LAB. EXERCISE 4
BOND DISSOCIATION IN THE HYDROGEN MOLECULE

PART 1: CALCULATION OF THE BOND DISSOCIATION PROFILE USING THE HF WAVEFUNCTION

1) Plot qualitatively the expected energy profile of the bond dissociation in the H_2 molecule. Comment on the asymptotes at short and long interatomic distances.

2) Write down the single determinant singlet ground-state wavefunction Ψ of the hydrogen molecule, based on a doubly occupied σ_g orbital.

3) Using the SCF-LCAO method, the σ_g and σ_u orbitals are expanded as linear combinations of the $1s_A$ and $1s_B$ atomic orbitals centered on hydrogens A and B, respectively:

$$\sigma_g = N_1\left(1s_A + 1s_B\right)$$
$$\sigma_u = N_2\left(1s_A - 1s_B\right)$$

where N_1 and N_2 are the normalization constants. Write the expression of N_1 and N_2 as a function of the overlap integral between $1s_A$ and $1s_B$:

$$S = \int 1s_A(\mathbf{r})1s_B(\mathbf{r})d\mathbf{r}$$

4) By using the LCAO expansion of the σ_g orbital, show that the ground state wavefunction Ψ corresponds to a combination of ionic and covalent electron configurations of same weights.

5) Use the AMPAC program to calculate the energy profile of the bond dissociation in the H_2 molecule at the RHF-AM1 level. Comment the asymptotic behavior of the total energy at long interatomic distances, in relation to the form of the HF wavefunction.

Note: the energy of the hydrogen molecule at infinite interatomic distance must be compared to the total electronic energy of the isolated H atom calculated the AM1 level.

PART 2: VALENCE BOND WAVEFUNCTION

6) One considers now the valence bond (VB) wavefunction built from the linear combination of two Slater determinants:

$$\Omega_1 = \left|1s_A\alpha \quad 1s_B\beta\right| \text{ and } \Omega_2 = \left|1s_A\beta \quad 1s_B\alpha\right|$$

The two eigenstates are thus expressed as:

$$\Psi_1 = A\left(\Omega_1 - \Omega_2\right) \text{ and } \Psi_2 = B\left(\Omega_1 + \Omega_2\right)$$

where A and B are normalization factors. Show that Ψ_1 and Ψ_2 correspond to a singlet and triplet state, respectively.

7) Compare the VB wavefunction Ψ_1 to the HF wavefunction written in Step 4. What can be expected regarding the asymptotic behavior of the total energy at long distances?

PART 3: CONFIGURATION INTERACTION WAVEFUNCTION

8) Using the LCAO expansion given in Step 3, write the expression of the atomic orbitals $1s_A$ and $1s_B$ with respect to the molecular orbitals σ_g and σ_u (the overlap integral S can be neglected for simplicity). Report these expressions into the expression of Ψ_1, and factorize. Show that the VB wavefuntion Ψ_1 corresponds to a combination of same weights of the fundamental σ_g^2 and doubly excited σ_u^2 configurations.

9) In the wavefunction written in Step 8, the fundamental σ_g^2 and doubly excited σ_u^2 configurations have the same weight, which is consistent in the infinite separation limit. How should evolve the relative weights of the fundamental and excited configurations with respect to the interatomic distance?

10) Use the AMPAC program to calculate the energy profile of the bond dissociation in the H_2 molecule at the CI-AM1 level. Plot in the same graph the energy profiles obtained at the HF and CI levels.

11) Plot the evolution of the weights of the fundamental σ_g^2 and doubly excited σ_u^2 configurations in the CI wavefunction.