve these simultaneous equations, or the matrix equation, and find the orbital energies, which are the ε's, and the atomic orbital coefficients, the c's, that define the molecular orbitals.

In the EH method we use an effective one electron Hamiltonian, h_{eff}, and then proceed to determine the energy of a molecular orbital

$$\varepsilon_j = \frac{\sum_r c_{jr}^* \sum_s c_{js} H_{rs}}{\sum_r c_{jr}^* \sum_s c_{js} S_{rs}} \qquad \{10\text{-}51\}$$

where $H_{rs} = \langle \varphi_r | h_{eff} | \varphi_s \rangle$ and $S_{rs} = \langle \varphi_r | \varphi_s \rangle$.

Minimization of the energy with respect to each of the coefficients again yields a set of simultaneous equations just like Equation {10-47}.

$$\sum_r c_r (H_{tr} - S_{tr} \varepsilon) = 0 \qquad \{10\text{-}52\}$$

As before, these equations can be written in matrix form

$$\mathbf{H} \mathbf{C}' = \mathbf{S} \mathbf{C}' \varepsilon . \qquad \{10\text{-}49\}$$

Equation {10-49} accounts for one molecular orbital. It has energy ε, and it is defined by the elements in the **C'** column vector, which are the coefficients that multiply the atomic orbital basis functions in the linear combination of atomic orbitals.

We can write one matrix equation for all the molecular orbitals.

$$\mathbf{H} \mathbf{C} = \mathbf{S} \mathbf{C} E \qquad \{10\text{-}53\}$$

where **H** is a square matrix containing the H_{rs}, the one electron energy integrals, and **C** is the matrix of coefficients for the atomic orbitals. Each column in **C** is the **C'** that defines one molecular orbital in terms of the basis functions. In

extended Hückel theory, the overlap is not neglected, and **S** is the matrix of overlap integrals. **E** is the diagonal matrix of orbital energies. All of these are square matrices with a size that equals the number of atomic orbitals used in the LCAO for the molecule under consideration.

Equation {10-53} represents an eigenvalue problem. For any extended Hückel calculation, we need to set up these matrices and then find the eigenvalues and eigenvectors. The eigenvalues are the orbital energies, and the eigenvectors are the atomic orbital coefficients that define the molecular orbital in terms of the basis functions.

Exercise 10.24 What is the size of the **H** matrix for HF? Write out the matrix elements in the **H** matrix using symbols for the wavefunctions appropriate to the HF molecule. Consider this matrix and determine if it is symmetric by examining pairs of off-diagonal elements. In a symmetric matrix, pairs of elements located by reflection across the diagonal are equal, i.e. $H_{rc} = H_{cr}$ where r and c represent the row and column, respectively. Why are such pairs of elements equal? Write out the **S** matrix in terms of symbols, showing the diagonal and the upper right portion of the matrix. This matrix also is symmetric, so if you compute the diagonal and the upper half of it, you know the values for the elements in the lower half. Why are pairs of **S** matrix elements across the diagonal equal?

The elements of the **H** matrix are assigned using experimental data. This approach makes the extended Hückel method a *semi-empirical* molecular orbital method. The basic structure of the method is based on the principles of physics and mathematics while the values of certain integrals are assigned by using educated guessing and experimental data. The H_{rr} are chosen as valence state ionization potentials with a minus sign to indicate binding. The values used by R. Hoffmann when he developed the extended Hückel technique were those of H.A. Skinner and H.O. Pritchard (Trans. Faraday Soc. **49** (1953), 1254). These values for C and H are listed in Table 10.1. The values for the heteroatoms (N, O, and F) are taken from Pople and Beveridge, *Approximate Molecular Orbital Theory*.

Table 10.1 Ionization potentials of various atomic orbitals.

Atomic orbital	Ionization potential (eV)
H 1s	13.6
C 2s	21.4
C 2p	11.4
N 2s	25.58
N 2p	13.9
O 2s	32.38
O 2p	15.85
F 2s	40.20
F 2p	18.66

The H_{rs} values are computed from the ionization potentials according to

$$H_{rs} = \frac{1}{2} K \left(H_{rr} + H_{ss} \right) S_{rs} \qquad \{10\text{-}54\}$$

The rationale for this expression is that the energy should be proportional to the energy of the atomic orbitals, and should be greater when the overlap of the atomic orbitals is greater. The contribution of these effects to the energy is scaled by the parameter K. Hoffmann assigned the value of K after a study of the effect of this parameter on the energies of the occupied orbitals of ethane. The conclusion was that a good value for K is K = 1.75.

Exercise 10.25 Fill in numerical values for the diagonal elements of the Extended Hückel Hamiltonian matrix for HF using the ionization potentials given in Table 10.1.

The overlap matrix also must be determined. The matrix elements are computed using the definition $S_{rs} = \langle \varphi_r | \varphi_s \rangle$ where ϕ_r and ϕ_s are the atomic orbitals. *Slater-type orbitals* (STO's) are used for the atomic orbitals rather than hydrogenic orbitals because integrals involving STO's can be computed more quickly on computers. Slater type orbitals have the form

$$\{10\text{-}55\}$$

where zeta, ζ, is a parameter describing the screened nuclear charge. In the extended Hückel calculations done by Hoffmann, the Slater orbital parameter ζ was 1.0 for the H_{1s} and 1.652 for the C_{2s} and C_{2p} orbitals.

Exercise 10.26 Describe the difference between Slater-type orbitals and hydrogenic orbitals.

Overlap integrals involve two orbitals on two different atoms or centers. Such integrals are called two-center integrals. In such integrals there are two variables to consider, corresponding to the distances from each of the atomic centers, r_A and r_B. Such integrals can be represented as

$$S_{A_{2s} B_{2s}} = \left(\frac{4\,\zeta^5}{3} \right) \int r_A \exp\left(-\zeta\, r_A \right) r_B \exp\left(-\zeta\, r_B \right) d\tau \qquad \{10\text{-}56\}$$

but elliptical coordinates must be used for the actual integration. Fortunately the software that does extended Hückel calculations contains the programming code to do overlap integrals. The interested reader will find sufficient detail on the evaluation of overlap integrals and the creation of the programmable mathematical form for any pair of Slater orbitals in Appendix B4 (pp. 199 - 200) of the book *Approximate Molecular Orbital Theory* by Pople and Beveridge. The values of the overlap integrals for HF are given in Table. 10.2.

Table 10.2 Overlap Integrals for HF

	F 2s	F $2p_x$	F $2p_y$	F $2p_z$	H 1s
F 2s					0.47428
F $2p_x$					0
F $2p_y$					0.38434
F $2p_z$					0
H 1s					

Our goal is to find the coefficients in the linear combinations of atomic orbitals and the energies of the molecular orbitals. For these results, we need to transform Equation {10-53}

$$\mathbf{H\,C} \;=\; \mathbf{S\,C\,E} \qquad\qquad \{10\text{-}53\}$$

into a form that allows us to use matrix diagonalization techniques. We are hampered here by the fact that the overlap matrix is not diagonal because the orbitals are not orthogonal. Mathematical methods do exist that can be used to transform a set of functions into an orthogonal set. Essentially these methods apply a transformation of the coordinates from the local coordinate system describing the molecule into one where the atomic orbitals in the LCAO are all orthogonal. Such a transformation can be accomplished through matrix algebra, and computer algorithms for this procedure are part of all molecular orbital

programs. The following paragraph describes how this transformation can be accomplished.

If the matrix $\mathbf{M}$ has an inverse $\mathbf{M}^{-1}$ then

$$\mathbf{M}\,\mathbf{M}^{-1} = 1 \qquad \{10\text{-}57\}$$

and we can place this product in a matrix equation without changing the equation. When this is done for Equation {10-53}, we obtain

$$\mathbf{H}\,\mathbf{M}\,\mathbf{M}^{-1}\,\mathbf{C} = \mathbf{S}\,\mathbf{M}\,\mathbf{M}^{-1}\,\mathbf{C}\,\mathbf{E} \qquad \{10\text{-}58\}$$

Next multiply on the left by $\mathbf{M^{-1}}$ and determine $\mathbf{M}$ so the product $\mathbf{M^{-1}SM}$ is the identity matrix, i.e. a matrix that has 1's on the diagonal and 0's off the diagonal is the case for an orthogonal basis set.

$$\mathbf{M}^{-1}\,\mathbf{H}\,\mathbf{M}\,\mathbf{M}^{-1}\,\mathbf{C} = \mathbf{M}^{-1}\,\mathbf{S}\,\mathbf{M}\,\mathbf{M}^{-1}\,\mathbf{C}\,\mathbf{E} \qquad \{10\text{-}59\}$$

which then can be written as

$$\mathbf{H}''\,\mathbf{C}'' = \mathbf{C}''\,\mathbf{E}'' \qquad \{10\text{-}60\}$$

where

$$\mathbf{C}' = \mathbf{M}^{-1}\,\mathbf{C} \qquad \{10\text{-}61\}$$

The identity matrix is not included because multiplying by the identity matrix is just like multiplying by the number 1. It doesn't change anything. The $\mathbf{H''}$ matrix can be diagonalized by multiplying on the left by the inverse of $\mathbf{C''}$ to find the energies of the molecular orbitals in the resulting diagonal matrix $\mathbf{E}$.

$$\mathbf{E} = \mathbf{C}''^{-1}\,\mathbf{H}''\,\mathbf{C}'' \qquad \{10\text{-}62\}$$

The matrix $\mathbf{C}''$ obtained in the diagonalization step is finally back transformed to the original coordinate system with the $\mathbf{M}$ matrix, $\mathbf{C} = \mathbf{M}\,\mathbf{C}''$ since $\mathbf{C}'' = \mathbf{M}^{-1}\mathbf{C}.$

Fortunately this process is automated in some computer software. For example, in Mathcad, the command genvals(H,S) returns a list of the eigenvalues for Equation {10-53}. These eigenvalues are the diagonal elements of **E**. The command genvecs(H,S) returns a matrix of the normalized eigenvectors corresponding to the eigenvalues. The ith eigenvalue in the list goes with the ith column in the eigenvector matrix. This problem, where **S** is not the identity matrix, is called a general eigenvalue problem, and *gen* in the Mathcad commands refers to *general*.

Exercise 10.29 Using your solution to Exercise 10.28, find the orbital energies and wavefunctions for HF given by an extended Hückel calculation. Construct an orbital energy level diagram, including both the atomic and molecular orbitals, and indicate the atomic orbital composition of each energy level. Draw lines from the atomic orbital levels to the molecular orbital levels to show which atomic orbitals contribute to which molecular orbitals. What insight does your calculation provide regarding the ionic or covalent nature of the chemical bond in HF?

10.7 Mulliken Populations

Mulliken populations (R.S. Mulliken, J. Chem. Phys. 23, 1833, 1841, 23389, 2343 (1955)) can be used to characterize the electronic charge distribution in a molecule and the bonding, antibonding, or nonbonding nature of the molecular orbitals for particular pairs of atoms. To develop the idea of these populations, consider a real, normalized molecular orbital composed from two normalized atomic orbitals.

$$\psi_i \;=\; c_{ij}\,\varphi_j + c_{ik}\,\varphi_k \qquad\qquad \{10\text{-}63\}$$

The charge distribution is described as a probability density by the square of this wavefunction.

$$\psi_i^2 \;=\; c_{ij}^2\,\varphi_j^2 + c_{ik}^2\,\varphi_k^2 + 2c_{ij}\,c_{ik}\,\varphi_j\,\varphi_k \qquad\qquad \{10\text{-}64\}$$

Integrating over all the electronic coordinates and using the fact that the molecular orbital and atomic orbitals are normalized produces

$$1 \ = \ c_{ij}^2 + c_{ik}^2 + 2c_{ij} \, c_{ik} \, S_{jk} \qquad\qquad \{10\text{-}65\}$$

where S_{jk} is the overlap integral involving the two atomic orbitals.

Mulliken's interpretation of this result is that one electron in molecular orbital ψ_ι contributes c_{ij}^2 to the electronic charge in atomic orbital ϕ_j, c_{ik}^2 to the electronic charge in atomic orbital ϕ_k, and $2c_{ij}c_{ik}S_{jk}$ to the electronic charge in the overlap region between the two atomic orbitals. He therefore call c_{ij}^2 and c_{ik}^2, the *atomic-orbital populations*, and $2c_{ij}c_{ik}S_{jk}$, the *overlap population*. The overlap population is >0 for a bonding molecular orbital, <0 for an antibonding molecular orbital, and 0 for a nonbonding molecular orbital.

It is convenient to tabulate these populations in matrix form for each molecular orbital. Such a matrix is called the *Mulliken population matrix*. If there are two electrons in the molecular orbital, then these populations are doubled. Each column and each row in a population matrix is corresponds to an atomic orbital, and the diagonal elements give the atomic-orbital populations, and the off-diagonal elements give the overlap populations. For our example, Equation {10-63}, the population matrix is

$$\mathbf{P_i} \ = \ \begin{pmatrix} c_{ij}^2 & 2c_{ij} \, c_{ik} \, S_{jk} \\ 2c_{ij} \, c_{ik} \, S_{jk} & c_{ik}^2 \end{pmatrix}. \qquad\qquad \{10\text{-}66\}$$

Since there is one population matrix for each molecular orbital, it generally is difficult to deal with all the information in the population matrices. Forming the *net population matrix* decreases the amount of data. The net population matrix is the sum of all the population matrices for the occupied orbitals.

$$\mathbf{NP} \ = \ \sum_{i=\text{occupied}} \mathbf{P_i} \qquad\qquad \{10\text{-}67\}$$

The net population matrix gives the atomic-orbital populations and overlap populations resulting from all the electrons in all the molecular orbitals. The diagonal elements give the total charge in each atomic orbital, and the off-diagonal elements give the total overlap population, which characterizes the total contribution of the two atomic orbitals to the bond between the two atoms.

The *gross population matrix* condenses the data in a different way. The net population matrix combines the contributions from all the occupied molecular orbitals. The gross population matrix combines the overlap populations with the atomic orbital populations for each molecular orbital. The columns of the gross population matrix correspond to the molecular orbitals, and the rows correspond to the atomic orbitals. A matrix element specifies the amount of charge, including the overlap contribution, that a particular molecular orbital contributes to a particular atomic orbital. Values for the matrix elements are obtained by dividing each overlap population in half and adding each half to the atomic-orbital populations of the participating atomic orbitals. The matrix elements provide the gross charge that a molecular orbital contributes to the atomic orbital. *Gross* means that overlap contributions are included. The gross population matrix therefore also is called the *charge matrix for the molecular orbitals*. An element of the gross population matrix (in the jth row and i^{th} column) is given by

$$\mathbf{GP}_{ji} \quad = \quad \mathbf{Pi}_{jj} + \frac{1}{2} \sum_{k \neq j} \mathbf{Pi}_{jk} \qquad \qquad \{10\text{-}68\}$$

where $\mathbf{Pi}$ is the population matrix for the ith molecular orbital, $\mathbf{Pi}_{jj}$ is the atomic-orbital population and the $\mathbf{Pi}_{jk}$ is the overlap population for atomic orbitals j and k in the ith molecular orbital.

Further condensation of the data can be obtained by considering atomic and overlap populations by atoms rather than by atomic orbitals. The resulting

matrix is called the *reduced-population matrix*. The reduced population is obtained from the net population matrix by adding the atomic orbital populations and the overlap populations of all the atomic orbitals of the same atom. The rows and columns of the reduced population matrix correspond to the atoms.

Atomic-orbital charges are obtained by adding the elements in the rows of the gross population matrix for the occupied molecular orbitals. Atomic charges are obtained from the atomic orbital charges by adding the atomic-orbital charges on the same atom. Finally, the net charge on an atom is obtained by subtracting the atomic charge from the nuclear charge adjusted for complete shielding by the 1s electrons.

> **Exercise 10.30** Using your results from Exercise 10.29 for HF, determine the Mulliken population matrix for each molecular orbital, the net population matrix, the charge matrix for the molecular orbitals, the reduced population matrix, the atomic orbital charges, the atomic charges, the net charge on each atom, and the dipole moment. Note: The bond length for HF is 91.7 pm and the experimental value for the dipole moment is 6.37×10^{-30} C m.

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.

$$\varphi_j \;=\; \sum_k c_{jk} \, \varphi_k \qquad\qquad \{10\text{-}69\}$$

The contracted Gaussian functions are composed from primitive Gaussian functions to match Slater-type orbitals. 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

$$E = \frac{\int \Psi^* \hat{H} \Psi \, d\tau}{\int \Psi^* \Psi \, d\tau} \qquad \{10\text{-}70\}$$

and find the optimum coefficients c_{jk} for each molecular orbital in Equation {10-69} 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.

$$V_{rs} = \sum_{r=1}^{N-1} \sum_{s=r+1}^{N} \frac{Z_r \, Z_s}{r_{rs}} \qquad \{10\text{-}71\}$$

Exercise 10.31   For a molecule with three nuclei, show that the sums in Equation {10-71} 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*.

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 $\psi_A(\mathbf{r_1})\alpha(1)$, and the spin orbital for electron 2 in a molecule could be $\psi_B(\mathbf{r_2})\beta(2)$, 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. $\psi_A(\mathbf{r_1})\alpha(1)$ and $\psi_A(\mathbf{r_2})\beta(2)$, 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.

Now consider the results of a self-consistent field calculation for carbon monoxide, C$-$O. 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, B24 (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

$$\psi_k \;=\; \sum_{j=1}^{10} C_{kj}\,\varphi_j \qquad\qquad \{10\text{-}72\}$$

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 10.3.5 gives the energy of the ground state,

$$E \;=\; \frac{\left\langle \Psi\middle|\hat{H}\middle|\Psi\right\rangle}{\left\langle \Psi\middle|\Psi\right\rangle}, \qquad\qquad \{10\text{-}73\}$$

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 mo's. Only the largest terms have been retained here. These functions are listed and discussed in order of increasing energy.

$1\sigma \approx 0.94\ 1s_O$. 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.

$2\sigma \approx 0.92\ 1s_C$. 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.

$3\sigma \approx (0.72\ 2s_O + 0.18\ 2p_{zO}) + (0.28\ 2s_C + 0.16\ 2p_{zC})$. 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.

$4\sigma \approx (0.37\ 2s_C + 0.1\ 2p_{zC}) + (0.54\ 2p_{zO} - 0.43\ 2s_O)$. 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.

$1\pi \approx 0.32\ 2p_{xC} + 0.44\ 2p_{xO}$ and $2\pi \approx 0.32\ 2p_{yC} + 0.44\ 2p_{yO}$. 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.

5σ ≈ 0.38 2$_{sC}$ - 0.38 2$_{pC}$ - 0.29 2p$_{zO}$. 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 10.33   Summarize how Quantum Mechanics is used to describe bonding and the electronic structure of molecules.

Exercise 10.34   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.

10.9   Correlation Energy and Configuration Interaction

The Hartree-Fock energy is not as low as the exact energy. The difference is due to electron correlation effects and is called the correlation energy. The Hartree-Fock wavefunction does not include these correlation effects because it describes the electrons as moving in the average potential field of all the other electrons. The instantaneous influence of electrons that come close together at some point is not taken into account. Electrons repel each other, and they will try to stay away from each other. Their motion

therefore is correlated, and this correlation reduces the energy of the system because it reduces the electron-electron repulsion. The Hartree-Fock wavefunction does not account for this correlation and therefore produces an energy that is too high.

One method for accounting for these correlation effects and the correlation energy is called *configuration interaction* (CI). In configuration interaction, Slater determinants are formed from two or more orbital occupation configurations. The CI wavefunction then is written as a linear combination of these determinants, and the coefficients are determined to minimize the energy.

$$\Psi_{CI} = c_1 D_1 + c_2 D_2 \qquad \{10\text{-}74\}$$

Exercise 10.35 Define correlation energy and explain why it is omitted in a SCF calculation and how it is included in a CI calculation.

Exercise 10.36 Write a CI wavefunction for helium using Slater determinants for the $1s^2$ and $1s^1 2s^1$ configurations. Explain how addition of the $1s^1 2s^1$ configuration to the wavefunction accounts for electron correlation in terms of keeping the electrons apart in different regions of space.

Good quality one-electron molecular orbitals are obtained by using a large basis set, by optimizing the parameters in the functions with the variational method, and by accounting for the electron-electron repulsion using the self-consistent field method. Electron correlation effects are taken into account with configuration interaction (CI). The CI methodology means that a wavefunction is written as a series of Slater Determinants involving different configurations, just as we discussed for the case of atoms. The limitation in this approach is that computer speed and capacity limit the size of the basis set and the number of configurations that can be used.

10.10　　　　Electronic States

The electronic configuration of an atom or molecule is a concept imposed by the orbital approximation. Spectroscopic transitions and other properties of atoms and molecules result from the states and not from the configurations, although it is useful to think about both the configuration and the state whenever possible. While a single determinant wavefunction generally is adequate for closed-shell systems (i.e. all electrons are paired in spatial orbitals), the best descriptions of the electronic states, especially for excited states and free radicals that have unpaired electrons, involve configuration interaction using multiple determinants. In these descriptions different configurations are mixed together and the picture of an orbital configuration disintegrates, and other properties, such as orbital and spin angular momentum and symmetry, are needed to identify and characterize the electronic states of molecules.

While a component of orbital angular momentum is preserved along the axis of a linear molecule, generally orbital angular momentum is quenched due to the irregular shapes of molecules. Angular momentum is quenched because circular motion is not possible when the potential energy function does not have circular symmetry.

The spin orbitals, however, still can be eigenfunctions of the spin angular momentum operators because the spin-orbit coupling usually is small. The resulting spin state depends on the orbital configuration, *e.g.* see Figure 10.2. For a closed-shell configuration, the spin state is a singlet and the spin angular momentum is 0 because the contributions from the α and β spins cancel. For an open shell configuration, which is characteristic of free radicals, there is an odd number of electrons and the spin quantum number $S = \frac{1}{2}$. This configuration produces a doublet spin state since $2S+1 = 2$. Excited configurations result when electromagnetic radiation or exposure to other sources of energy promotes an electron from an occupied orbital to a previously unoccupied orbital. An

excited configuration for a closed shell system produces two states, a singlet state (2S+1 = 0) and a triplet state (2S+1 = 3) depending on how the electron spins are paired. The z-components of the angular momentum for 2 electrons can add to give +1, 0, or −1 in units of $\hbar$. The three spin functions for a triplet state are

$$\alpha(1)\,\alpha(2)$$
$$\frac{1}{\sqrt{2}}\left[\alpha(1)\,\beta(2) + \alpha(2)\,\beta(1)\right] \qquad \{10\text{-}75\}$$
$$\beta(1)\,\beta(2)$$

and the singlet spin function is

$$\frac{1}{\sqrt{2}}\left[\alpha(1)\,\beta(2) - \alpha(2)\,\beta(1)\right] \qquad \{10\text{-}76\}$$

The singlet and triplet states differ in energy even though the electron configuration is the same. This difference results from the antisymmetry condition imposed on the wavefunctions. The antisymmetry condition reduces the electron-electron repulsion for triplet states, so triplet states have the lower energy.

The electronic states of molecules therefore are labeled and identified by their spin and orbital angular momentum and symmetry properties, as appropriate. For example, the ground state of the hydrogen molecule is designated as $X^1\Sigma_g^+$. In this symbol, the X identifies the state as the ground state, the superscript 1 identifies it as a singlet state, the sigma says the orbital angular momentum is 0, and the g identifies the wavefunction as symmetric with respect to inversion. Other states with the same symmetry and angular momentum properties are labeled as A, B, C, etc in order of increasing energy or order of discovery. States with different spin multiplicities from that of the ground state are labeled with lower case letters, a, b, c, etc.

For polyatomic molecules the symmetry designation and spin multiplicity are used. For example, an excited state of naphthalene is identified as $^1B_{1u}$. The superscript 1 identifies it as a singlet state, The letter B and subscript 1 identifies the symmetry with respect to rotations, and the subscript u says the wavefunction is antisymmetric with respect to inversion.

Good quality descriptions of the electronic states of molecules are obtained by using a large basis set, by optimizing the parameters in the functions with the variational method, and by accounting for the electron-electron repulsion using the self-consistent field method. Electron correlation effects are taken into account with configuration interaction (CI). The CI methodology means that a wavefunction is written as a series of Slater Determinants involving different configurations, just as we discussed for the case of atoms. The limitation in this approach is that computer speed and capacity limit the size of the basis set and the number of configurations that can be used.

Study Guide

- What is meant by the expression *ab initio* calculation?

- List all the terms in a complete molecular Hamiltonian.

- Why are calculations on closed-shell systems more easily done than on open-shell systems?

- How is it possible to reduce a multi-electron Hamiltonian operator to a single-electron Fock operator?

- Why is the calculation with the Fock operator called a self-consistent field calculation?

- What is the physical meaning of a SCF one-electron energy?

- Why is the nonlinear variational method not used in every case to optimize basis functions, and what usually is done instead?

- Why is it faster for a computer to use the variational principle to determine the coefficients in a linear combination of functions than to determine the parameters in the functions?

- Identify the characteristics of hydrogenic, Slater, and Gaussian basis sets.

- What is meant by the Hartree-Fock wavefunction and energy?

- What is the difference between a restricted and unrestricted Hartree-Fock calculation?

- What is neglected that makes the Hartree-Fock energy necessarily greater than the exact energy?

- What is meant by correlation energy?

- What purpose is served by including configuration interaction in a calculation?

Problems

1. Produce computer-generated graphs like those in Figure 10.1 that plot the amplitude of the atomic and molecular orbitals along the inter-nuclear axis (defined as the z-axis) of the H_2^+ molecule.

    a) Plot the four basis functions for the H_2^+ molecule ($\varphi_{1sA}, \varphi_{1sB}, \varphi_{2p_zA}, \varphi_{2p_zB}$).

    b) Construct and graph a bonding molecular orbital using these basis functions with a parameter λ multiplying the $2p_z$ functions, for a few values of the parameter λ between 0 and 1. Determine the normalization constant N for each value of λ by assuming that the atomic overlap

integrals are either 0 or 1.

$$\psi = \frac{1}{N}\left[\varphi_{1sA} + \varphi_{1sB} + \lambda\left(\varphi_{2p_zA} + \varphi_{2p_zB}\right)\right]$$

c) Explain why the molecular orbital you graphed is a bonding orbital.

d) Explain why a value for λ greater than 0 should improve the description of a bonding orbital.

2. Construct energy level diagrams for B_2 and O_2 that show both the atomic orbitals and the molecular orbitals and use these diagrams to explain why both molecules are paramagnetic. Label the molecular orbitals to reveal both their symmetry and their atomic orbital parentage. Note: one diagram and labeling does not apply to both molecules.

3. Defend or shoot down the following statement. The Born-Oppenheimer approximation predicts that vibrational frequencies, vibrational force constants, and bond dissociation energies should be independent of isotopic substitution.

4. From the following bond lengths and dipole moments, compute the charges on the hydrogen atom and the halide atom. Compare the results with the electronegativities predicted from the order of these elements in the Periodic Table. What do these charges tell you about the contribution of the hydrogen 1s atomic orbital to the molecular orbitals for each molecule? Use the insight you gained from this problem, to define ionic and covalent bonding.

Molecule	R_0 in pm	μ in 10^{-30} C m
HF	91.7	6.37

HCl	127.5	3.44
HBr	141.4	2.64
HI	160.9	1.40

5. Explain in terms of both the electronic charge density and the electronic energy, why chemists describe the overlap of atomic orbitals as being important for bond formation.

6. Compare the extended Hückel calculation on HF with the SCF calculation reported in

B.j. Ransil, Rev. Mod. Phys. 32, 239, 245 (1960) in J.A. Pople and D.L. Beveridge, Approximate Molecular Orbital Theory (McGraw-Hill, 1970) pp. 46-51.

Activity 1   Extended Hückel calculations on formaldehyde

A Mathcad worksheet for this activity is provided.

Acrobat file: FormaldehydeMC11.pdf

Mathcad 11 file: FormaldehydeMC11.mcd

Mathcad 2000 file: FormaldehydeMC2000.mcd

Activity 2   Analysis of a photoelectron spectrum

A photoelectron spectrum is obtained by measuring the kinetic energy, E_K, of electrons emitted from a molecule by ionization with a high-energy

source with energy $h\nu_0$. The ionization energy or potential, I_E, of these electrons is given by

$$I_E = h\nu_0 - E_K. \hspace{3cm} \{10\text{-}77\}$$

Koopmans' Theorem or Approximation says that an orbital wave function, ϕ_k, and orbital energy, ε_k, obtained by a SCF calculation doesn't change if an electron is added or removed from this orbital. Consequently, the peaks or bands appearing in a photoelectron spectrum can be assigned to ionization from particular molecular orbitals in a molecule by comparing the SCF orbital energies with the ionization energies determined from the photoelectron spectrum.

In this activity, Hyperchem (or the software provided by your instructor) will be used to calculate orbital energies to provide the information needed to analyze the photoelectron spectrum of formamide. Formamide is the simplest manifestation of the amide bond. The amide bond, also known as the peptide linkage, joins amino acids to form peptides and proteins.

Data for you to analyze is provided in the Mathcad or Acrobat links above.

a) Use Hyperchem to perform a 6-31G SCF calculation on formamide.

b) Use the data to identify the orbitals being ionized to produce the peaks labeled 1 through 6 in the formamide photoelectron spectrum given below.

c) Characterize these orbitals by specifying their atomic orbital parentage and their bonding, antibonding, and nonbonding properties.

Using Hyperchem for an *ab initio* calculation:

- Double click on the Draw tool to produce the Periodic Table.

- Click on the Element in the Table and then click on the Workspace to produce that element. Close the Periodic Table when finished.

- Drag from one atom to another to produce single bonds.

- Left-Click on a bond to produce a double bond. Right-Click to remove a bond.

- On the Build menu select Add H and Model Build.

- On the Setup menu select ab initio.

- Select Basis Set Other 6-31G. Use default parameters for all options.

- Make sure Options/Configuration Interaction is None.

- Under File menu select Start Log. Type Title and identify a Directory for the file.

- Under Compute menu select Geometry Optimization.

- Log information level should be Level 4. Assume this is the case by default.

- When calculation is finished, Stop Log under the File menu.

- Examine data pertaining to the orbitals in the File menu.

- Examine the orbitals using Orbitals under the Compute menu.

- Experiment with other Basis Sets and Configuration Interaction if you have time.
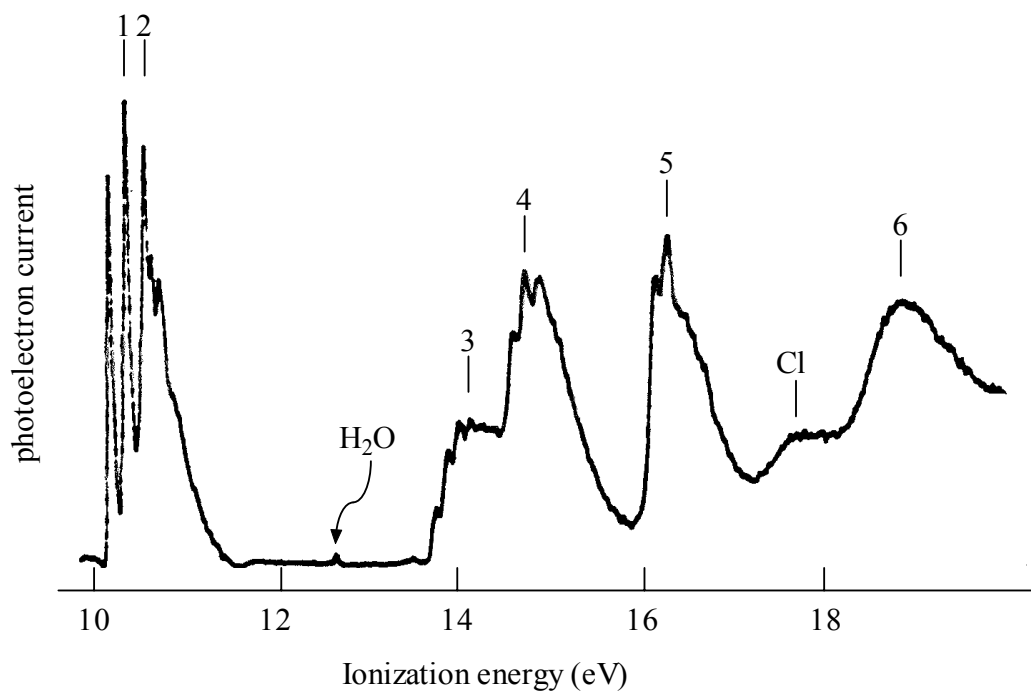
Figure 10.8   Photoelectron Spectrum of formamide H₂NCHO. (from Kimura, permission pending)

Activity 3

Carry out an Extended Hückel Calculation on CO and compare the results with the SCF calculation reported by Huo J. (Chem. Phys. 43, B24 (1965)).

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