

# An Introduction to Theoretical Chemistry

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## Chapter 6

# Electronic structures

Electrons are the “glue” that holds the nuclei together in the chemical bonds of molecules and ions. Of course, it is the nuclei’s positive charges that bind the electrons to the nuclei. The competitions among Coulomb repulsions and attractions as well as the existence of non-zero electronic and nuclear kinetic energies make the treatment of the full electronic–nuclear Schrödinger equation an extremely difficult problem. Electronic structure theory deals with the quantum states of the electrons, usually within the Born–Oppenheimer approximation (i.e., with the nuclei held fixed). It also addresses the forces that the electrons’ presence creates on the nuclei; it is these forces that determine the geometries and energies of various stable structures of the molecule as well as transition states connecting these stable structures. Because there are ground and excited electronic states, each of which has different electronic properties, there are different stable-structure and transition-state geometries for each such electronic state. Electronic structure theory deals with all of these states, their nuclear structures, and the spectroscopies (e.g., electronic, vibrational, rotational) connecting them.

### **Theoretical treatment of electronic structure: atomic and molecular orbital theory**

In Chapter 5’s discussion of molecular structure, I introduced you to the strategies that theory uses to interpret experimental data relating to such matters, and how and why theory can also be used to simulate the behavior of molecules. In carrying out simulations, the Born–Oppenheimer electronic energy  $E(R)$  as a function of the  $3N$  coordinates of the  $N$  atoms in the molecule plays a central role. It is on this landscape that one searches for stable isomers and transition states, and it is the second derivative (Hessian) matrix of this function that provides the harmonic vibrational frequencies of such isomers. In the present chapter, I want to provide you with an introduction to the tools that we use to solve the electronic Schrödinger equation to generate  $E(R)$  and the electronic wave function  $\Psi(r | R)$ . In essence, this treatment will focus on orbitals of atoms and molecules and how we obtain and interpret them.

For an atom, one can approximate the orbitals by using the solutions of the hydrogenic Schrödinger equation discussed in the Background Material. Although such functions are not proper solutions to the actual  $N$ -electron Schrödinger equation (believe it or not, no one has ever solved exactly any such equation for  $N > 1$ ) of any atom, they can be used as perturbation or variational starting-point approximations when one may be satisfied with qualitatively accurate answers. In particular, the solutions of this one-electron hydrogenic problem form the qualitative basis for much of atomic and molecular orbital theory. As discussed in detail in the Background Material, these orbitals are labeled by  $n$ ,  $l$ , and  $m$  quantum numbers for the bound states and by  $l$  and  $m$  quantum numbers and the energy  $E$  for the continuum states.

Much as the particle-in-a-box orbitals are used to qualitatively describe  $\pi$ -electrons in conjugated polyenes or electronic bands in solids, these so-called hydrogen-like orbitals provide qualitative descriptions of orbitals of atoms with more than a single electron. By introducing the concept of screening as a way to represent the repulsive interactions among the electrons of an atom, an effective nuclear charge  $Z_{\text{eff}}$  can be used in place of  $Z$  in the hydrogenic  $\psi_{n,l,m}$  and  $E_{n,l}$  formulas of the Background Material to generate approximate atomic orbitals to be filled by electrons in a many-electron atom. For example, in the crudest approximation of a carbon atom, the two 1s electrons experience the full nuclear attraction, so  $Z_{\text{eff}} = 6$  for them, whereas the 2s and 2p electrons are screened by the two 1s electrons, so  $Z_{\text{eff}} = 4$  for them. Within this approximation, one then occupies two 1s orbitals with  $Z = 6$ , two 2s orbitals with  $Z = 4$  and two 2p orbitals with  $Z = 4$  in forming the full six-electron product wave function of the lowest-energy state of carbon:

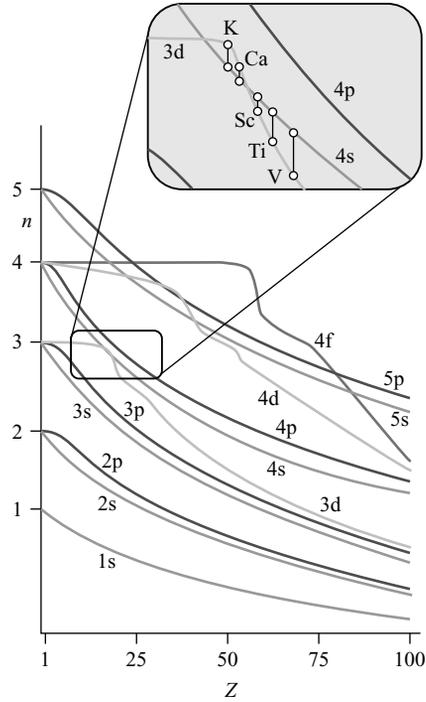
$$\Psi(1, 2, \dots, 6) = \psi_{1s\alpha}(1)\psi_{1s\beta}(2)\psi_{2s\alpha}(3) \dots \psi_{2p(0)\beta}(6). \quad (6.1)$$

However, such approximate orbitals are not sufficiently accurate to be of use in quantitative simulations of atomic and molecular structure. In particular, their energies do not properly follow the trends in atomic orbital (AO) energies that are taught in introductory chemistry classes and that are shown pictorially in Fig. 6.1. For example, the relative energies of the 3d and 4s orbitals are not adequately described in a model that treats electron repulsion effects in terms of a simple screening factor. So, now it is time to examine how we can move beyond the screening model and take the electron repulsion effects, which cause the inter-electronic couplings that render the Schrödinger equation insoluble, into account in a more reliable manner.

## 6.1 Orbitals

### 6.1.1 The Hartree description

The energies and wave functions within the most commonly used theories of atomic structure are assumed to arise as solutions of a Schrödinger equation



**Figure 6.1** Energies of atomic orbitals as functions of nuclear charge for neutral atoms.

whose Hamiltonian  $h_e(r)$  possess three kinds of energies:

- (i) Kinetic energy, whose average value is computed by taking the expectation value of the kinetic energy operator  $-\hbar^2/2m\nabla^2$  with respect to any particular solution  $\phi_J(r)$  to the Schrödinger equation:  $\text{KE} = \langle \phi_J | -\hbar^2/2m\nabla^2 | \phi_J \rangle$ ;
- (ii) Coulomb attraction energy with the nucleus of charge  $Z$ :  $\langle \phi_J | -Ze^2/r | \phi_J \rangle$ ;
- (iii) Coulomb repulsion energies with all of the  $n - 1$  other electrons, which are assumed to occupy other atomic orbitals (AOs) denoted  $\phi_K$ , with this energy computed as  $\sum_K \langle \phi_J(r)\phi_K(r') | (e^2/|r - r'|) | \phi_J(r)\phi_K(r') \rangle$ .

The so-called Dirac notation  $\langle \phi_J(r)\phi_K(r') | (e^2/|r - r'|) | \phi_J(r)\phi_K(r') \rangle$  is used to represent the six-dimensional Coulomb integral  $J_{J,K} = \int |\phi_J(r)|^2 |\phi_K(r')|^2 (e^2/|r - r'|) dr dr'$  that describes the Coulomb repulsion between the charge density  $|\phi_J(r)|^2$  for the electron in  $\phi_J$  and the charge density  $|\phi_K(r')|^2$  for the electron in  $\phi_K$ . Of course, the sum over  $K$  must be limited to exclude  $K = J$  to avoid counting a “self-interaction” of the electron in orbital  $\phi_J$  with itself.

The total energy  $\varepsilon_J$  of the orbital  $\phi_J$  is the sum of the above three contributions:

$$\begin{aligned} \varepsilon_J = & \langle \phi_J | -\frac{\hbar^2}{2m} \nabla^2 | \phi_J \rangle + \langle \phi_J | -\frac{Ze^2}{|r|} | \phi_J \rangle \\ & + \sum_K \langle \phi_J(r)\phi_K(r') | \frac{e^2}{|r - r'|} | \phi_J(r)\phi_K(r') \rangle. \end{aligned} \quad (6.2)$$

This treatment of the electrons and their orbitals is referred to as the Hartree-level of theory. As stated above, when screened hydrogenic AOs are used to approximate the  $\phi_J$  and  $\phi_K$  orbitals, the resultant  $\varepsilon_J$  values do not produce accurate predictions. For example, the negative of  $\varepsilon_J$  should approximate the ionization energy for removal of an electron from the AO  $\phi_J$ . Such ionization potentials (IPs) can be measured, and the measured values do not agree well with the theoretical values when a crude screening approximation is made for the AOs.

### 6.1.2 The LCAO expansion

To improve upon the use of screened hydrogenic AOs, it is most common to approximate each of the Hartree AOs  $\{\phi_K\}$  as a linear combination of so-called basis AOs  $\{\chi_\mu\}$ :

$$\phi_J = \sum_{\mu} C_{J,\mu} \chi_{\mu}, \quad (6.3)$$

using what is termed the linear-combination-of-atomic-orbitals (LCAO) expansion. In this equation, the expansion coefficients  $\{C_{J,\mu}\}$  are the variables that are to be determined by solving the Schrödinger equation

$$h_e \phi_J = \varepsilon_J \phi_J. \quad (6.4)$$

After substituting the LCAO expansion for  $\phi_J$  into this Schrödinger equation, multiplying on the left by one of the basis AOs  $\chi_\nu$ , and then integrating over the coordinates of the electron in  $\phi_J$ , one obtains

$$\sum_{\mu} \langle \chi_\nu | h_e | \chi_\mu \rangle C_{J,\mu} = \varepsilon_J \sum_{\mu} \langle \chi_\nu | \chi_\mu \rangle C_{J,\mu}. \quad (6.5)$$

This is a matrix eigenvalue equation in which the  $\varepsilon_J$  and  $\{C_{J,\mu}\}$  appear as eigenvalues and eigenvectors. The matrices  $\langle \chi_\nu | h_e | \chi_\mu \rangle$  and  $\langle \chi_\nu | \chi_\mu \rangle$  are called the Hamiltonian and overlap matrices, respectively. An explicit expression for the former is obtained by introducing the earlier definition of  $h_e$ :

$$\begin{aligned} \langle \chi_\nu | h_e | \chi_\mu \rangle = & \langle \chi_\nu | -\frac{\hbar^2}{2m} \nabla^2 | \chi_\mu \rangle + \langle \chi_\nu | -\frac{Ze^2}{|r|} | \chi_\mu \rangle \\ & + \sum_{K,\eta,\gamma} C_{K,\eta} C_{K,\gamma} \langle \chi_\nu(r) \chi_\eta(r') | \left( \frac{e^2}{|r-r'|} \right) | \chi_\mu(r) \chi_\gamma(r') \rangle. \end{aligned} \quad (6.6)$$

An important thing to notice about the form of the matrix Hartree equations is that to compute the Hamiltonian matrix, one must know the LCAO coefficients  $\{C_{K,\gamma}\}$  of the orbitals which the electrons occupy. On the other hand, these LCAO coefficients are supposed to be found by solving the Hartree matrix eigenvalue equations. This paradox leads to the need to solve these equations iteratively in a so-called self-consistent field (SCF) technique. In the SCF process, one inputs an initial approximation to the  $\{C_{K,\gamma}\}$  coefficients. This then

allows one to form the Hamiltonian matrix defined above. The Hartree matrix equations  $\sum_{\mu} \langle \chi_v | h_e | \chi_{\mu} \rangle C_{J,\mu} = \varepsilon_J \sum_{\mu} \langle \chi_v | \chi_{\mu} \rangle C_{J,\mu}$  are then solved for “new”  $\{C_{K,\gamma}\}$  coefficients and for the orbital energies  $\{\varepsilon_K\}$ . The new LCAO coefficients of those orbitals that are occupied are then used to form a “new” Hamiltonian matrix, after which the Hartree equations are again solved for another generation of LCAO coefficients and orbital energies. This process is continued until the orbital energies and LCAO coefficients obtained in successive iterations do not differ appreciably. Upon such convergence, one says that a self-consistent field has been realized because the  $\{C_{K,\gamma}\}$  coefficients are used to form a Coulomb field potential that details the electron–electron interactions.

### 6.1.3 AO basis sets

#### *STOs and GTOs*

As noted above, it is possible to use the screened hydrogenic orbitals as the  $\{\chi_{\mu}\}$ . However, much effort has been expended at developing alternative sets of functions to use as basis orbitals. The result of this effort has been to produce two kinds of functions that currently are widely used.

The basis orbitals commonly used in the LCAO process fall into two primary classes:

- (i) Slater-type orbitals (STOs)  $\chi_{n,l,m}(r, \theta, \phi) = N_{n,l,m,\zeta} Y_{l,m}(\theta, \phi) r^{n-1} \exp(-\zeta r)$  are characterized by quantum numbers  $n$ ,  $l$ , and  $m$  and exponents (which characterize the orbital’s radial “size”)  $\zeta$ . The symbol  $N_{n,l,m,\zeta}$  denotes the normalization constant.
- (ii) Cartesian Gaussian-type orbitals (GTOs)  $\chi_{a,b,c}(r, \theta, \phi) = N'_{a,b,c,\alpha} x^a y^b z^c \exp(-\alpha r^2)$  are characterized by quantum numbers  $a$ ,  $b$ , and  $c$ , which detail the angular shape and direction of the orbital, and exponents  $\alpha$  which govern the radial “size”.

For both types of AOs, the coordinates  $r$ ,  $\theta$ , and  $\phi$  refer to the position of the electron relative to a set of axes attached to the nucleus on which the basis orbital is located. Note that Slater-type orbitals (STOs) are similar to hydrogenic orbitals in the region close to the nucleus. Specifically, they have a non-zero slope near the nucleus (i.e.,  $d/dr(\exp(-\zeta r))_{r=0} = -\zeta$ ). In contrast, GTOs have zero slope near  $r = 0$  because  $d/dr(\exp(-\alpha r^2))_{r=0} = 0$ . We say that STOs display a “cusp” at  $r = 0$  that is characteristic of the hydrogenic solutions, whereas GTOs do not.

Although STOs have the proper “cusp” behavior near nuclei, they are used primarily for atomic and linear-molecule calculations because the multi-center integrals  $\langle \chi_{\mu}(1) \chi_{\nu}(2) | e^2 / |r_1 - r_2| \chi_{\nu}(1) \chi_{\mu}(2) \rangle$  which arise in polyatomic-molecule calculations (we will discuss these integrals later in this chapter) can not efficiently

be evaluated when STOs are employed. In contrast, such integrals can routinely be computed when GTOs are used. This fundamental advantage of GTOs has led to the dominance of these functions in molecular quantum chemistry.

To overcome the primary weakness of GTO functions (i.e., their radial derivatives vanish at the nucleus), it is common to combine two, three, or more GTOs, with combination coefficients which are fixed and not treated as LCAO parameters, into new functions called contracted GTOs or CGTOs. Typically, a series of radially tight, medium, and loose GTOs are multiplied by contraction coefficients and summed to produce a CGTO which approximates the proper “cusp” at the nuclear center (although no such combination of GTOs can exactly produce such a cusp because each GTO has zero slope at  $r = 0$ ).

Although most calculations on molecules are now performed using Gaussian orbitals, it should be noted that other basis sets can be used as long as they span enough of the regions of space (radial and angular) where significant electron density resides. In fact, it is possible to use plane wave orbitals of the form  $\chi(r, \theta, \phi) = N \exp[i(k_x r \sin \theta \cos \phi + k_y r \sin \theta \sin \phi + k_z r \cos \theta)]$ , where  $N$  is a normalization constant and  $k_x$ ,  $k_y$ , and  $k_z$  are quantum numbers detailing the momenta of the orbital along the  $x$ ,  $y$ , and  $z$  Cartesian directions. The advantage to using such “simple” orbitals is that the integrals one must perform are much easier to handle with such functions. The disadvantage is that one must use many such functions to accurately describe sharply peaked charge distributions of, for example, inner-shell core orbitals.

Much effort has been devoted to developing and tabulating in widely available locations sets of STO or GTO basis orbitals for main-group elements and transition metals. This ongoing effort is aimed at providing standard basis set libraries which:

- (i) Yield predictable chemical accuracy in the resultant energies.
- (ii) Are cost effective to use in practical calculations.
- (iii) Are relatively transferable so that a given atom's basis is flexible enough to be used for that atom in various bonding environments (e.g., hybridization and degree of ionization).

### *The fundamental core and valence basis*

In constructing an atomic orbital basis, one can choose from among several classes of functions. First, the size and nature of the primary core and valence basis must be specified. Within this category, the following choices are common:

- (i) A minimal basis in which the number of CGTO orbitals is equal to the number of core and valence atomic orbitals in the atom.
- (ii) A double-zeta (DZ) basis in which twice as many CGTOs are used as there are core and valence atomic orbitals. The use of more basis functions is motivated by a desire to provide additional variational flexibility so the LCAO process can

generate molecular orbitals of variable diffuseness as the local electronegativity of the atom varies.

- (iii) A triple-zeta (TZ) basis in which three times as many CGTOs are used as the number of core and valence atomic orbitals (of course, there are quadruple-zeta and higher-zeta bases also).

Optimization of the orbital exponents ( $\zeta$ s or  $\alpha$ s) and the GTO-to-CGTO contraction coefficients for the kind of bases described above have undergone explosive growth in recent years. The theory group at the Pacific Northwest National Labs (PNNL) offer a World Wide Web site from which one can find (and even download in a form prepared for input to any of several commonly used electronic structure codes) a wide variety of Gaussian atomic basis sets. This site can be accessed at <http://www.emsl.pnl.gov:2080/forms/basisform.html>.

### *Polarization functions*

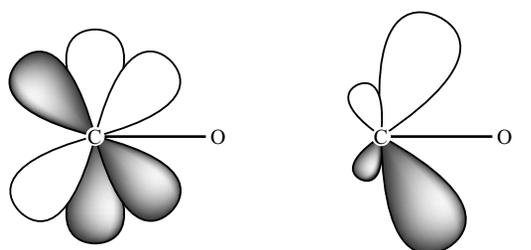
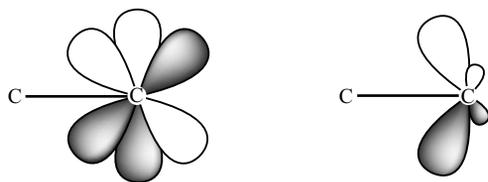
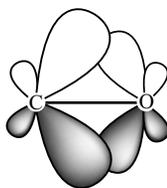
One usually enhances any core and valence basis set with a set of so-called polarization functions. They are functions of one higher angular momentum than appears in the atom's valence orbital space (e.g.,  $d$ -functions for C, N, and O and  $p$ -functions for H), and they have exponents ( $\zeta$  or  $\alpha$ ) which cause their radial sizes to be similar to the sizes of the valence orbitals (i.e., the polarization  $p$  orbitals of the H atom are similar in size to the  $1s$  orbital). Thus, they are not orbitals which describe the atom's valence orbital with one higher  $l$ -value; such higher- $l$  valence orbitals would be radially more diffuse.

The primary purpose of polarization functions is to give additional angular flexibility to the LCAO process in forming bonding orbitals between pairs of valence atomic orbitals. This is illustrated in Fig. 6.2 where polarization  $d_\pi$  orbitals on C and O are seen to contribute to formation of the bonding  $\pi$  orbital of a carbonyl group by allowing polarization of the carbon atom's  $p_\pi$  orbital toward the right and of the oxygen atom's  $p_\pi$  orbital toward the left. Polarization functions are essential in strained ring compounds because they provide the angular flexibility needed to direct the electron density into regions between bonded atoms, but they are also important in unstrained compounds when high accuracy is required.

### *Diffuse functions*

When dealing with anions or Rydberg states, one must further augment the AO basis set by adding so-called diffuse basis orbitals. The valence and polarization functions described above do not provide enough radial flexibility to adequately describe either of these cases. The PNNL web site data base cited above offers a good source for obtaining diffuse functions appropriate to a variety of atoms.

Once one has specified an atomic orbital basis for each atom in the molecule, the LCAO-MO procedure can be used to determine the  $C_{\mu,i}$  coefficients that describe the occupied and virtual (i.e., unoccupied) orbitals. It is important to

Carbon  $p_\pi$  and  $d_\pi$  orbitals combining to form a bent  $\pi$  orbitalOxygen  $p_\pi$  and  $d_\pi$  orbitals combining to form a bent  $\pi$  orbital $\pi$  bond formed from C and O bent ( $\pi$  polarized) AOs

**Figure 6.2** Oxygen and carbon form a  $\pi$  bond that uses the polarization functions on each atom.

keep in mind that the basis orbitals are not themselves the SCF orbitals of the isolated atoms; even the proper atomic orbitals are combinations (with atomic values for the  $C_{\mu,i}$  coefficients) of the basis functions. The LCAO-MO-SCF process itself determines the magnitudes and signs of the  $C_{\mu,i}$ . In particular, it is alternations in the signs of these coefficients that allow radial nodes to form.

### 6.1.4 The Hartree–Fock approximation

Unfortunately, the Hartree approximation discussed above ignores an important property of electronic wave functions – their permutational antisymmetry. The full Hamiltonian

$$H = \sum_j \left( -\frac{\hbar^2}{2m} \nabla_j^2 - \frac{Ze^2}{r_j} \right) + \frac{1}{2} \sum_{j,k} \frac{e^2}{|r_j - r_k|} \quad (6.7)$$

is invariant (i.e., is left unchanged) under the operation  $P_{i,j}$  in which a pair of electrons have their labels ( $i, j$ ) permuted. We say that  $H$  commutes with the permutation operator  $P_{i,j}$ . This fact implies that any solution  $\Psi$  to  $H\Psi = E\Psi$  must also be an eigenfunction of  $P_{i,j}$ . Because permutation operators are

idempotent, which means that if one applies  $P$  twice, one obtains the identity  $PP = 1$ , it can be seen that the eigenvalues of  $P$  must be either  $+1$  or  $-1$ . That is, if  $P\Psi = c\Psi$ , then  $PP\Psi = cc\Psi$ , but  $PP = 1$  means that  $cc = 1$ , so  $c = +1$  or  $-1$ .

As a result of  $H$  commuting with electron permutation operators and of the idempotency of  $P$ , the eigenfunctions  $\Psi$  must either be odd or even under the application of any such permutation. Particles whose wave functions are even under  $P$  are called Bose particles or bosons, those for which  $\Psi$  is odd are called fermions. Electrons belong to the latter class of particles.

The simple spin-orbital product function used in Hartree theory

$$\Psi = \prod_{k=1, N} \phi_k \quad (6.8)$$

does not have the proper permutational symmetry. For example, the Be atom function  $\Psi = 1s\alpha(1) 1s\beta(2) 2s\alpha(3) 2s\beta(4)$  is not odd under the interchange of the labels of electrons 3 and 4; instead one obtains  $1s\alpha(1) 1s\beta(2) 2s\alpha(4) 2s\beta(3)$ . However, such products of spin-orbitals (i.e., orbitals multiplied by  $\alpha$  or  $\beta$  spin functions) can be made into properly antisymmetric functions by forming the determinant of an  $N \times N$  matrix whose row index labels the spin-orbital and whose column index labels the electrons. For example, the Be atom function  $1s\alpha(1) 1s\beta(2) 2s\alpha(3) 2s\beta(4)$  produces the  $4 \times 4$  matrix whose determinant is shown below

$$\begin{vmatrix} 1s\alpha(1) & 1s\alpha(2) & 1s\alpha(3) & 1s\alpha(4) \\ 1s\beta(1) & 1s\beta(2) & 1s\beta(3) & 1s\beta(4) \\ 2s\alpha(1) & 2s\alpha(2) & 2s\alpha(3) & 2s\alpha(4) \\ 2s\beta(1) & 2s\beta(2) & 2s\beta(3) & 2s\beta(4) \end{vmatrix} \quad (6.9)$$

Clearly, if one interchanges any columns of this determinant, one changes the sign of the function. Moreover, if a determinant contains two or more rows that are identical (i.e., if one attempts to form such a function having two or more spin-orbitals equal), it vanishes. This is how such antisymmetric wave functions embody the Pauli exclusion principle.

A convenient way to write such a determinant is as follows:

$$\sum_P (-1)^P \phi_{P_1}(1) \phi_{P_2}(2) \dots \phi_{P_N}(N), \quad (6.10)$$

where the sum is over all  $N!$  permutations of the  $N$  spin-orbitals and the notation  $(-1)^P$  means that a  $-1$  is affixed to any permutation that involves an odd number of pairwise interchanges of spin-orbitals and a  $+1$  sign is given to any that involves an even number. To properly normalize such a determinantal wave function, one must multiply it by  $(N!)^{-1/2}$ . So, the final result is that wave functions of the form

$$\Psi = (N!)^{-1/2} \sum_P (-1)^P \phi_{P_1}(1) \phi_{P_2}(2) \dots \phi_{P_N}(N) \quad (6.11)$$

have the proper permutational antisymmetry. Note that such functions consist of a sum of  $N!$  factors, all of which have exactly the same number of electrons occupying the same number of spin orbitals; the only difference among the  $N!$  terms involves which electron occupies which spin-orbital. For example, in the  $1s\alpha 2s\alpha$  function appropriate to the excited state of He, one has

$$\Psi = (2)^{-1/2} \{1s\alpha(1)2s\alpha(2) - 2s\alpha(1)1s\alpha(2)\}. \quad (6.12)$$

This function is clearly odd under the interchange of the labels of the two electrons, yet each of its two components has one electron in a  $1s\alpha$  spin-orbital and another electron in a  $2s\alpha$  spin-orbital.

Although having to make  $\Psi$  antisymmetric appears to complicate matters significantly, it turns out that the Schrödinger equation appropriate to the spin-orbitals in such an antisymmetrized product wave function is nearly the same as the Hartree Schrödinger equation treated earlier. In fact, the resultant equation is

$$\begin{aligned} h_e \phi_J &= \left[ -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{r} + \sum_K \langle \phi_K(r') | \frac{e^2}{|r-r'|} | \phi_K(r') \rangle \right] \phi_J(r) \\ &\quad - \sum_K \langle \phi_K(r') | \frac{e^2}{|r-r'|} | \phi_J(r') \rangle \phi_K(r) \\ &= \varepsilon_J \phi_J(r). \end{aligned} \quad (6.13)$$

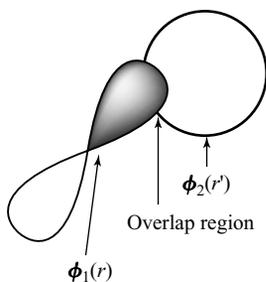
In this expression, which is known as the Hartree–Fock equation, the same kinetic and nuclear attraction potentials occur as in the Hartree equation. Moreover, the same Coulomb potential

$$\begin{aligned} \sum_K \int \phi_K(r') e^2 / |r-r'| \phi_K(r') dr' &= \sum_K \langle \phi_K(r') | e^2 / |r-r'| | \phi_K(r') \rangle \\ &= \sum_K J_K(r) \end{aligned} \quad (6.14)$$

appears. However, one also finds a so-called exchange contribution to the Hartree–Fock potential that is equal to  $\sum_L \langle \phi_L(r') | (e^2 / |r-r'|) | \phi_J(r') \rangle \phi_L(r)$  and is often written in short-hand notation as  $\sum_L K_L \phi_J(r)$ . Notice that the Coulomb and exchange terms cancel for the  $L = J$  case; this causes the artificial self-interaction term  $J_L \phi_L(r)$  that can appear in the Hartree equations (unless one explicitly eliminates it) to automatically cancel with the exchange term  $K_L \phi_L(r)$  in the Hartree–Fock equations.

When the LCAO expansion of each Hartree–Fock (HF) spin-orbital is substituted into the above HF Schrödinger equation, a matrix equation is again obtained:

$$\sum_{\mu} \langle \chi_{\nu} | h_e | \chi_{\mu} \rangle C_{J,\mu} = \varepsilon_J \sum_{\mu} \langle \chi_{\nu} | \chi_{\mu} \rangle C_{J,\mu}, \quad (6.15)$$



**Figure 6.3** An s and a p orbital and their overlap region.

where the overlap integral  $\langle \chi_\nu | \chi_\mu \rangle$  is as defined earlier, and the  $h_e$  matrix element is

$$\begin{aligned} \langle \chi_\nu | h_e | \chi_\mu \rangle = & \langle \chi_\nu | -\frac{\hbar^2}{2m} \nabla^2 | \chi_\mu \rangle + \left\langle \chi_\nu | -\frac{Ze^2}{|r|} \chi_\mu \right\rangle \\ & + \sum_{K,\eta,\gamma} C_{K,\eta} C_{K,\gamma} \left[ \langle \chi_\nu(r) \chi_\eta(r') | \left( \frac{e^2}{|r-r'|} \right) | \chi_\mu(r) \chi_\gamma(r') \rangle \right. \\ & \left. - \langle \chi_\nu(r) \chi_\eta(r') | \left( \frac{e^2}{|r-r'|} \right) | \chi_\gamma(r) \chi_\mu(r') \rangle \right]. \end{aligned} \quad (6.16)$$

Clearly, the only difference between this expression and the corresponding result of Hartree theory is the presence of the last term, the exchange integral. The SCF iterative procedure used to solve the Hartree equations is again used to solve the HF equations.

Next, I think it is useful to reflect on the physical meaning of the Coulomb and exchange interactions between pairs of orbitals. For example, the Coulomb integral  $J_{1,2} = \int |\phi_1(r)|^2 e^2/|r-r'| |\phi_2(r')|^2 dr dr'$  appropriate to the two orbitals shown in Fig. 6.3 represents the Coulomb repulsion energy  $e^2/|r-r'|$  of two charge densities,  $|\phi_1|^2$  and  $|\phi_2|^2$ , integrated over all locations  $r$  and  $r'$  of the two electrons.

In contrast, the exchange integral  $K_{1,2} = \int \phi_1(r) \phi_2(r') e^2/|r-r'| \phi_2(r) \phi_1(r') dr dr'$  can be thought of as the Coulomb repulsion between two electrons whose coordinates  $r$  and  $r'$  are both distributed throughout the “overlap region”  $\phi_1 \phi_2$ . This overlap region is where both  $\phi_1$  and  $\phi_2$  have appreciable magnitude, so exchange integrals tend to be significant in magnitude only when the two orbitals involved have substantial regions of overlap.

Finally, a few words are in order about one of the most computer time-consuming parts of any Hartree–Fock calculation (or those discussed later) – the task of evaluating and transforming the two-electron integrals  $\langle \chi_\nu(r) \chi_\eta(r') | (e^2/|r-r'|) | \chi_\mu(r) \chi_\gamma(r') \rangle$ . Even when  $M$  GTOs are used as basis functions, the evaluation of  $M^4/8$  of these integrals poses a major hurdle. For example, with 500 basis orbitals, there will be of the order of  $7.8 \times 10^9$  such integrals. With each integral requiring 2 words of disk storage, this would require at least  $1.5 \times 10^4$  Mwords of disk storage. Even in the era of modern computers that possess 100 Gby disks, this is a significant requirement. One of the more important technical advances that is under much current development is the efficient calculation of such integrals when the product functions  $\chi_\nu(r) \chi_\mu(r)$  and  $\chi_\gamma(r') \chi_\eta(r')$  that display the dependence on the two electrons' coordinates  $r$  and  $r'$  are spatially distant. In particular, multipolar expansions of these product functions are used to obtain more efficient approximations to their integrals when these functions are far apart. Moreover, such expansions offer a reliable way to “ignore” (i.e., approximate as zero) many integrals whose product functions are sufficiently distant. Such approaches show considerable promise for reducing the  $M^4/8$  two-electron

integral list to one whose size scales much less strongly with the size of the AO basis.

### Koopmans' theorem

The HF-SCF equations  $h_e\phi_i = \varepsilon_i\phi_i$  imply that the orbital energies  $\varepsilon_i$  can be written as

$$\begin{aligned}\varepsilon_i &= \langle \phi_i | h_e | \phi_i \rangle = \langle \phi_i | T + V | \phi_i \rangle + \sum_{j(\text{occupied})} \langle \phi_i | J_j - K_j | \phi_i \rangle \\ &= \langle \phi_i | T + V | \phi_i \rangle + \sum_{j(\text{occupied})} [J_{i,j} - K_{i,j}],\end{aligned}\quad (6.17)$$

where  $T + V$  represents the kinetic ( $T$ ) and nuclear attraction ( $V$ ) energies, respectively. Thus,  $\varepsilon_i$  is the average value of the kinetic energy plus Coulomb attraction to the nuclei for an electron in  $\phi_i$  plus the sum over all of the spin-orbitals occupied in  $\Psi$  of Coulomb minus exchange interactions.

If  $\phi_i$  is an occupied spin-orbital, the  $j = i$  term [ $J_{i,i} - K_{i,i}$ ] disappears in the above sum and the remaining terms in the sum represent the Coulomb minus exchange interaction of  $\phi_i$  with all of the  $N - 1$  other occupied spin-orbitals. If  $\phi_i$  is a virtual spin-orbital, this cancellation does not occur because the sum over  $j$  does not include  $j = i$ . So, one obtains the Coulomb minus exchange interaction of  $\phi_i$  with all  $N$  of the occupied spin-orbitals in  $\Psi$ . Hence the energies of occupied orbitals pertain to interactions appropriate to a total of  $N$  electrons, while the energies of virtual orbitals pertain to a system with  $N + 1$  electrons.

Let us consider the following model of the detachment or attachment of an electron in an  $N$ -electron system.

- (i) In this model, both the parent molecule and the species generated by adding or removing an electron are treated at the single-determinant level.
- (ii) The Hartree–Fock orbitals of the parent molecule are used to describe both species. It is said that such a model neglects “orbital relaxation” (i.e., the reoptimization of the spin-orbitals to allow them to become appropriate to the daughter species).

Within this model, the energy difference between the daughter and the parent can be written as follows ( $\phi_k$  represents the particular spin-orbital that is added or removed): for electron detachment:

$$E^{N-1} - E^N = -\varepsilon_k;\quad (6.18)$$

and for electron attachment:

$$E^N - E^{N+1} = -\varepsilon_k.\quad (6.19)$$

So, within the limitations of the HF, frozen-orbital model, the ionization potentials (IPs) and electron affinities (EAs) are given as the negative of the occupied and virtual spin-orbital energies, respectively. This statement is referred to as

Koopmans' theorem; it is used extensively in quantum chemical calculations as a means of estimating IPs and EAs and often yields results that are qualitatively correct (i.e.,  $\pm 0.5$  eV).

### *Orbital energies and the total energy*

The total HF-SCF electronic energy can be written as

$$E = \sum_{i(\text{occupied})} \langle \phi_i | T + V | \phi_i \rangle + \sum_{i > j(\text{occupied})} [J_{i,j} - K_{i,j}], \quad (6.20)$$

and the sum of the orbital energies of the occupied spin-orbitals is given by

$$\sum_{i(\text{occupied})} \varepsilon_i = \sum_{i(\text{occupied})} \langle \phi_i | T + V | \phi_i \rangle + \sum_{i,j(\text{occupied})} [J_{i,j} - K_{i,j}]. \quad (6.21)$$

These two expressions differ in a very important way; the sum of occupied orbital energies double counts the Coulomb minus exchange interaction energies. Thus, within the Hartree–Fock approximation, the sum of the occupied orbital energies is not equal to the total energy. This finding teaches us that we can not think of the total electronic energy of a given orbital occupation in terms of the orbital energies alone. We need to also keep track of the inter-electron Coulomb and exchange energies.

## 6.1.5 Molecular orbitals

Before moving on to discuss methods that go beyond the HF model, it is appropriate to examine some of the computational effort that goes into carrying out an SCF calculation on molecules. The primary differences that appear when molecules rather than atoms are considered are:

- (i) The electronic Hamiltonian  $h_e$  contains not only one nuclear-attraction Coulomb potential  $\sum_j Z e^2 / r_j$  but a sum of such terms, one for each nucleus in the molecule  $\sum_a \sum_j Z_a e^2 / |r_j - R_a|$ , whose locations are denoted  $R_a$ .
- (ii) One has AO basis functions of the type discussed above located on each nucleus of the molecule. These functions are still denoted  $\chi_{\mu}(r - R_a)$ , but their radial and angular dependences involve the distance and orientation of the electron relative to the particular nucleus on which the AO is located.

Other than these two changes, performing a SCF calculation on a molecule (or molecular ion) proceeds just as in the atomic case detailed earlier. Let us briefly review how this iterative process occurs.

Once atomic basis sets have been chosen for each atom, the one- and two-electron integrals appearing in the  $h$  and overlap matrices must be evaluated. There are numerous highly efficient computer codes that allow such integrals to

be computed for s, p, d, f, and even g, h, and i basis functions. After executing one of these “integral packages” for a basis with a total of  $M$  functions, one has available (usually on the computer’s hard disk) of the order of  $M^2/2$  one-electron ( $\langle \chi_\mu | h_e | \chi_\nu \rangle$  and  $\langle \chi_\mu | \chi_\nu \rangle$ ) and  $M^4/8$  two-electron ( $\langle \chi_\mu \chi_\delta | \chi_\nu \chi_\kappa \rangle$ ) integrals. When treating extremely large atomic orbital basis sets (e.g., 500 or more basis functions), modern computer programs calculate the requisite integrals but never store them on the disk. Instead, their contributions to the  $\langle \chi_\mu | h_e | \chi_\nu \rangle$  matrix elements are accumulated “on the fly” after which the integrals are discarded.

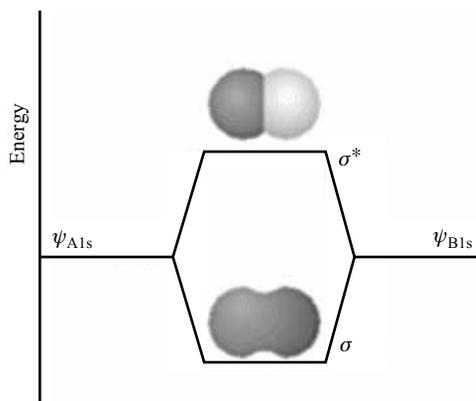
### Shapes, sizes, and energies of orbitals

Each molecular spin-orbital (MO) that results from solving the HF-SCF equations for a molecule or molecular ion consists of a sum of components involving all of the basis AOs:

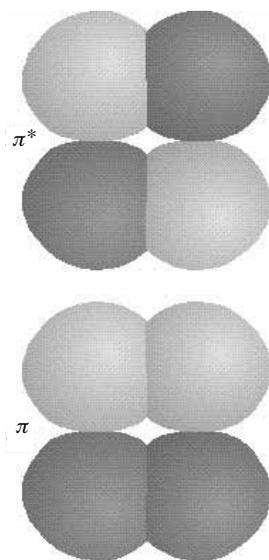
$$\phi_j = \sum_{\mu} C_{j,\mu} \chi_{\mu}. \quad (6.22)$$

In this expression, the  $C_{j,\mu}$  are referred to as LCAO-MO coefficients because they tell us how to linearly combine AOs to form the MOs. Because the AOs have various angular shapes (e.g., s, p, or d shapes) and radial extents (i.e., different orbital exponents), the MOs constructed from them can be of different shapes and radial sizes. Let’s look at a few examples to see what I mean.

The first example arises when two H atoms combine to form the  $H_2$  molecule. The valence AOs on each H atom are the 1s AOs; they combine to form the two valence MOs ( $\sigma$  and  $\sigma^*$ ) depicted in Fig. 6.4. The bonding MO labeled  $\sigma$  has LCAO-MO coefficients of equal sign for the two 1s AOs, as a result of which this MO has the same sign near the left H nucleus (A) as near the right H nucleus (B). In contrast, the antibonding MO labeled  $\sigma^*$  has LCAO-MO coefficients of different sign for the A and B 1s AOs. As was the case in the Hückel or



**Figure 6.4** Two 1s hydrogen atomic orbitals combine to form a bonding and antibonding molecular orbital.



**Figure 6.5** Two  $p_\pi$  atomic orbitals on carbon atoms combine to form a bonding and antibonding molecular orbital.

tight-binding model outlined in the Background Material, the energy splitting between the two MOs depends on the overlap  $\langle \chi_{1sA} | \chi_{1sB} \rangle$  between the two AOs.

An analogous pair of bonding and antibonding MOs arises when two p orbitals overlap “sideways” as in ethylene to form  $\pi$  and  $\pi^*$  MOs which are illustrated in Fig. 6.5. The shapes of these MOs clearly are dictated by the shapes of the AOs that comprise them and the relative signs of the LCAO-MO coefficients that relate the MOs to AOs. For the  $\pi$  MO, these coefficients have the same sign on the left and right atoms; for the  $\pi^*$  MO, they have opposite signs.

I should stress that the signs and magnitudes of the LCAO-MO coefficients arise as eigenvectors of the HF-SCF matrix eigenvalue equation:

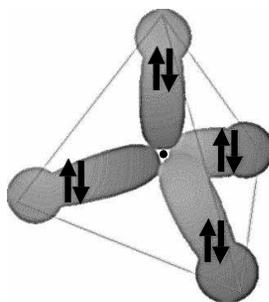
$$\sum_{\mu} \langle \chi_{\nu} | h_e | \chi_{\mu} \rangle C_{j,\mu} = \varepsilon_j \sum_{\mu} \langle \chi_{\nu} | \chi_{\mu} \rangle C_{j,\mu}. \quad (6.23)$$

It is a characteristic of such eigenvalue problems for the lower energy eigenfunctions to have fewer nodes than the higher energy solutions as we learned from several examples that we solved in the Background Material.

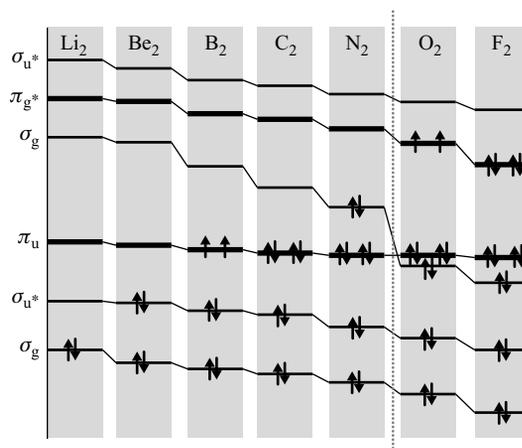
Another thing to note about the MOs shown above is that they will differ in their quantitative details, but not in their overall shapes, when various functional groups are attached to the ethylene molecule’s C atoms. For example, if electron withdrawing groups such as Cl, OH or Br are attached to one of the C atoms, the attractive potential experienced by a  $\pi$  electron near that C atom will be enhanced. As a result, the bonding MO will have larger LCAO-MO coefficients  $C_{k,\mu}$  belonging to the “tighter” basis AOs  $\chi_{\mu}$  on this C atom. This will make the bonding  $\pi$  MO more radially compact in this region of space, although its nodal character and gross shape will not change. Alternatively, an electron donating group such as  $\text{H}_3\text{C}$ – or *t*-butyl attached to one of the C centers will cause the  $\pi$  MO to be more diffuse (by making its LCAO-MO coefficients for more diffuse basis AOs larger).

In addition to MOs formed primarily of AOs of one type (i.e., for  $\text{H}_2$  it is primarily s-type orbitals that form the  $\sigma$  and  $\sigma^*$  MOs; for ethylene’s  $\pi$  bond, it is primarily the C 2p AOs that contribute), there are bonding and antibonding MOs formed by combining several AOs. For example, the four equivalent C–H bonding MOs in  $\text{CH}_4$  shown in Fig. 6.6 each involve C 2s and 2p as well as H 1s basis AOs.

The energies of the MOs depend on two primary factors: the energies of the AOs from which the MOs are constructed and the overlap between these AOs. The pattern in energies for valence MOs formed by combining pairs of first-row atoms to form homonuclear diatomic molecules is shown in Fig. 6.7. In this figure, the core MOs formed from the 1s AOs are not shown, but only those MOs formed from 2s and 2p AOs appear. The clear trend toward lower orbital



**Figure 6.6** The four C–H bonds in methane.



**Figure 6.7** Energies of the valence molecular orbitals in homonuclear diatomic molecules involving first-row atoms.

energies as one moves from left to right is due primarily to the trends in orbital energies of the constituent AOs. That is, F being more electronegative than N has a lower-energy 2p orbital than does N.

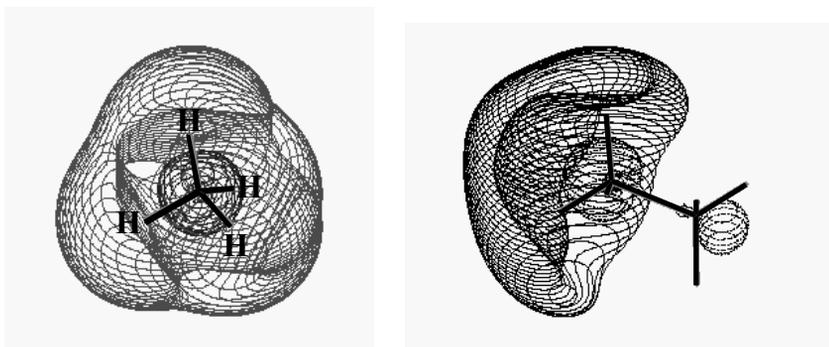
### *Bonding, antibonding, non-bonding, and Rydberg orbitals*

As noted above, when valence AOs combine to form MOs, the relative signs of the combination coefficients determine, along with the AO overlap magnitudes, the MO's energy and nodal properties. In addition to the bonding and antibonding MOs discussed and illustrated earlier, two other kinds of MOs are important to know about.

Non-bonding MOs arise, for example, when an orbital on one atom is not directed toward and overlapping with an orbital on a neighboring atom. For example, the lone pair orbitals on  $\text{H}_2\text{O}$  or on the oxygen atom of  $\text{H}_2\text{C}=\text{O}$  are non-bonding orbitals. They still are described in the LCAO-MO manner, but their  $C_{\mu,i}$  coefficients do not contain dominant contributions from more than one atomic center.

Finally, there is a type of orbital that all molecules possess but that is ignored in most elementary discussions of electronic structure. All molecules have so-called Rydberg orbitals. These orbitals can be thought of as large diffuse orbitals that describe the regions of space an electron would occupy if it were in the presence of the corresponding molecular cation. Two examples of such Rydberg orbitals are shown in Fig. 6.8. On the left, we see the Rydberg orbital of  $\text{NH}_4$  and on the right, that of  $\text{H}_3\text{N}-\text{CH}_3$ . The former species can be thought of as a closed-shell ammonium cation  $\text{NH}_4^+$  around which a Rydberg orbital resides. The latter is protonated methyl amine with its Rydberg orbital.

**Figure 6.8** Rydberg orbitals of  $\text{NH}_4^+$  and of protonated methyl amine.



## 6.2 Deficiencies in the single determinant model

To achieve reasonable chemical accuracy (e.g.,  $\pm 5$  kcal mol $^{-1}$ ) in electronic structure calculations, one can not describe the wave function  $\Psi$  in terms of a single determinant. The reason such a wave function is inadequate is because the spatial probability density functions are not correlated. This means the probability of finding one electron at position  $\mathbf{r}$  is independent of where the other electrons are, which is absurd because the electrons' mutual Coulomb repulsion causes them to "avoid" one another. This mutual avoidance is what we call electron correlation because the electrons' motions, as reflected in their spatial probability densities, are correlated (i.e., inter-related). Let us consider a simple example to illustrate this problem with single determinant functions. The  $|1s\alpha(r) 1s\beta(r')|$  determinant, when written as

$$|1s\alpha(r) 1s\beta(r')| = 2^{-1/2} \{1s\alpha(r) 1s\beta(r') - 1s\alpha(r') 1s\beta(r)\} \quad (6.24)$$

can be multiplied by itself to produce the two-electron spin- and spatial-probability density:

$$P(r, r') = 1/2 \{ [1s\alpha(r) 1s\beta(r')]^2 + [1s\alpha(r') 1s\beta(r)]^2 - 1s\alpha(r) 1s\beta(r') 1s\alpha(r') 1s\beta(r) - 1s\alpha(r') 1s\beta(r) 1s\alpha(r) 1s\beta(r') \}. \quad (6.25)$$

If we now integrate over the spins of the two electrons and make use of

$$\langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1, \quad \text{and} \quad \langle \alpha | \beta \rangle = \langle \beta | \alpha \rangle = 0, \quad (6.26)$$

we obtain the following spatial (i.e., with spin absent) probability density:

$$P(r, r') = |1s(r)|^2 |1s(r')|^2. \quad (6.27)$$

This probability, being a product of the probability density for finding one electron at  $r$  times the density of finding another electron at  $r'$ , clearly has no correlation in it. That is, the probability of finding one electron at  $r$  does not depend on where ( $r'$ ) the other electron is. This product form for  $P(r, r')$  is a direct result of the

single-determinant form for  $\Psi$ , so this form must be wrong if electron correlation is to be accounted for.

### 6.2.1 Electron correlation

Now, we need to ask how  $\Psi$  should be written if electron correlation effects are to be taken into account. As we now demonstrate, it turns out that one can account for electron avoidance by taking  $\Psi$  to be a combination of two or more determinants that differ by the promotion of two electrons from one orbital to another orbital. For example, in describing the  $\pi^2$  bonding electron pair of an olefin or the  $ns^2$  electron pair in alkaline earth atoms, one mixes in doubly excited determinants of the form  $(\pi^*)^2$  or  $np^2$ , respectively.

Briefly, the physical importance of such doubly excited determinants can be made clear by using the following identity involving determinants:

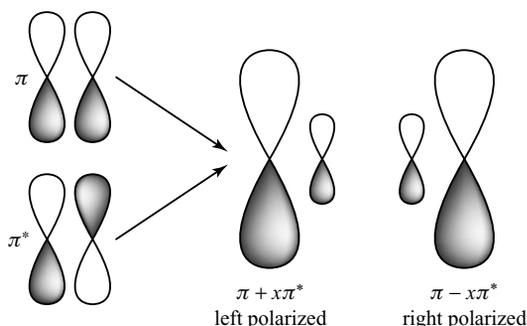
$$C_1 |\dots \phi \alpha \phi \beta \dots| - C_2 |\dots \phi' \alpha \phi' \beta \dots| = C_1/2 \{ |\dots (\phi - x\phi') \alpha (\phi + x\phi') \beta \dots| - |\dots (\phi - x\phi') \beta (\phi + x\phi') \alpha \dots| \}, \quad (6.28)$$

where

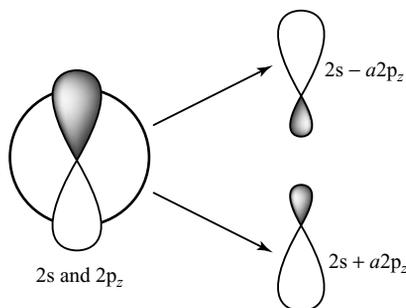
$$x = (C_2/C_1)^{1/2}. \quad (6.29)$$

This allows one to interpret the combination of two determinants that differ from one another by a double promotion from one orbital ( $\phi$ ) to another ( $\phi'$ ) as equivalent to a singlet coupling (i.e., having  $\alpha\beta$ - $\beta\alpha$  spin function) of two different orbitals ( $\phi - x\phi'$ ) and ( $\phi + x\phi'$ ) that comprise what are called polarized orbital pairs. In the simplest embodiment of such a configuration interaction (CI) description of electron correlation, each electron pair in the atom or molecule is correlated by mixing in a configuration state function (CSF) in which that electron pair is “doubly excited” to a correlating orbital.

In the olefin example mentioned above, the two non-orthogonal polarized orbital pairs involve mixing the  $\pi$  and  $\pi^*$  orbitals to produce two left-right polarized orbitals as depicted in Fig. 6.9. In this case, one says that the  $\pi^2$  electron pair



**Figure 6.9** Left and right polarized orbitals of an olefin.



**Figure 6.10** Angularly polarized orbital pairs.

undergoes left-right correlation when the  $(\pi^*)^2$  determinant is mixed into the CI wave function.

In the alkaline earth atom case, the polarized orbital pairs are formed by mixing the  $ns$  and  $np$  orbitals (actually, one must mix in equal amounts of  $p_x$ ,  $p_y$ , and  $p_z$  orbitals to preserve overall  $^1S$  symmetry in this case), and give rise to angular correlation of the electron pair. Such a pair of polarized orbitals is shown in Fig. 6.10. More specifically, the following four determinants are found to have the largest amplitudes in  $\Psi$ :

$$\Psi \cong C_1 |1s^2 2s^2| - C_2 [|1s^2 2p_x^2| + |1s^2 2p_y^2| + |1s^2 2p_z^2|]. \quad (6.30)$$

The fact that the latter three terms possess the same amplitude  $C_2$  is a result of the requirement that a state of  $^1S$  symmetry is desired. It can be shown that this function is equivalent to:

$$\begin{aligned} \Psi \cong & 1/6 C_1 |1s\alpha 1s\beta| \{ [(2s - a2p_x)\alpha(2s + a2p_x)\beta - (2s - a2p_x)\beta(2s + a2p_x)\alpha] \\ & + [(2s - a2p_y)\alpha(2s + a2p_y)\beta - (2s - a2p_y)\beta(2s + a2p_y)\alpha] \\ & + [(2s - a2p_z)\alpha(2s + a2p_z)\beta - (2s - a2p_z)\beta(2s + a2p_z)\alpha] \}, \end{aligned} \quad (6.31)$$

where  $a = \sqrt{3C_2/C_1}$ .

Here two electrons occupy the  $1s$  orbital (with opposite,  $\alpha$  and  $\beta$  spins), and are thus not being treated in a correlated manner, while the other pair resides in  $2s/2p$  polarized orbitals in a manner that instantaneously correlates their motions. These polarized orbital pairs ( $2s \pm a2p_{x,y, \text{ or } z}$ ) are formed by combining the  $2s$  orbital with the  $2p_{x,y, \text{ or } z}$  orbital in a ratio determined by  $C_2/C_1$ .

This ratio  $C_2/C_1$  can be shown using perturbation theory to be proportional to the magnitude of the coupling  $\langle 1s^2 2s^2 | H | 1s^2 2p^2 \rangle$  between the two configurations involved and inversely proportional to the energy difference  $[\langle 1s^2 2s^2 | H | 1s^2 2s^2 \rangle - \langle 1s^2 2p^2 | H | 1s^2 2p^2 \rangle]$  between these configurations. In general, configurations that have similar Hamiltonian expectation values and that are coupled strongly give rise to strongly mixed (i.e., with large  $|C_2/C_1|$  ratios) polarized orbital pairs.

In each of the three equivalent terms in the alkaline earth wave function, one of the valence electrons moves in a  $2s + a2p$  orbital polarized in one direction while

the other valence electron moves in the  $2s - a2p$  orbital polarized in the opposite direction. For example, the first term  $[(2s - a2p_x)\alpha (2s + a2p_x)\beta - (2s - a2p_x)\beta (2s + a2p_x)\alpha]$  describes one electron occupying a  $2s - a2p_x$  polarized orbital while the other electron occupies the  $2s + a2p_x$  orbital. The electrons thus reduce their Coulomb repulsion by occupying different regions of space; in the SCF picture  $1s^2 2s^2$ , both electrons reside in the same  $2s$  region of space. In this particular example, the electrons undergo angular correlation to avoid one another.

The use of doubly excited determinants is thus seen as a mechanism by which  $\Psi$  can place electron pairs, which in the single-configuration picture occupy the same orbital, into different regions of space (i.e., each one into a different member of the polarized orbital pair) thereby lowering their mutual Coulombic repulsion. Such electron correlation effects are extremely important to include if one expects to achieve chemically meaningful accuracy (i.e.,  $\pm 5$  kcal mol<sup>-1</sup>).

## 6.2.2 Essential configuration interaction

There are occasions in which the inclusion of two or more determinants in  $\Psi$  is essential to obtaining even a qualitatively correct description of the molecule's electronic structure. In such cases, we say that we are including essential correlation effects. To illustrate, let us consider the description of the two electrons in a single covalent bond between two atoms or fragments that we label X and Y. The fragment orbitals from which the bonding  $\sigma$  and antibonding  $\sigma^*$  MOs are formed we will label  $s_X$  and  $s_Y$ , respectively.

Several spin- and spatial-symmetry adapted two-electron determinants can be formed by placing two electrons into the  $\sigma$  and  $\sigma^*$  orbitals. For example, to describe the singlet determinant corresponding to the closed-shell  $\sigma^2$  orbital occupancy, a single Slater determinant

$${}^1\sum(0) = |\sigma\alpha\sigma\beta| = (2)^{-1/2}\{\sigma\alpha(1)\sigma\beta(2) - \sigma\beta(1)\sigma\alpha(2)\} \quad (6.32)$$

suffices. An analogous expression for the  $(\sigma^*)^2$  determinant is given by

$${}^1\sum^{**}(0) = |\sigma^*\alpha\sigma^*\beta| = (2)^{-1/2}\{\sigma^*\alpha(1)\sigma^*\beta(2) - \sigma^*\alpha(2)\sigma^*\beta(1)\}. \quad (6.33)$$

Also, the  $M_S = 1$  component of the triplet state having  $\sigma\sigma^*$  orbital occupancy can be written as a single Slater determinant:

$${}^3\sum^*(1) = |\sigma\alpha\sigma^*\alpha| = (2)^{-1/2}\{\sigma\alpha(1)\sigma^*\alpha(2) - \sigma^*\alpha(1)\sigma\alpha(2)\}, \quad (6.34)$$

as can the  $M_S = -1$  component of the triplet state

$${}^3\sum^*(-1) = |\sigma\beta\sigma^*\beta| = (2)^{-1/2}\{\sigma\beta(1)\sigma^*\beta(2) - \sigma^*\beta(1)\sigma\beta(2)\}. \quad (6.35)$$