

### 4.3 Illustrating how CI Accounts for Electron Correlation, and the RHF Dissociation Problem

Consider the  $\text{H}_2$  molecule in a minimum basis consisting of one  $s$ -function on each centre,  $\chi_A$  and  $\chi_B$ . An RHF calculation will produce two MOs,  $\phi_1$  and  $\phi_2$ , being the sum and difference of the two AOs. The sum of the two AOs is a bonding MO, with increased probability of finding the electrons between the two nuclei, while the difference is an antibonding MO, with decreased probability of finding the electrons between the two nuclei.

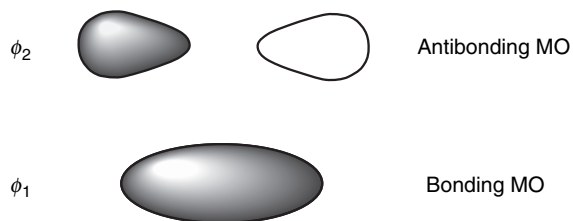


Figure 4.6 Molecular orbitals for  $\text{H}_2$

The HF wave function will have two electrons in the lowest energy (bonding) MO.

$$\begin{aligned}\phi_1 &= (\chi_A + \chi_B) \\ \phi_2 &= (\chi_A - \chi_B) \\ \Phi_0 &= \begin{vmatrix} \phi_1(1) & \overline{\phi_1(1)} \\ \phi_1(2) & \overline{\phi_1(2)} \end{vmatrix}\end{aligned}\quad (4.16)$$

We have here neglected the normalization constants for both the MOs and the determinantal wave function. The bar above the MO indicates that the electron has a  $\beta$  spin function, no bar indicates an  $\alpha$  spin function. In this basis, there are one doubly ( $\Phi_1$ ) and four singly excited Slater determinants ( $\Phi_{2-5}$ ).

$$\begin{aligned}\Phi_1 &= \begin{vmatrix} \phi_2(1) & \overline{\phi_2(1)} \\ \phi_2(2) & \overline{\phi_2(2)} \end{vmatrix} \\ \Phi_2 &= \begin{vmatrix} \phi_1(1) & \overline{\phi_2(1)} \\ \phi_1(2) & \overline{\phi_2(2)} \end{vmatrix} \\ \Phi_3 &= \begin{vmatrix} \overline{\phi_1(1)} & \phi_1(1) \\ \overline{\phi_1(2)} & \phi_1(2) \end{vmatrix} \\ \Phi_4 &= \begin{vmatrix} \phi_1(1) & \phi_2(1) \\ \phi_1(2) & \phi_2(2) \end{vmatrix} \\ \Phi_5 &= \begin{vmatrix} \overline{\phi_1(1)} & \overline{\phi_2(1)} \\ \overline{\phi_1(2)} & \overline{\phi_2(2)} \end{vmatrix}\end{aligned}\quad (4.17)$$

Configurations  $\Phi_4$  and  $\Phi_5$  are clearly the  $S_z = 1$  and  $S_z = -1$  components of a triplet state. The plus combination of  $\Phi_2$  and  $\Phi_3$  is the  $S_z = 0$  component of the triplet, and the minus combination is a singlet configuration, Figure 4.4. The  $H_2$  molecule belongs to the  $D_{\infty h}$  point group, and the two MOs transform as the  $\sigma_g$  ( $\phi_1$ ) and  $\sigma_u$  ( $\phi_2$ ) representations. The singly excited CSF ( $\Phi_2 - \Phi_3$ ) has overall  $\Sigma_u$  symmetry, while the HF ( $\Phi_0$ ) and doubly excited determinant ( $\Phi_1$ ) have  $\Sigma_g$ . The full  $6 \times 6$  CI problem therefore blocks into a  $2 \times 2$  block of singlet  $\Sigma_g$  states, a  $1 \times 1$  block of singlet  $\Sigma_u$ , and a  $3 \times 3$  block of triplet  $\Sigma_u$  states. Owing to the orthogonality of the spin functions, the triplet block is already diagonal.

The full CI for the  $^1\Sigma_g$  states involves only two configurations, the reference HF and the doubly excited determinant.

$$\begin{pmatrix} {}^1\Phi_{0,\Sigma_g} & {}^1\Phi_{1,\Sigma_g} & {}^1(\Phi_2 - \Phi_3)_{\Sigma_u} & {}^3\Phi_{4,\Sigma_u} & {}^3(\Phi_2 + \Phi_3)_{\Sigma_u} & {}^3\Phi_{5,\Sigma_u} \end{pmatrix} \begin{pmatrix} E_0 & H_{01} & 0 & 0 & 0 & 0 \\ H_{01} & E_1 & 0 & 0 & 0 & 0 \\ 0 & 0 & E_2 & 0 & 0 & 0 \\ 0 & 0 & 0 & E_3 & 0 & 0 \\ 0 & 0 & 0 & 0 & E_4 & 0 \\ 0 & 0 & 0 & 0 & 0 & E_5 \end{pmatrix}$$

**Figure 4.7** Structure of the full CI matrix for the  $H_2$  system in a minimum basis

$$\begin{aligned}\Phi_0 &= \phi_1(1)\overline{\phi_1(2)} - \overline{\phi_1(1)}\phi_1(2) = \phi_1\phi_1(\alpha\beta - \beta\alpha) \\ \Phi_1 &= \phi_2(1)\overline{\phi_2(2)} - \overline{\phi_2(1)}\phi_2(2) = \phi_2\phi_2(\alpha\beta - \beta\alpha)\end{aligned}\quad (4.18)$$

In eq. (4.18) the electron coordinate is given implicitly by the order in which the orbitals are written, i.e.  $\phi_1\phi_1[\alpha\beta - \beta\alpha] = \phi_1(1)\phi_1(2)[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$ . Ignoring the spin functions (which may be integrated out since  $\mathbf{H}$  is spin independent), the determinants can be expanded in AOs.

$$\begin{aligned}\Phi_0 &= (\chi_A(1) + \chi_B(1))(\chi_A(2) + \chi_B(2)) = \chi_A\chi_A + \chi_B\chi_B + \chi_A\chi_B + \chi_B\chi_A \\ \Phi_1 &= (\chi_A(1) - \chi_B(1))(\chi_A(2) - \chi_B(2)) = \chi_A\chi_A + \chi_B\chi_B - \chi_A\chi_B - \chi_B\chi_A\end{aligned}\quad (4.19)$$

The first two terms on the right-hand side have both electrons on the same nuclear centre, and they describe *ionic* contributions to the wave function,  $\text{H}^+\text{H}^-$ . The later two terms describe *covalent* contributions to the wave function,  $\text{H}\cdot\text{H}\cdot$ . The HF wave function thus contains equal amounts of ionic and covalent contributions.

The full CI wave function may be written in terms of AOs as in eq. (4.20), with the optimum values of the  $a_0$  and  $a_1$  coefficients determined by the variational procedure.

$$\begin{aligned}\Psi_{\text{CI}} &= a_0\Phi_0 + a_1\Phi_1 \\ \Psi_{\text{CI}} &= (a_0 + a_1)(\chi_A\chi_A + \chi_B\chi_B) + (a_0 - a_1)(\chi_A\chi_B + \chi_B\chi_A)\end{aligned}\quad (4.20)$$

The HF wave function constrains both electrons to move in the same bonding orbital. By allowing the doubly excited state to enter the wave function, the electrons can better avoid each other, as the antibonding MO is now also available. The antibonding MO has a nodal plane (where  $\phi_2 = 0$ ) perpendicular to the molecular axis (Figure 4.6), and the electrons are able to correlate their movements by being on opposite sides of this plane. This *left-right* correlation is a molecular equivalent of the atomic radial correlation discussed in Section 5.2.

Consider now the behaviour of the HF wave function  $\Phi_0$  (eq. (4.19)) as the distance between the two nuclei is increased toward infinity. Since the HF wave function is an equal mixture of ionic and covalent terms, the dissociation limit is 50%  $\text{H}^+\text{H}^-$  and 50%  $\text{H}\cdot\text{H}\cdot$ . In the gas phase, all bonds dissociate homolytically, and the ionic contribution should be 0%. The HF dissociation energy is therefore much too high. This is a general problem with RHF type wave functions: the constraint of doubly occupied MOs is inconsistent with breaking bonds to produce radicals. In order for an RHF wave function to dissociate correctly, an even-electron molecule must break into two even-electron fragments, each being in the lowest electronic state. Furthermore, the orbital symmetries must match. There are only a few covalently bonded systems that obey these requirements (the simplest example is  $\text{HHe}^+$ ). The wrong dissociation limit for RHF wave functions has several consequences:

- (1) The energy for stretched bonds is too high. Most transition structures have partly formed/broken bonds, thus activation energies are too high at the RHF level.
- (2) The too steep increase in energy as a function of the bond length causes the minimum on a potential energy curve to occur too “early” for covalently bonded systems, and equilibrium bond lengths are too short at the RHF level.

- (3) The too steep increase in energy as a function of the bond length causes the curvature of the potential energy surface near the equilibrium to be too large, and vibrational frequencies, especially those describing bond stretching, are in general too high.
- (4) The wave function contains too much “ionic” character, and RHF dipole moments (and also atomic charges) are in general too large.

It should be noted that dative bonds, such as in metal complexes and charge transfer species, in general have RHF wave functions that dissociate correctly, and the equilibrium bond lengths in these cases are normally too long.

The dissociation problem is solved in the case of a full CI wave function in this minimum basis. As seen from eq. (4.20), the ionic term can be made to disappear by setting  $a_1 = -a_0$ . The full CI wave function generates the lowest possible energy (within the limitations of the chosen basis set) at all distances, with the optimum weights of the HF and doubly excited determinant determined by the variational principle. In the general case of a polyatomic molecule and large basis set, correct dissociation of all bonds can be achieved if the CI wave function contains all determinants generated by a full CI in the valence orbital space. The latter corresponds to a full CI if a minimum basis is employed, but is much smaller than a full CI if an extended basis is used.