4.1 MULTICONFIGURATIONAL WAVE FUNCTIONS AND THE STRUCTURE OF THE FULL CI MATRIX

For the sake of simplicity, we assume in this chapter that our molecule of interest has an even number of electrons and is adequately represented, to a first approximation, by a closed-shell restricted HF determinant, $|\Psi_0\rangle$. Suppose we have solved Roothaan's equations in a finite basis set and obtained a set of $2K$ spin orbitals $\{\chi_i\}$. The determinant formed from the N lowest energy spin orbitals is $|\Psi_0\rangle$. As we have seen in Chapter 2, we can form, in addition to $|\Psi_0\rangle$, a large number of other N-electron determinants from the $2K$ spin orbitals. It is convenient to describe these other determinants by stating how they differ from $|\Psi_0\rangle$. Thus the set of possible determinants include $|\Psi_0\rangle$, the singly excited determinants $|\Psi_a^r\rangle$ (which differ from $|\Psi_0\rangle$ in having the spin orbital χ_a replaced by χ_r), the doubly excited determinants $|\Psi_{ab}^{rs}\rangle$, etc., up to and including N-tuply excited determinants. We can use these many-electron wave functions as a basis in which to expand the exact many-electron wave function $|\Phi_0\rangle$. If $|\Psi_0\rangle$ is a reasonable approximation to $|\Phi_0\rangle$, then we know from the variation principle that a better approximation (which becomes exact as the basis becomes complete) is

$$|\Phi_0\rangle = c_0|\Psi_0\rangle + \sum_{ar} c_a^r|\Psi_a^r\rangle + \sum_{\substack{a<b\\r<s}} c_{ab}^{rs}|\Psi_{ab}^{rs}\rangle + \sum_{\substack{a<b<c\\r<s<t}} c_{abc}^{rst}|\Psi_{abc}^{rst}\rangle + \sum_{\substack{a<b<c<d\\r<s<t<u}} c_{abcd}^{rstu}|\Psi_{abcd}^{rstu}\rangle + \cdots \tag{4.2a}$$

This is the form of the full CI wave function. The restrictions on the summation indices (e.g., $a < b$, $r < s$, etc.) insure that a given excited determinant is included in the sum only once. When doing formal manipulations it is sometimes convenient to remove this restriction and rewrite Eq. (4.2a) as

$$|\Phi_0\rangle = c_0|\Psi_0\rangle + \left(\frac{1}{1!}\right)^2 \sum_{ar} c_a^r|\Psi_a^r\rangle + \left(\frac{1}{2!}\right)^2 \sum_{abrs} c_{ab}^{rs}|\Psi_{ab}^{rs}\rangle + \left(\frac{1}{3!}\right)^2 \sum_{\substack{abc\\rst}} c_{abc}^{rst}|\Psi_{abc}^{rst}\rangle + \left(\frac{1}{4!}\right)^2 \sum_{\substack{abcd\\rstu}} c_{abcd}^{rstu}|\Psi_{abcd}^{rstu}\rangle + \cdots \tag{4.2b}$$

A factor $(1/n!)^2$ is included in front of the summation involving n-tuply excited determinants to insure that a given excitation is really counted but once. For example, the unrestricted summations for double excitations include the following terms

$$c_{ab}^{rs}|\Psi_{ab}^{rs}\rangle, \quad c_{ba}^{rs}|\Psi_{ba}^{rs}\rangle, \quad c_{ab}^{sr}|\Psi_{ab}^{sr}\rangle, \quad \text{and} \quad c_{ba}^{sr}|\Psi_{ba}^{sr}\rangle$$

Now, if we require the coefficient c_{ab}^{rs} to be antisymmetric with respect to the interchange of a and b or r and s just as the wave functions, then all four

terms are equal. Thus the factor of 1/4 insures that each determinant is counted only once.

How many n-tuple excitations are there? If we have $2K$ spin orbitals, N will be occupied in $|\Psi_0\rangle$ and $2K - N$ will be unoccupied. We can choose n spin orbitals from those occupied in $|\Psi_0\rangle$ in $\binom{N}{n}$ ways. Similarly, we can choose n orbitals from the $2K - N$ virtual orbitals in $\binom{2K-N}{n}$ ways. Thus the total number of n-tuply excited determinants is $\binom{N}{n}\binom{2K-N}{n}$. Even for small molecules and one-electron basis sets of only moderate size, the number of n-tuply excited determinants is extremely large for all n except 0 and 1. A significant number of these determinants can be eliminated (although in most cases not enough!) by exploiting the fact that there is no mixing of wave functions with different spin (i.e., $\langle\Psi_i|\mathscr{H}|\Psi_j\rangle = 0$ if $|\Psi_i\rangle$ and $|\Psi_j\rangle$ have different spin). Suppose we are interested in the singlet states of a molecule. Then we can immediately eliminate from the trial function those determinants which do not have the same number of α and β spin orbitals (i.e., keep only those which are eigenfunctions of $\mathscr{S}_z$ with eigenvalue 0). Moreover, as we have seen in Section 2.5, by taking appropriate linear combinations of these remaining determinants we can form *spin-adapted configurations* which are eigenfunctions of $\mathscr{S}^2$. Thus if we are interested in singlet states we need only include singlet spin-adapted configurations in the trial function. Although actual calculations always use spin-adapted configurations, it will be convenient, however, to develop the formalism in terms of determinants, since the resulting expressions have a simpler structure.

Given the trial function of Eq. (4.2) we can find the corresponding energies by using the linear variational method. As we have seen in Chapter 1, this consists of forming the matrix representation of the Hamiltonian in the basis of the N-electron functions of expansion (4.2) and then finding the eigenvalues of this matrix. This is called the full CI matrix, and the method is referred to as full CI. The lowest eigenvalue will be an upper bound to the ground state energy of the system. The higher eigenvalues will be upper bounds to excited states of the system. Here we will focus only on the lowest eigenvalue. The difference between the lowest eigenvalue ($\mathscr{E}_0$) and the Hartree-Fock energy (E_0) obtained within the same one-electron basis is called *the basis set correlation energy*. As the one-electron basis set approaches completeness, this basis set correlation energy approaches the exact correlation energy. The basis set correlation energy obtained by performing a full CI is, however, exact within the subspace spanned by the one-electron basis. Thus it constitutes a benchmark by which all other approaches to the calculation of the correlation energy performed with the same basis set should be judged. For a given one-electron basis set, full CI is the best that one can do.

To examine the structure of the full CI matrix it is convenient to rewrite the expansion of Eq. (4.2) in a symbolic form

$$|\Phi_0\rangle = c_0|\Psi_0\rangle + c_S|S\rangle + c_D|D\rangle + c_T|T\rangle + c_Q|Q\rangle + \cdots \tag{4.3}$$

where $|S\rangle$ represents the terms involving single excitations, $|D\rangle$ represents the terms involving double excitations, and so on. Using this notation, the full CI matrix is presented in Fig. 4.1. The following observations are important:

1. There is no coupling between the HF ground state and single excitations (i.e., $\langle\Psi_0|\mathscr{H}|S\rangle = 0$). This is a consequence of Brillouin's theorem (see Subsection 3.3.2), which states that all matrix elements of the form $\langle\Psi_0|\mathscr{H}|\Psi_a^r\rangle$ are zero.
2. There is no coupling between $|\Psi_0\rangle$ and triples or quadruples. Similarly, singles do not mix with quadruples. This is a consequence of the fact that all matrix elements of the Hamiltonian between Slater determinants which differ by more than 2 spin orbitals are zero. A corollary of this is that the blocks that are not zero are sparse. For example, the symbol $\langle D|\mathscr{H}|Q\rangle$ represents

$$\langle D|\mathscr{H}|Q\rangle \leftrightarrow \langle\Psi_{ab}^{rs}|\mathscr{H}|\Psi_{cdef}^{tuvw}\rangle$$

   For a matrix element of this type to be nonzero, the indices a and b must be included in the set $\{c, d, e, f\}$ and the indices r and s must be included in the set $\{t, u, v, w\}$.
3. Because single excitations do not mix *directly* with $|\Psi_0\rangle$, they can be expected to have a very small effect on the ground state energy. Their effect is not zero because they do mix *indirectly*; that is, they interact with the doubles which in turn interact with $|\Psi_0\rangle$. Although they have

$$\begin{array}{c} \\ |\Psi_0\rangle \\ \langle\Psi_0| \\ \langle S| \\ \langle D| \\ \langle T| \\ \langle Q| \\ \cdot \end{array}
\begin{array}{c}
\begin{array}{ccccccc} & |\Psi_a^r\rangle & |\Psi_{ab}^{rs}\rangle & |\Psi_{abc}^{rst}\rangle & |\Psi_{abcd}^{rstu}\rangle & \cdot\cdot \\ |\Psi_0\rangle & |S\rangle & |D\rangle & |T\rangle & |Q\rangle & \cdot \end{array} \\
\begin{bmatrix}
\langle\Psi_0|\mathscr{H}|\Psi_0\rangle & 0 & \langle\Psi_0|\mathscr{H}|D\rangle & 0 & 0 & \cdots \\
 & \langle S|\mathscr{H}|S\rangle & \langle S|\mathscr{H}|D\rangle & \langle S|\mathscr{H}|T\rangle & 0 & \cdots \\
 & & \langle D|\mathscr{H}|D\rangle & \langle D|\mathscr{H}|T\rangle & \langle D|\mathscr{H}|Q\rangle & \cdots \\
 & & & \langle T|\mathscr{H}|T\rangle & \langle T|\mathscr{H}|Q\rangle & \cdots \\
 & & & & \langle Q|\mathscr{H}|Q\rangle & \cdot\cdot \\
 & & & & & \vdots
\end{bmatrix}
\end{array}$$

$$\langle S|\mathscr{H}|T\rangle \leftrightarrow \langle\Psi_a^r|\mathscr{H}|\Psi_{cde}^{tuv}\rangle$$
$$\langle D|\mathscr{H}|D\rangle \leftrightarrow \langle\Psi_{ab}^{rs}|\mathscr{H}|\Psi_{cd}^{tu}\rangle$$

Figure 4.1 Structure of the full CI matrix. The matrix is Hermitian and only the upper triangle is shown.

almost negligible effect on the *energy* of the ground state, they do influence the charge distribution and, as we shall see later, single excitations are needed for a proper description of one-electron properties such as the dipole moment. The situation is entirely different for excited-electronic states. In the calculation of the electronic spectra of molecules the single excitations play the primary role.

4. Because it is the double excitations that mix directly with $|\Psi_0\rangle$, it is to be expected that these excitations play an important, and, for small systems, a predominant role in determining the correlation energy. Moreover, it turns out that quadruple excitations are more important than triple or single excitations if one is concerned solely with the ground state energy.
5. All the matrix elements required for actual calculations can be found using the rules described in Chapter 2. As mentioned previously, calculations are performed using spin-adapted configurations. These have been discussed in detail in Section 2.5 for singly and doubly excited determinants. Some of the matrix elements in the CI matrix involving these configurations are given in Table 4.1. They will be used several times later in the book. You might like to test your facility with the rules for evaluation of matrix elements and your stamina by checking the entries in the table.

Table 4.1 Some matrix elements between singlet symmetry-adapted configurations constructed from real orbitals

SINGLE EXCITATIONS

$$\langle \Psi_0 | \mathscr{H} | \Psi_a^r \rangle = 0$$

$$\langle {}^1\Psi_a^r | \mathscr{H} - E_0 | {}^1\Psi_b^s \rangle = (\varepsilon_r - \varepsilon_a)\delta_{rs}\delta_{ab} - (rs|ba) + 2(ra|bs)$$

DOUBLE EXCITATIONS

$$\langle \Psi_0 | \mathscr{H} | {}^1\Psi_{aa}^{rr} \rangle = K_{ra}$$

$$\langle \Psi_0 | \mathscr{H} | {}^1\Psi_{aa}^{rs} \rangle = 2^{1/2}(sa|ra)$$

$$\langle \Psi_0 | \mathscr{H} | {}^1\Psi_{ab}^{rr} \rangle = 2^{1/2}(rb|ra)$$

$$\langle \Psi_0 | \mathscr{H} | {}^A\Psi_{ab}^{rs} \rangle = 3^{1/2}((ra|sb) - (rb|sa))$$

$$\langle \Psi_0 | \mathscr{H} | {}^B\Psi_{ab}^{rs} \rangle = (ra|sb) + (rb|sa)$$

$$\langle {}^1\Psi_{aa}^{rr} | \mathscr{H} - E_0 | {}^1\Psi_{aa}^{rr} \rangle = 2(\varepsilon_r - \varepsilon_a) + J_{aa} + J_{rr} - 4J_{ra} + 2K_{ra}$$

$$\langle {}^1\Psi_{aa}^{rs} | \mathscr{H} - E_0 | {}^1\Psi_{aa}^{rs} \rangle = \varepsilon_r + \varepsilon_s - 2\varepsilon_a + J_{aa} + J_{rs} + K_{rs} - 2J_{sa} - 2J_{ra} + K_{sa} + K_{ra}$$

$$\langle {}^1\Psi_{ab}^{rr} | \mathscr{H} - E_0 | {}^1\Psi_{ab}^{rr} \rangle = 2\varepsilon_r - \varepsilon_a - \varepsilon_b + J_{rr} + J_{ab} + K_{ab} - 2J_{rb} - 2J_{ra} + K_{rb} + K_{ra}$$

$$\langle {}^A\Psi_{ab}^{rs} | \mathscr{H} - E_0 | {}^A\Psi_{ab}^{rs} \rangle = \varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b + J_{ab} + J_{rs} - K_{ab} - K_{rs} - J_{sb} - J_{sa} - J_{rb} - J_{ra} + \tfrac{3}{2}(K_{sb} + K_{sa} + K_{rb} + K_{ra})$$

$$\langle {}^B\Psi_{ab}^{rs} | \mathscr{H} - E_0 | {}^B\Psi_{ab}^{rs} \rangle = \varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b + J_{ab} + J_{rs} + K_{ab} + K_{rs} - J_{sb} - J_{sa} - J_{rb} - J_{ra} + \tfrac{1}{2}(K_{sb} + K_{sa} + K_{rb} + K_{ra})$$

$$\langle {}^A\Psi_{ab}^{rs} | \mathscr{H} | {}^B\Psi_{ab}^{rs} \rangle = (3/4)^{1/2}(K_{sb} - K_{sa} - K_{rb} + K_{ra})$$

4.1.1 Intermediate Normalization and an Expression for the Correlation Energy

Now that we have examined the general features of the full CI matrix, we will study the CI formalism in greater detail, as applied to the ground state of the system. When $|\Psi_0\rangle$ is a reasonable approximation to the exact ground state wave function $|\Phi_0\rangle$, the coefficient c_0 in the CI expansion (see Eq. (4.2)) will be much larger than any of the others. It is convenient to write $|\Phi_0\rangle$ in an *intermediate normalized form*

$$|\Phi_0\rangle = |\Psi_0\rangle + \sum_{ct} c_c^t |\Psi_c^t\rangle + \sum_{\substack{c<d\\t<u}} c_{cd}^{tu} |\Psi_{cd}^{tu}\rangle + \sum_{\substack{c<d<e\\t<u<v}} c_{cde}^{tuv} |\Psi_{cde}^{tuv}\rangle + \sum_{\substack{c<d<e<f\\t<u<v<w}} c_{cdef}^{tuvw} |\Psi_{cdef}^{tuvw}\rangle + \cdots \tag{4.4}$$

Because

$$\langle\Phi_0|\Phi_0\rangle = 1 + \sum_{ct} (c_c^t)^2 + \sum_{\substack{c<d\\t<u}} (c_{cd}^{tu})^2 + \cdots$$

this wave function is not normalized. However, it has the property that

$$\langle\Psi_0|\Phi_0\rangle = 1 \tag{4.5}$$

Given the intermediate normalized $|\Phi_0\rangle$ we can always normalize it, if we so desire, by multiplying each term in the expansion by a constant (i.e., $|\Phi_0'\rangle = c'|\Phi_0\rangle$, chosen so that $\langle\Phi_0'|\Phi_0\rangle = 1$.)

As discussed in Chapter 1, an equivalent formulation of the linear variation method is simply to write

$$\mathscr{H}|\Phi_0\rangle = \mathscr{E}_0|\Phi_0\rangle \tag{4.6}$$

where $|\Phi_0\rangle$ is given by Eq. (4.4) and then successively multiply this equation by $\langle\Psi_0|$, $\Psi_a^r|$, $\langle\Psi_{ab}^{rs}|$, etc. Before we do this, it is convenient to rewrite Eq. (4.6) by subtracting $E_0|\Phi_0\rangle$ from both sides to obtain

$$(\mathscr{H} - E_0)|\Phi_0\rangle = (\mathscr{E}_0 - E_0)|\Phi_0\rangle = E_{\text{corr}}|\Phi_0\rangle \tag{4.7}$$

where E_{corr} is the correlation energy. If we multiply both sides of this equation by $\langle\Psi_0|$ we obtain

$$\langle\Psi_0|\mathscr{H} - E_0|\Phi_0\rangle = E_{\text{corr}}\langle\Psi_0|\Phi_0\rangle = E_{\text{corr}} \tag{4.8}$$

where we have used the fact that $|\Phi_0\rangle$ is intermediately normalized. Now consider the left-hand side of the equation. Using the expansion in Eq. (4.4), we have

$$\langle\Psi_0|\mathscr{H} - E_0|\Phi_0\rangle = \langle\Psi_0|\mathscr{H} - E_0\left(|\Psi_0\rangle + \sum_{ct} c_c^t|\Psi_c^t\rangle + \sum_{\substack{c<d\\t<u}} c_{cd}^{tu}|\Psi_{cd}^{tu}\rangle + \cdots\right)$$

$$= \sum_{\substack{c<d\\t<u}} c_{cd}^{tu}\langle\Psi_0|\mathscr{H}|\Psi_{cd}^{tu}\rangle \tag{4.9}$$

where we have used Brillouin's theorem ($\langle\Psi_0|\mathscr{H}|\Psi_c^t\rangle = 0$) and the fact that triple and higher excitations do not mix with $|\Psi_0\rangle$ because they differ from $|\Psi_0\rangle$ by more than two spin orbitals. Combining Eqs. (4.8) and (4.9) we have the following explicit expression for the correlation energy:

$$E_{\text{corr}} = \sum_{\substack{a<b \\ r<s}} c_{ab}^{rs}\langle\Psi_0|\mathscr{H}|\Psi_{ab}^{rs}\rangle \tag{4.10}$$

Thus the correlation energy is determined solely by the coefficients of the double excitations in the intermediate normalized CI function. This does *not* mean that only double excitations need to be included for an exact CI description of the ground state; the coefficients $\{c_{ab}^{rs}\}$ are affected by the presence of other excitations. To see this, multiply Eq. (4.7) by $\langle\Psi_a^r|$ to obtain

$$\langle\Psi_a^r|\mathscr{H} - E_0|\Phi_0\rangle = E_{\text{corr}}\langle\Psi_a^r|\Phi_0\rangle$$

Using the expansion for $|\Phi_0\rangle$ and Brillouin's theorem this becomes

$$\sum_{ct} c_c^t\langle\Psi_a^r|\mathscr{H} - E_0|\Psi_c^t\rangle + \sum_{\substack{c<d \\ t<u}} c_{cd}^{tu}\langle\Psi_a^r|\mathscr{H}|\Psi_{cd}^{tu}\rangle + \sum_{\substack{c<d<e \\ t<u<v}} c_{cde}^{tuv}\langle\Psi_a^r|\mathscr{H}|\Psi_{cde}^{tuv}\rangle$$

$$= E_{\text{corr}}c_a^r \tag{4.11}$$

This expression can be simplified somewhat by taking into account the fact that there are nonzero matrix elements between singles and triples only when a equals c, d, or e and r equals t, u, or v. This allows us to rewrite Eq. (4.11) as

$$\sum_{ct} c_c^t\langle\Psi_a^r|\mathscr{H} - E_0|\Psi_c^t\rangle + \sum_{\substack{c<d \\ t<u}} c_{cd}^{tu}\langle\Psi_a^r|\mathscr{H}|\Psi_{cd}^{tu}\rangle + \sum_{\substack{c<d \\ t<u}} c_{acd}^{rtu}\langle\Psi_a^r|\mathscr{H}|\Psi_{acd}^{rtu}\rangle$$

$$= E_{\text{corr}}c_a^r \tag{4.12}$$

The important point about this equation is that it contains, and hence couples, the coefficients of the singles, doubles, and triples. If we continue the above procedure by multiplying Eq. (4.7) by $\langle\Psi_{ab}^{rs}|$, $\langle\Psi_{abc}^{rst}|$, etc., we would end up with a hierarchy of equations that must be solved simultaneously to obtain the correlation energy. This set of coupled equations is extremely large if all possible excitations are included. This is just another way of saying that the full CI matrix is extremely large. After illustrating the formalism developed so far, by applying it to minimal basis H_2, we will return to the problem of truncating the CI matrix to a manageable size.

Exercise 4.1 Obtain Eq. (4.12) from (4.11). It will prove convenient to use unrestricted summations.

Let us consider the application of the above formalism to minimal basis H_2. Since this is a two-electron system, full CI involves only single and double excitations. Recall that in this model we have two molecular orbitals: ψ_1 is the bonding orbital with gerade symmetry and ψ_2 is the antibonding

orbital with ungerade symmetry. The HF ground state wave function is

$$|\Psi_0\rangle = |\psi_1\bar{\psi}_1\rangle = |1\bar{1}\rangle \tag{4.13}$$

Since we have four spin orbitals ($\chi_1 \equiv 1$, $\chi_2 \equiv \bar{1}$, $\chi_3 \equiv 2$, $\chi_4 \equiv \bar{2}$) we can form in addition to $|\Psi_0\rangle$, five other determinants namely, $|1\bar{2}\rangle$, $|2\bar{1}\rangle$, $|12\rangle$, $|\bar{2}\bar{1}\rangle$, and $|2\bar{2}\rangle$. Using these determinants, the full CI wave function can be written as

$$|\Phi_0\rangle = |\Psi_0\rangle + c_1^2|2\bar{1}\rangle + c_{\bar{1}}^{\bar{2}}|1\bar{2}\rangle + c_{\bar{1}}^{2}|12\rangle + c_{1}^{\bar{2}}|\bar{2}\bar{1}\rangle + c_{1\bar{1}}^{2\bar{2}}|2\bar{2}\rangle \tag{4.14}$$

We can rewrite this in terms of spin-adapted configurations as follows. Since the exact ground state is a singlet we know that only configurations of singlet symmetry need be included in the expansion. The doubly excited state is a closed-shell and hence a singlet. Out of the four singly excited determinants $|2\bar{1}\rangle$, $|1\bar{2}\rangle$, $|12\rangle$, $|\bar{2}\bar{1}\rangle$ we can form one singlet state and three triplets. The singlet state is (see Eq. (2.260))

$$|^1\Psi_1^2\rangle = 2^{-1/2}(|1\bar{2}\rangle + |2\bar{1}\rangle)$$

Thus the spin-adapted expansion is

$$|\Phi_0\rangle = |\Psi_0\rangle + c_1^2|^1\Psi_1^2\rangle + c_{1\bar{1}}^{2\bar{2}}|2\bar{2}\rangle \tag{4.15}$$

Finally, we can simplify the expansion further by taking into account the spatial symmetry of the system. Both $|\Psi_0\rangle$ and $|2\bar{2}\rangle$ are of gerade symmetry while $|^1\Psi_1^2\rangle$ is of ungerade symmetry because it contains one orbital with gerade and one with ungerade symmetry. Therefore, this single excitation will not mix with $|\Psi_0\rangle$ or $|2\bar{2}\rangle$. Thus we can write the CI expansion, which is both symmetry and spin-adapted, as

$$|\Phi_0\rangle = |\Psi_0\rangle + c_{1\bar{1}}^{2\bar{2}}|2\bar{2}\rangle = |\Psi_0\rangle + c_{1\bar{1}}^{2\bar{2}}|\Psi_{1\bar{1}}^{2\bar{2}}\rangle \tag{4.16}$$

Given this trial function, the variational method tells us that the corresponding energy ($\mathscr{E}_0$) is the lowest eigenvalue of the CI matrix

$$\mathbf{H} = \begin{pmatrix} \langle\Psi_0|\mathscr{H}|\Psi_0\rangle & \langle\Psi_0|\mathscr{H}|\Psi_{1\bar{1}}^{2\bar{2}}\rangle \\ \langle\Psi_{1\bar{1}}^{2\bar{2}}|\mathscr{H}|\Psi_0\rangle & \langle\Psi_{1\bar{1}}^{2\bar{2}}|\mathscr{H}|\Psi_{1\bar{1}}^{2\bar{2}}\rangle \end{pmatrix}$$

The required matrix elements are readily evaluated using the rules o Chapter 2. Since the molecular orbitals are real, we have

$$\langle\Psi_0|\mathscr{H}|\Psi_0\rangle = E_0 = 2h_{11} + J_{11} \tag{4.17a}$$

$$\langle\Psi_0|\mathscr{H}|\Psi_{1\bar{1}}^{2\bar{2}}\rangle = \langle 1\bar{1}||2\bar{2}\rangle = (12|12) = K_{12} = \langle\Psi_{1\bar{1}}^{2\bar{2}}|\mathscr{H}|\Psi_0\rangle \tag{4.17b}$$

$$\langle\Psi_{1\bar{1}}^{2\bar{2}}|\mathscr{H}|\Psi_{1\bar{1}}^{2\bar{2}}\rangle = 2h_{22} + J_{22} \tag{4.17c}$$

Using the HF orbital energies (see Eqs. (3.130) and (3.131))

$$\varepsilon_1 = h_{11} + J_{11}$$

$$\varepsilon_2 = h_{22} + 2J_{12} - K_{12}$$

the diagonal matrix elements can be rewritten as

$$E_0 = 2\varepsilon_1 - J_{11} \tag{4.17d}$$

$$\langle \Psi_{1\bar{1}}^{2\bar{2}} | \mathscr{H} | \Psi_{1\bar{1}}^{2\bar{2}} \rangle = 2\varepsilon_2 - 4J_{12} + J_{22} + 2K_{12} \tag{4.17e}$$

Having evaluated the matrix elements, it is a straightforward matter to find the lowest eigenvalue of the matrix using the secular determinant or unitary transformation approach discussed in Chapter 1. Here we wish to solve the problem by a somewhat different but completely equivalent way, that we shall use many times in this book. We start by substituting Eq. (4.16) into Eq. (4.7):

$$(\mathscr{H} - E_0)(|\Psi_0\rangle + c|\Psi_{1\bar{1}}^{2\bar{2}}\rangle) = E_{\text{corr}}(|\Psi_0\rangle + c|\Psi_{1\bar{1}}^{2\bar{2}}\rangle) \tag{4.18}$$

where we have written c for $c_{1\bar{1}}^{2\bar{2}}$. Multiplying this equation by $\langle \Psi_0|$ we have

$$E_{\text{corr}} = c\langle \Psi_0 | \mathscr{H} | \Psi_{1\bar{1}}^{2\bar{2}} \rangle = cK_{12} \tag{4.19a}$$

Similarly, multiplying by $\langle \Psi_{1\bar{1}}^{2\bar{2}}|$ we have

$$\langle \Psi_{1\bar{1}}^{2\bar{2}} | \mathscr{H} | \Psi_0 \rangle + c\langle \Psi_{1\bar{1}}^{2\bar{2}} | \mathscr{H} - E_0 | \Psi_{1\bar{1}}^{2\bar{2}} \rangle = cE_{\text{corr}} \tag{4.19b}$$

Defining

$$2\Delta = \langle \Psi_{1\bar{1}}^{2\bar{2}} | \mathscr{H} - E_0 | \Psi_{1\bar{1}}^{2\bar{2}} \rangle = 2(\varepsilon_2 - \varepsilon_1) + J_{11} + J_{22} - 4J_{12} + 2K_{12} \tag{4.20}$$

where we have used the matrix elements in Eq. (4.17), we can rewrite Eq. (4.19b) as

$$K_{12} + 2\Delta c = cE_{\text{corr}} \tag{4.21}$$

The two simultaneous equations (4.19a) and (4.21) can be combined into the matrix equation

$$\begin{pmatrix} 0 & K_{12} \\ K_{12} & 2\Delta \end{pmatrix} \begin{pmatrix} 1 \\ c \end{pmatrix} = E_{\text{corr}} \begin{pmatrix} 1 \\ c \end{pmatrix} \tag{4.22}$$

We could have obtained this result directly from the CI eigenvalue problem:

$$\begin{pmatrix} E_0 & K_{12} \\ K_{12} & \langle \Psi_{1\bar{1}}^{2\bar{2}} | \mathscr{H} | \Psi_{1\bar{1}}^{2\bar{2}} \rangle \end{pmatrix} \begin{pmatrix} c_0 \\ c_1 \end{pmatrix} = \mathscr{E} \begin{pmatrix} c_0 \\ c_1 \end{pmatrix}$$

by simply subtracting

$$\begin{pmatrix} E_0 & 0 \\ 0 & E_0 \end{pmatrix} \begin{pmatrix} c_0 \\ c_1 \end{pmatrix}$$

from both sides, using the definition of 2Δ (Eq. (4.20)) and setting $c_0 = 1$ (intermediate normalization), $\mathscr{E} - E_0 = E_{\text{corr}}$, and $c_1 = c$. To obtain the lowest eigenvalue we solve Eq. (4.21) for c:

$$c = \frac{K_{12}}{E_{\text{corr}} - 2\Delta}$$

and substitute this into Eq. (4.19a) to obtain

$$E_{\text{corr}} = \frac{K_{12}^2}{E_{\text{corr}} - 2\Delta}$$

This equation is a quadratic equation for E_{corr}, which can be solved for the lowest root, i.e.,

$$E_{\text{corr}} = \Delta - (\Delta^2 + K_{12}^2)^{1/2} \tag{4.23}$$

This is the exact correlation energy of H_2 within the minimal basis set of atomic orbitals.

Exercise 4.2 Using the secular determinant approach show that the lowest eigenvalue of the matrix

$$\begin{pmatrix} 0 & K_{12} \\ K_{12} & 2\Delta \end{pmatrix}$$

is given by Eq. (4.23).

The exact energy of minimal basis H_2 is

$$\mathscr{E}_0 = E_0 + E_{\text{corr}} = 2h_{11} + J_{11} + \Delta - (\Delta^2 + K_{12}^2)^{1/2} \tag{4.24}$$

In contrast to E_0, this full CI energy properly describes the dissociation of H_2, as might be expected, since it is the exact energy in the basis. To see this, recall that as $R \to \infty$, $h_{11} = h_{22} \to E(\text{H})$, where $E(\text{H})$ is the energy of the hydrogen atom in the basis and that *all* molecular orbital two-electron integrals tend to $\frac{1}{2}(\phi_1\phi_1|\phi_1\phi_1)$, where ϕ_1 is a hydrogenic orbital. It then follows that $\Delta \to 0$ as $R \to \infty$ and hence $E_{\text{corr}} \to -K_{12} = -\frac{1}{2}(\phi_1\phi_1|\phi_1\phi_1)$ which exactly cancels the long range limit of J_{11} thus ensuring that $\mathscr{E}_0$ approaches $2E(\text{H})$. The full CI, RHF, and UHF potential energy curves for STO-3G H_2 are compared in Fig. 4.2. Note that although, in contrast to RHF, UHF does describe dissociation properly, the UHF potential curve is significantly different from the full CI one. For comparison the essentially exact nonrelativistic results of Kolos and Wolniewicz are shown. Their calculations, which exploit the simplifications inherent in a two-electron system, use wave functions which explicitly contain the interelectronic distance (i.e., r_{12}). One can see that although full CI is exact in the STO-3G basis, it gives a potential curve which does not agree very well with the exact one. Although the full CI STO-3G well depth is greater than the exact result, this does not imply that the variation principle has been violated. The STO-3G full CI energy of H_2 and the STO-3G energy of the hydrogen atom are both higher than the corresponding exact results. However, the STO-3G potential energy curve is obtained by subtracting the energy of two isolated H atoms from the energy of H_2 and thus need not be an upper bound to the exact curve. The STO-3G UHF and full CI well depths are greater than the exact result because the STO-3G basis is so poor for the hydrogen atom.

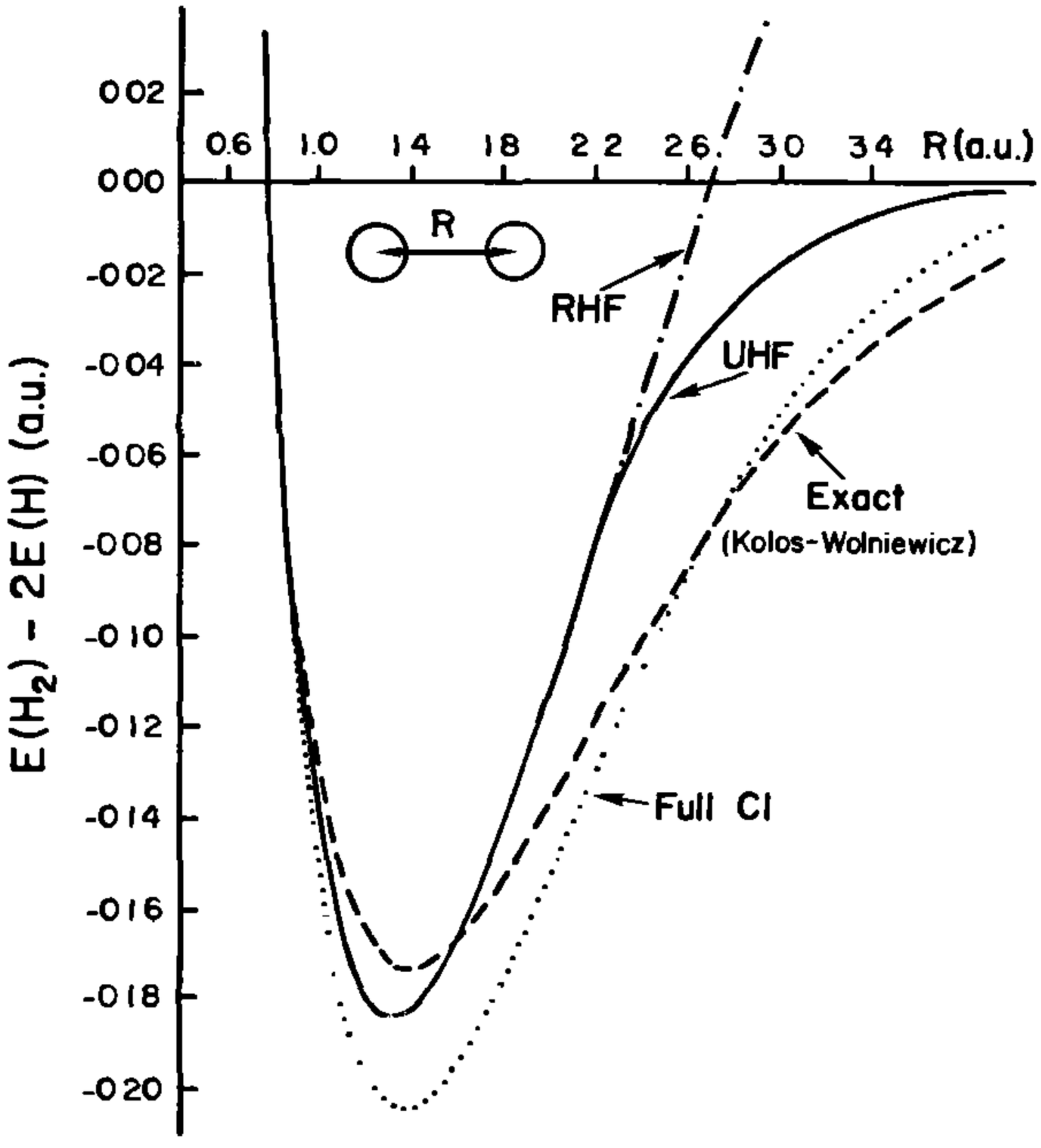

Figure 4.2 STO-3G potential energy curves for H_2.

Exercise 4.3 Calculate the coefficient of the double excitation (c) in the intermediate normalized CI wave function at $R = 1.4$ a.u., using the STO-3G integrals given in Appendix D. Show analytically that as $R \to \infty$, $c \to -1$, and hence that at large distances the Hartree-Fock ground state and the doubly excited configuration have equal weight in the CI ground state. Finally, show that the CI wave function, when normalized to unity, becomes (at $R = \infty$)

$$2^{-1/2}(|\phi_1\bar{\phi}_2\rangle + |\phi_2\bar{\phi}_1\rangle)$$

where ϕ_1 and ϕ_2 are atomic orbitals on centers one and two, respectively.

4.2 DOUBLY EXCITED CI

For all but the smallest molecules, even with a minimal basis set, full CI is a computationally impractical procedure. With a one-electron basis of moderate size, there are so many possible spin-adapted configurations that the full CI matrix becomes impossibly large (e.g., its dimensionality is greater than $10^9 \times 10^9$). To obtain a computationally viable scheme one must trun-