LAB. EXERCISE 5
CALCULATION OF THE GROUND AND EXCITED STATES OF THE HYDROGEN MOLECULE USING THE CONFIGURATIONS INTERACTION METHOD

PART 1: CI EIGENSTATES

1) Write the four electron configurations based on the possible occupancies of the σ_g and σ_u orbitals (we consider that the two electrons have different spins). Write the Slater's determinant corresponding to each configuration.

2) Using the SCF-LCAO method, expand the σ_g and σ_u orbitals as normalized linear combinations of the $1s_A$ and $1s_B$ atomic orbitals centered on hydrogens A and B, respectively (the overlap between $1s_A$ and $1s_B$ will be neglected).

3) Use the AMPAC program to optimize the internuclear distance at the RHF/AM1 level, and use the keyword '`1ELEC`' to print the 1-electron integrals in the AOs basis. Take the value of the electronic energy.

4) Using the 1-electron integrals in the AOs basis obtained in Step 3, calculate the 1-electron integrals in the MOs basis.

5) One gives the non-zero 2-electrons integrals in the MOs basis, as calculated at the AM1 level:

$$\int \sigma_g(\mathbf{r}_1)\sigma_g(\mathbf{r}_1)\frac{1}{r_{12}}\sigma_g(\mathbf{r}_2)\sigma_g(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 = \left(gg|gg\right) = 11.923$$

$$\int \sigma_u(\mathbf{r}_1)\sigma_u(\mathbf{r}_1)\frac{1}{r_{12}}\sigma_u(\mathbf{r}_2)\sigma_u(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 = \left(uu|uu\right) = 11.923$$

$$\int \sigma_g(\mathbf{r}_1)\sigma_g(\mathbf{r}_1)\frac{1}{r_{12}}\sigma_u(\mathbf{r}_2)\sigma_u(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 = \left(gg|uu\right) = 11.923$$

$$\int \sigma_g(\mathbf{r}_1)\sigma_u(\mathbf{r}_1)\frac{1}{r_{12}}\sigma_g(\mathbf{r}_2)\sigma_u(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 = \left(gu|gu\right) = 0.92462$$

Build the CI matrix in the basis of the Slater determinants.

6) Use the AMPAC program to check the values of the CI matrix elements, by specifying the following list of keywords:

```
AM1 C.I.=2 CISTATE=4 SINGLET MECI MATCI 1SCF DEBUG
```

8) Calculate the energies of the two eigenstates issued from the coupling between the reference and the doubly excited configuration (RD-block). Deduce the CI expansion coefficients of these two eigenstates in the basis of the Slater determinants.

9) Same question as Step 8 for the S-block. Show that the lower energy state issued from the coupling between singly excited configurations corresponds to a triplet state, while the higher energy state is a singlet.

10) Check the results of Step 8 and 9 with those obtained using AMPAC, and calculate the correlation energy for the ground state.

PART 2: TRIPLET STATES WITH $S_z = \pm 1$

11) Calculate the energy of the two possible triplet configurations in which the σ_g and σ_u orbitals are singly occupied with electrons of same spin.

12) Check the result with AMPAC using the additional keyword '`MICROS=1`'. Report on a same diagram the energy of the 6 eigenstates of the H_2 molecule.