Appendix A

Overview of ab Initio Molecular Orbital Theory

A Born-Oppenheimer electronic wavefunction ϕ must obey the "clamped nuclei" Schrödinger equation described in Chapter 1,

 $h_{e}(\mathbf{r} | \mathbf{R})\phi(\mathbf{r} | \mathbf{R}) = E(\mathbf{R})\phi(\mathbf{r} | \mathbf{R}).$ (A.1)

Here, h_e , the electronic Hamiltonian, might include spin-orbit operators as well as the usual kinetic energy, electron-nuclear, nuclear-nuclear, and electronelectron interaction terms. For any system containing more than one electron, equation A.1 has never been solved exactly, and one must resort to approximation methods to obtain a description of the wavefunction ϕ and a value for the electronic energy $E(\mathbf{R})$.

• The two most commonly employed approximation techniques are perturbation theory (PT) and the variational method (VM) (Pilar, 1968; Eyring, Walter and Kimball, 1944). The implementation of either approximation begins with finding an appropriate set of molecular orbitals that can subsequently be used to construct a basis of N-electron functions in terms of which ϕ is expanded. Let us first analyze how the molecular orbitals are obtained.

A.1. Orbitals

In the Hartree-Fock (HF) or self-consistent field (SCF) method (Cook, 1978), one uses the variational principle to determine those spin-orbitals $\{\psi_i\}$ —orbitals multiplied by a spin function α or β having $m_s = \pm 1/2$ —that minimize the energy of a single Slater-determinant trial wavefunction ϕ_{SD} (Cook, 1978; Pilar, 1968)

$$\phi_{\rm SD} = \det[\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\cdots\psi_N(\mathbf{r}_N)]. \tag{A.2}$$

This energy-minimization process results in a set of HF or SCF equations that the spin orbitals must obey, namely,

$$F\psi_1 = \epsilon_i \psi_i, \tag{A.3}$$

in which ϵ_i is the orbital energy corresponding to spin orbital ψ_i and F is the Fock operator in atomic units (Pilar, 1968), or

$$F = -\frac{1}{2}\nabla_r^2 - \sum_a \frac{Z_a}{|\mathbf{r} - \mathbf{R}_a|} + \sum_{j_{occ}}^N \int \psi f(\mathbf{r}') \frac{1 - P_{rr'}}{|\mathbf{r} - \mathbf{r}'|} \psi_j(\mathbf{r}') d\mathbf{r}'. \quad (A.4)$$

in which $P_{rr'}$ permutes the coordinates **r** and **r'**, and N is the number of electrons in the system. In the operator F, the sum over j_{occ} refers to those spin orbitals that are *occupied* in ϕ_{SD} . It is through this choice of occupancy that one determines the state (e.g., $1s\alpha 1s\beta$ or $1s\alpha 2s\beta$) for which the SCF calculation is being performed.

In writing the trial variational wavefunction as a single Slater determinant, one assumes that the major component of the true electronic wavefunction ϕ describes uncorrelated motion of the electrons. In other words, although the electrons certainly interact, their motion is not strongly affected by the *instantaneous* positions of the other electrons. The regions of space in which they move (the orbitals) are primarily determined by the *average* interactions among the electrons. This nearly independent-motion ansatz leads to the postulate that ϕ can be approximated as an antisymmetrized product of oneelectron spin orbitals (Pilar, 1961; Cook, 1978); this approximation is similar to giving the probabilities of uncorrelated events as products of probabilities of the individual events.

If the orbitals used to construct ϕ_{SD} are allowed complete variational flexibility, the resulting calculation is referred to as an unrestricted HF (UHF) calculation. In this most general case, the resulting HF spatial orbitals associated with α and β spins will not necessarily be identical. For example, a UHF calculation on the $1s\alpha 1s'\beta 2s\alpha$ occupancy of Li does not yield two identical 1s orbitals ($1s \neq 1s'$). As a result, the Slater determinant det($1s\alpha 1s'\beta 2s\alpha$) is not a pure doublet (s = 1/2) spin eigenfunction (Pauncz, 1979). Although this is indeed an unattractive feature of such UHF wavefunctions, this SCF procedure is widely used as a method for generating molecular orbitals (Pople, 1976). Subsequent to the UHF calculation of the molecular orbitals, the improper spin-symmetry behavior of ϕ_{SD} can be removed by applying a spinprojection operator P, (Pauncz, 1979) to ϕ_{SD} to give a correct spin eigenstate

$$\phi_{s,\text{SD}} = P_{s}\phi_{\text{SD}}.\tag{A.5}$$

The resulting *projected* UHF wavefunction $\phi_{s,SD}$ is generally no longer a single Slater determinant. For example, a doublet (s = 1/2) projection of the $1s\alpha 1s'\beta 2s\alpha$ Slater determinant yields

 $\frac{1}{\sqrt{2}} \left[\det(1s\alpha 1s'\beta 2s\alpha) + \det(1s\beta 1s'\alpha 2s\alpha) \right].$

However, it is still straightforward to compute the energy of $\phi_{s,SD}$ using the Slater-Condon rules (Cook, 1978) discussed below.

As an alternative to projecting a spin-unrestricted Slater determinant, one can force the orbitals that belong to paired electrons to be identical at the start of the SCF procedure and to remain so. For example, one can use the determinant det($1s\alpha 1s\beta 2s\alpha$), which contains only two (1s and 2s) spatial orbitals rather than three (1s, 1s', and 2s). The energy of this spin-restricted HF (RHF) trial function can be minimized to give a set of equations (Roothaan, 1960) analogous to equation A.3, which determine the restricted HF orbitals. This RHF process has the advantage that it does not yield different spatial orbitals for paired electrons. Thus, for the Li example, the RHF ϕ_{sp} automatically has doublet spin symmetry (Pauncz, 1979). A disadvantage of the RHF method is that it is computationally more difficult. Furthermore, its derivation is not entirely free from arbitrary assumptions (Jørgensen and Simons, 1981), which makes it difficult to associate the orbital energies $\{\epsilon_i\}$ with ionization potentials by means of Koopman's theorem (Pilar, 1968; Cook, 1978). In contrast, the UHF method permits the approximate evaluation of (vertical) ionization energies as $-\epsilon_i$.

The UHF or RHF self-consistent-field equations are usually solved by the Roothaan-matrix procedure in which the ψ_i functions are expanded in an atomic orbital (AO) basis $\{X_b\}$. When this expansion is used in equation A.3, one obtains Roothaan-matrix HF equations of either the UHF or RHF variety (Cook, 1978). If M atomic orbitals are used in the expansion, the resulting matrix eigenvalue problem generates N occupied molecular orbitals and 2M - N excited or virtual molecular orbitals.

$$\psi_i = \sum_b C_{ib} X_b(\alpha \text{ or } \beta).$$
(A.6)

The most commonly used atomic orbitals are Slater-type orb.tals (STO), namely,

$$X_b = N_b Y_{l_b m_b} r^{n_b - 1} \exp(-\zeta_b |\mathbf{r} - \mathbf{R}_b|)$$
(A.7)

and Gaussian-type orbitals (GTO),

$$X_a = N_a' X^{k_a} Y^{u_a} Z^{v_a} \exp[-\alpha_a (\mathbf{r} - \mathbf{R}_a)^2].$$
(A.8)

In these defining equations, Y_{lm} is a spherical harmonic, N_b and $N_{a'}$ are normalization constants, $R_{a,b}$ is the position of the nucleus on which the atomic orbital is located, n_b , l_b , m_b , k_a , u_a and v_a are orbital quantum numbers, and ζ_b and α_a are orbital exponents that determine the radial sizes of the atomic orbital.

Slater-type orbitals are to be preferred on fundamental grounds because they display proper cusp behavior at the nuclear centers. For example, the

$$\left[\frac{d}{dr}N\exp(-\zeta r)\right]_{r=0} = -N\zeta.$$
(A.9)

This is precisely the behavior displayed by hydrogenlike orbitals that are eigenfunctions of the one-electron Schrödinger equation having only kinetic and electron-nuclear attraction energies. In contrast, all GTO have zero slope at the nucleus; for example, for the 1s GTO

$$\left[\frac{d}{dr}N\exp(-\alpha r^2)\right]_{r=0} = 0.$$
 (A.10)

Near a nucleus the full Schrödinger differential equation is dominated by the same kinetic and nuclear-electron attraction terms that constitute the hydrogenlike Hamiltonian; thus, the correct wavefunction ϕ must display hydrogenlike cusps at the nuclei. The STO fulfill this criterion; the GTO do not.

The deficiencies of the GTO raise the question of why and how they are used. GTO's are convenient in studies of polyatomic molecules because they allow efficient handling of the multicenter integrals that arise. In integrals containing a product of two orbitals X_a and X_b that have origins on different nuclei \mathbf{R}_a and \mathbf{R}_b , the Gaussian orbitals allow this product to be written in terms of a single common origin. For example, the product of two 1*s*-type GTO's can be expressed as

$$\exp[-\alpha_{a}(\mathbf{r} - \mathbf{R}_{a})^{2}]\exp[-\alpha_{b}(\mathbf{r} - \mathbf{R}_{b})^{2}]$$
$$= \exp[-(\alpha_{a} + \alpha_{b})\mathbf{r}^{2}]\exp\left(-\frac{\alpha_{a}\alpha_{b}}{\alpha_{a} + \alpha_{b}}\mathbf{R}^{2}\right) \qquad (A.11)$$

in which the origin of the final *r*-dependent function is located between \mathbf{R}_a and \mathbf{R}_b at a distance $\alpha_a R/(\alpha_a + \alpha_b)$ from \mathbf{R}_a and $\alpha_b R/(\alpha_a + \alpha_b)$ from \mathbf{R}_b $(R = |\mathbf{R}_a - \mathbf{R}_b|)$. The fact that the product $X_a X_b$ that involves GTO's having different origins can be expressed as a single new GTO at a new origin makes the use of GTO's in evaluating integrals efficient.

To attempt to overcome the improper cusp behavior of GTO's, one often employs *contracted* GTO's (CGTO) (Schaefer, 1972; Dunning, 1970, 1971; Huzinaga, 1965). A CGTO (X_a^c) is a linear combination of the GTO's

$$X_a^c = \sum_b A_{ab} X_b \tag{A.12}$$

in which the GTO $\{X_b\}$ have common quantum numbers (e.g., 1s, 2p, 3d) but different orbital exponents (α_b) . By combining a tight GTO (one having large



Figure A-1 Formation of an STO by addition of loose and tight GTO's.

 α_b) with other GTO's having progressively smaller exponents, one might fit the cusp behavior of the STO. This is shown for 1s-type functions in Figure A-1. By choosing the contraction coefficients $\{A_{ab}\}$ properly, it is possible to generate a CGTO which, in a least-squares sense, reproduces the proper STO cusp behavior (Pople, 1969). Alternatively, the contraction coefficients can be chosen to minimize the SCF energy of the lowest energy state of the atom of interest (Dunning, 1970, 1971). For either of these CGTO for any atom, the CGTO itself can be viewed as the atomic-orbital basis function that is to be used in subsequent molecular SCF calculations. In the literature, tabulations of optimal CGTO's are available for most first-, second-, and third-row atoms based either upon the STO fitting procedure (Pople, 1969) or the atomic-energy optimization procedure (Dunning, 1970, 1971).

In summary, the SCF method can be used to generate a set of molecular orbitals that are expressed in terms of a chosen set of Gaussian- or Slater-type atomic basis functions. The nature of the occupied molecular orbitals, as displayed in the molecular-orbital expansion coefficients of equation A.6, describes the charge density and bonding characteristics of these orbitals. The energies $\{\epsilon_i\}$ of the occupied orbitals give us, via Koopmans' theorem, ionization potentials of the system. However, one must remember that the entire SCF method, including the concept of molecular orbital, is predicated upon the assumption that ϕ is accurately represented by ϕ_{SD} .

128 APPENDIX A

A.2. Configuration Interaction

In Chapter 3 it was shown that it is not always possible to describe the electronic wavefunction ϕ in terms of a *single* orbital-occupancy list (configuration). For example, the fragmentation of heteropolar bonds to give radical products was shown to require both σ^2 and $\sigma\sigma^*$ configurations to describe ϕ throughout the entire bond-dissociation process. For these reasons one must often extend the description of ϕ to include more than one Slater determinant or configuration. Moreover, such a multiconfigurational description should be examined whenever high accuracy in the resulting wavefunction and energy is desired. Hence, even when ϕ is dominated (~95%) by a single Slater determinant, that determinant does not accurately represent the true wavefunction because the Slater determinant describes electrons moving in orbitals determined only by the average interactions with the other electrons and not by the instantaneous interactions. No electron correlation is present in the SCF (single determinant) description.

By writing ϕ as a linear combination of all Slater determinants $\{\phi_I\}$ that can be constructed from the 2M (occupied and virtual) SCF spin orbitals,

$$\phi = \sum_{I} C_{I} \phi_{I}, \tag{A.13}$$

the SCF treatment is improved. In most such configuration-interaction calculations the ϕ_I are symmetry-projected functions (each of which may contain several Slater determinants) describing the various configurations (spin-orbital occupancies) that can be made from 2M orbitals and N electrons (Pauncz, 1979; Shavitt, 1977).

Clearly, the number 2M!/N!(2M-N)! of these configurations becomes extremely large as the basis size (M) and the number of electrons increases. Therefore, various procedures have evolved for selecting the most important of the 2M!/N!(2M-N)! configurations (Shavitt, 1977). The most commonly used criterion for judging the importance of a configuration ϕ_I is to evaluate its interaction strength using the one or few configurations that are absolutely essential to describe ϕ . For example, for the case of heteropolar bond rupture (mentioned above and in Chapter 3) the σ^2 and $\sigma\sigma^*$ configurations are essential. Other configurations ϕ_I (e.g., $\sigma\sigma'$, π^2 , and so forth) are evaluated for their importance by computing their interaction strengths $\langle \phi_I | H | \phi_{essential} \rangle$ for all of the essential configurations. If the interaction strength is large, ϕ_I is considered to be important.

Unfortunately, ranking configurations according to the value of their interaction strengths provides little physical interpretation for the nonessential configurations. However, it is possible to ascribe meaning to those configurations that are either singly (ϕ_n) or doubly (ϕ_n) excited relative to a dominant essential configuration ϕ_e . The contributions to ϕ made by a configuration in which one electron is promoted from ψ_{μ} (occupied in ϕ_e) to ψ_p (unoccupied in ϕ_e) can be denoted $\phi_{s\mu}^p$. The trial wavefunction $\phi_e + C_s \phi_{s\mu}^p$ consisting of two Slater determinants is (because the two determinants differ by one column only) equivalent to another single Slater determinant having the property that the column in which ϕ_e and $\phi_{s\mu}^p$ differ (ϕ_e having ψ_{μ} and $\phi_{s\mu}^p$ having ψ_p) is replaced by a column containing the modified spin orbital $\psi' = \psi_{\mu} + C_s \psi_p$. The fact that $\phi_e + C_s \phi_{s\mu}^p$ is equivalent to a modified Slater determinant in which ψ_{μ} has been replaced by ψ' is the basis for saying that such singly excited determinants ψ_{μ}^p produce either orbital modification or orbital relaxation.

If the SCF orbitals are used to construct the Slater determinants, one finds (by using the Slater-Condon rules discussed below) that the interaction strength between the SCF determinant (which is presumably one of the essential configurations) and singly excited determinants vanishes—that is,

$$\langle \phi_{\rm HF} | H | \phi_s \rangle = 0. \tag{A.14}$$

This equation, known as the Brillouin theorem (Schaefer, 1972; Cook, 1978; Pilar, 1968), simply states that singly excited determinants are not important (in the interaction strength case) when SCF orbitals are used to construct the determinants because these orbitals are already optimal—further optimization (modification or relaxation) or the orbitals is not needed.

For doubly excited configurations $\phi_{D,\mu\nu}^{pq}$ in which ψ_{μ} and ψ_{ν} (which are occupied in ϕ_e) are replaced by ψ_p and ψ_q , the trial function $\phi_e - C_D \phi_{D,\mu\nu}^{pq}$ can be rewritten as a combination of two other determinants, each of which include *pairs* of polarized orbitals:

$$\phi_{e} - C_{D}\phi_{D,\mu\nu}^{pq} = \det[...(\psi_{\mu} - \sqrt{C_{D}} \psi_{p})(\psi_{\nu} + \sqrt{C_{D}} \psi_{q})] + \det[...(\psi_{\mu} + \sqrt{C_{D}} \psi_{p})(\psi_{\nu} - \sqrt{C_{D}} \psi_{q})].$$
(A.15)

Notice that in each of these two determinants, each electron moves in separate polarized orbitals. For example, in describing the rupture of the H₂ bond discussed in Chapter 3, a configuration-interaction wavefunction including both the σ_e^2 and σ_μ^2 configurations was used:

$$\phi = \sigma_g^2 - C\sigma_u^2. \tag{A.16}$$

The polarized orbitals corresponding to this doubly excited configurationinteraction wavefunction are $\sigma_g \pm \sqrt{C}\sigma_u$. Such double excitations give rise to electron-pair correlations because, in the polarized-orbital determinantal description, the electron pair residing in the orbitals ψ_{μ} and ψ_{ν} are correlated in the sense that one electron is in one polarized orbital when the other electron is





Figure A-2 Polarized orbitals.

in the other polarized orbital. Doubly excited determinants that include excitations of orbitals differing in their left-right symmetry (as above) give rise to polarized orbitals that are left-right polarized. Double excitations of the form $\sigma^2 \rightarrow \pi_x^2$ give rise to polarized orbitals ($\sigma \pm \sqrt{C}\pi_x$) that differ in their angular characteristics as shown in Figure A-2. Double excitations of the form $2s^2 \rightarrow 3s^2$ give polarized orbitals ($2s \pm \sqrt{C}3s$) that differ in their radial or inout character. This polarized orbital-*pair* description of the contributions made by double excitations is the basis for saying that such configurations give rise to electron correlations. As one electron is in one polarized orbital, the second is in the other orbital; this is what is meant by correlated motion.

In summary, configuration interaction is used to improve upon the SCF description of the electronic wavefunction. Such improvement is often essential as, for example, in describing heteropolar bond rupture to give radical products. However, configuration interaction can also be used simply to improve the accuracy of the wavefunction ϕ and energy *E*. Configurations that are singly or doubly excited relative to a dominant (essential) configuration allow orbital relaxation and electron-pair correlation effects to be included in the configuration-interaction wavefunction. Numerical procedures for adding configurations above and beyond these singles and doubles, which are included on physical grounds, are usually based upon evaluating the interaction strength of each such configuration with all of the essential configurations.

A.3. Slater-Condon Rules

After obtaining a list of configurations that includes the essential configurations and perhaps some set of singly, doubly, or more highly excited configurations that have been chosen as discussed in section A.2, the C_I expansion coefficients of equation A.13 must be evaluated. In the configuration-interaction procedure, the wavefunction of equation A.13 is used in the variational method to minimize the electronic energy. This approach leads to the well-known configuration-interaction matrix eigenvalue problem (Shavitt, 1977; Pilar, 1968)

$$\sum_{J=1}^{Q} H_{IJ}C_J = EC_I \qquad I = 1, \dots Q$$
 (A.17)

in which Q is the number of configurations included in the configurationinteraction wavefunction and E is the configuration-interaction approximation to the electronic energy. The $Q \times Q$ matrix **H** clearly has Q eigenvalues $\{E_i, i = 1, \ldots, Q\}$ and Q independent eigenvectors $\{C_{i,J}, i = 1, \ldots, Q; J = 1, \ldots, Q\}$. The various E_i represent the configuration-interaction approximations to the ground- and excited-state energies; the coefficients $\{C_{i,J}; J = 1, \ldots, Q\}$ describe the configuration-interaction wavefunction for this *i*th state.

The elements of the **H** matrix are given as integrals over the configurations ϕ_I :

$$H_{IJ} = \int \phi_I^* h_c \phi_J \, d\tau_1 \, \dots \, d\tau_N, \qquad (A.18)$$

in which h_e is the full Born-Oppenheimer electronic Hamiltonian described earlier and $d\tau_j$ denotes the space- and spin-integration volume element for the *j*th electron. The evaluation of these integrals is nontrivial because the ϕ_I are antisymmetrized N-electron functions. The derivation of closed expressions for the $H_{I,J}$ matrix elements is given in many texts on quantum chemistry (Cook, 1978; Condon and Shortley, 1957). The resulting set of so-called Slater-Condon rules can be summarized as follows. Two configuration functions ϕ_I and ϕ_J are first decomposed into their constituent Slater determinants det_{Ik} and det_J (each ϕ_I consists of one or more Slater determinants). To compute the matrix element $\langle \det_{I_k} | h_e | \det_{J_i} \rangle$ the spin-orbital occupancies of these two determinants are compared. If the occupancies differ by more than two spin orbitals (e.g., $1s^22s^2$ and $1s_{\alpha}2p_x^23s_{\beta}$ differ by three), then the matrix element vanishes. If the occupancies differ by two spin orbitals (with ψ_{μ} and ψ_{ν} in det_{Ik} and ψ_p and ψ_q in det _{J_i}), then the matrix element has a value $\pm [\langle \mu\nu | pq \rangle - \langle \mu\nu | qp \rangle]$ in which

$$\langle \mu\nu | pq \rangle \equiv \int \psi^*_{\mu}(\mathbf{r}) \psi^*_{\nu}(\mathbf{r}') | \mathbf{r} - \mathbf{r}' |^{-1} \psi_p(\mathbf{r}) \psi_q(\mathbf{r}') d\tau d\tau'.$$
(A.19)

The choice of + or - in the \pm sign is determined by how many spin-orbital interchanges are needed to arrange det_{J_i} to have exactly the same spin-orbital ordering as det_{I_k}, except that ψ_p replaces ψ_μ and ψ_q replaces ψ_ν . If the number of interchanges needed is odd (even), then the minus (plus) sign results. When det_{I_k} and det_{J_i} differ by only one spin orbital (with ψ_μ in det_{I_k} and ψ_p in det_{J_i}), then the value of the matrix element is

$$\pm \left[\left\langle \psi_{\mu} \right| - \frac{1}{2} \nabla_{r}^{2} - \sum_{a} \frac{Z_{a}}{|\mathbf{r} - \mathbf{R}_{a}|} \left| \psi_{p} \right\rangle + \sum_{\nu} \left(\left\langle \psi_{\mu} \psi_{\nu} \right| \psi_{p} \psi_{\nu} \right\rangle - \left\langle \psi_{\mu} \psi_{\nu} \right| \psi_{\nu} \psi_{p} \right\rangle \right]$$

in which the sum over ν runs over all of the spin orbitals common to det_{*I*_k} and det_{*J*_l}. The sign \pm is computed as just described by determining how many spin-orbital interchanges are needed to bring det_{*J*_l} into the same order (except for the ψ_p and ψ_{μ} mismatch) as det_{*I*_k}. If det_{*J*_k and det_{*J*_l} have identical spin-orbital occupancies, their Hamiltonian matrix element is given as above, but with $\psi_p = \psi_{\mu}$, and summed over the index μ that runs over all occupied spin orbitals.}}

Once the Slater-Condon rules are used to compute the Hamiltonian matrix elements over the determinants \det_{I_k} , the evaluation of the configurationbased matrix elements $\langle \phi_I | h_e | \phi_J \rangle$ is straightforward. Knowing that ϕ_I is expressed as a linear combination of the \det_{I_k}

$$\phi_I = \sum_k B_{I_k} \det_{I_k}, \tag{A.20}$$

one can write

$$\langle \phi_I | h_e | \phi_J \rangle = \sum_{k,l} B_{I_k} B_{J_l} \langle \det_{I_k} | h_e | \det_{J_l} \rangle.$$
 (A.21)

The final result of using the Slater-Condon rules is that the configurationinteraction **H** matrix, whose dimension is equal to the number of configurations selected, can be computed in terms of the one-electron $(\langle \psi_i | -1/2\nabla^2 | \psi_j \rangle,$ $\langle \psi_i | -Z_a / | \mathbf{r} - \mathbf{R}_a | | \psi_j \rangle)$ and two-electron $(\langle \psi_i \psi_j | \psi_k \psi_l \rangle)$ integrals over the spin orbitals used to form the configurations. These integrals can be evaluated in terms of the molecular-orbital expansion coefficients C_{ia} and the one- and two-electron integrals over the atomic-basis orbitals $\{X_a\}$, which must be explicitly calculated for the GTO or STO basis. For example, the two-electron integrals are expressed as

$$\langle \psi_i \psi_j | \psi_k \psi_l \rangle = \sum_{abcd} C_{ia} C_{jb} C_{kc} C_{ld} \langle X_a X_b | X_c X_d \rangle.$$
(A.22)

After forming the $Q \times Q$ configuration-interaction **H** matrix, the eigenvalues (E_I) and eigenvectors $(C_{IJ}; J = 1 \dots Q)$ are found by diagonalization. Each of the resulting approximate energy levels E_I can be shown (Hylleraas, 1930) to be an upper bound to the *I*th exact energy level of the system. The eigenvector $\{C_{IJ}; J = 1 \dots Q\}$ tell us to express the approximate configuration-interaction wavefunction (ϕ_I) for the *I*th energy level in terms of the configura-

$$\phi_i = \sum_{I=1}^{Q} C_{iI} \phi_I.$$
 (A.23)

By including in a configuration-interaction wavefunction the essential configurations (which are usually straightforward to guess) as well as configurations that are singly and doubly excited relative to any of these essential components, a satisfactory description of orbital relaxation and electron-pair correlation effects can often be achieved. This truncated configurationinteraction treatment, based upon low-order excitations out of essential configurations, has a significant weakness that should be made clear. This kind of configuration-interaction method suffers from what is called size inconsistency (Pople, 1976). To illustrate the problem, consider how one would compute the configuration-interaction energy of two separated and noninteracting beryllium atoms. Assume that a configuration-interaction calculation has already been performed on a single Be atom from which it was decided that only two configurations $(1s^22s^2)$ and $1s^22p^2$ need to be included in the one-atom configuration-interaction wavefunction to achieve a reasonable description-that is, evidence is available that supports the inclusion of only double excitations $(2s^2 \rightarrow 2p^2)$ in the Be atom configuration-interaction wavefunctions. If the same level of configuration interaction (dominant configuration $1s_A^2 2s_A^2 1s_B^2 2s_B^2$ plus double excitations $2s_A^2 \rightarrow 2p_A^2$, $2s_A^2 \rightarrow 2p_A 2p_B$, $2s_B^2 \rightarrow 2p_B^2$, $2s_A 2s_B \rightarrow 2p_B^2$ $2p_A 2p_B$, $2s_A 2s_B \rightarrow 2p_A$, and $2s_A 2s_B \rightarrow 2p_B^2$) were applied to the Be + Be system, the lowest resultant configuration-interaction energy would not be equal to twice the configuration-interaction energy obtained above for the single Be atom. One says that this configuration-interaction treatment is size-inconsistent because the energy obtained for noninteracting systems is not the sum of the configuration-interaction energies of the individual systems.

What is wrong with the above configuration-interaction wavefunction is that the wavefunction for Be + Be should (because the atoms are noninteracting) be the antisymmetrized product of the wavefunctions for the two Be atoms (A and B):

$$\phi_{\mathrm{Be}+\mathrm{Be}} = \phi_{\mathrm{Be}_{\mathrm{A}}}\phi_{\mathrm{Be}_{\mathrm{B}}}.\tag{A.24}$$

Because ϕ_{Be_A} and ϕ_{Be_B} contain both $1s^22s^2$ and $1s^22p^2$ configurations, $\phi_{Be + Be}$ should contain $2s_A^2 2s_B^2$, $2s_A^2 2p_B^2$, $2p_A^2 2s_B^2$, and $2p_A^2 2p_B^2$ (the $1s_A^2 1s_B^2$ is suppressed). This last configuration is quadruply excited relative to the dominant $2s_A^2 2s_B^2$ configuration, but it must be included if $\phi_{Be + Be}$ is to be size-consistent.

From the above example, it should be clear that a configurationinteraction wavefunction that is truncated to any level of excitation (e.g., doubly) when separately treating individual systems, A and B, will not be appropriate for use when treating the combined system AB even when A and B are for removed (let alone when they are interacting or chemically bonded). Correct treatment of AB requires inclusion of excitations up through the sum of the excitation levels used when separately treating A and B. Clearly, this size-consistency problem of the truncated configuration-interaction method may cause serious errors when using these techniques for computing energy differences such as bond-dissociation energies, intermolecular forces, and energy or enthalpy changes in chemical reactions.

The realization that truncated configuration-interaction approximations are not size-consistent has led to much recent interest in the use of perturbation theory for treating electron correlation effects (Pople, 1976). In these manybody perturbation theories (MBPT) the electronic Hamiltonian h_e is usually decomposed into h_e^0 and V in which h_e^0 is a sum of one-electron Fock operators

$$h_{c}^{0} = \sum_{i=1}^{N} F(i),$$
 (A.25)

in which F(i) is the Fock operator for the *i*th electron defined in equation A.4. The perturbation V then consists of the instantaneous electron-electron interaction minus the average (coulomb minus exchange) interaction contained in the Fock operator

$$\mathbf{V} = \frac{1}{2} \sum_{i \neq j}^{N} \frac{1}{|\mathbf{r}_{i} - \mathbf{r}_{j}|} - \sum_{i=1}^{N} \nu(\mathbf{r}_{i})$$
(A.26)

in which

$$v(\mathbf{r}_i) = \sum_{j_{occ}} \int \psi_j^*(\mathbf{r}') \frac{1 - P_{\mathbf{r}_i,\mathbf{r}'}}{|\mathbf{r}_i - \mathbf{r}'|} \psi_j(\mathbf{r}') d\mathbf{r}'.$$
(A.27)

In addition to the above decomposition of h_e , the exact electronic wavefunction ϕ is assumed to be given as a zeroth-order component ϕ^0 plus higher-order corrections ($\phi^{(n)}$; n = 1, 2, ...) with ϕ^0 taken to be a *single*configuration wavefunction. Such a single-configuration wavefunction, if it is constructed from the SCF spin orbitals, is an eigenfunction of the above-defined h_e^0 with eigenvalue E^0 equal to the sum of the SCF orbital energies belonging to the spin orbitals occupied in ϕ^0 .

Although such MBPT-based treatments of electron correlations have been successfully carried out by several research workers (Pople, 1976; Bartlett, 1975), major problems arise when the physical situation dictates that the true wavefunction ϕ is not dominated by a *single* configuration. As we saw earlier, description of processes with heteropolar or homopolar bond rupture usually requires a description of two or more essential configurations. By using a spinunrestricted SCF configuration as ϕ^0 , it is possible to describe bond rupture length of, for example, HCl, the single configuration is det(. $..\sigma\alpha\sigma'\beta$) with $\sigma = \sigma'$. Upon bond rupture the single-configuration wavefunction becomes det(. $..\sigma\alpha\sigma'\beta$) in which σ is the hydrogen 1s orbital and σ' is a chlorine 3p orbital. Unfortunately, such a UHF treatment suffers from the spin-impurity difficulty discussed in section A.1. Moreover, chemical problems (e.g., strong configuration mixing arising in concerted reactions involving breaking and forming more than one bond) exist for which *any* single-configuration description is inappropriate, and these limit the application of MBPT to large numbers of species arising in a variety of chemical reactions.

At present, a great deal of research is aimed at extending the machinery of MBPT (which does not suffer from the size-consistency problems) to permit ϕ^0 to consist of more than one essential configuration; however, this problem is not resolved yet. As a result, a perturbation theory tool that can be used in the avoided-crossing situations arising in many of the concerted reactions treated in Chapters 4 and 7 is not available. Thus, we shall not pursue further the use of MBPT to treat correlation in a manner that overcomes the sizeconsistency difficulty of the configuration-interaction method. The most essential point is that configuration interaction is not size-consistent. Thus, although the inclusion of singly and doubly excited configurations is attractive because of their significance with respect to relaxation and pair correlation, use of the variational configuration-interaction method for determining the amplitudes of these configurations may be questionable. Unfortunately, the MBPT method has not yet been extended to allow multiconfigurational zeroth-order functions, so it also cannot (at present) be employed for reliable evaluation of the desired amplitudes.