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.

$$\sigma_g^{\,2}: \Phi_1 = \left|\sigma_g \overline{\sigma}_g\right| = \frac{1}{\sqrt{2}}\sigma_g(1)\sigma_g(2)\left(\alpha(1)\beta(2) - \beta(1)\alpha(2)\right)$$

$$\sigma_g^{\,1}\sigma_u^{\,1}: \begin{cases} \Phi_2 = \left|\sigma_g \overline{\sigma}_u\right| = \frac{1}{\sqrt{2}}\left(\sigma_g(1)\alpha(1)\sigma_u(2)\beta(2) - \sigma_u(1)\beta(1)\sigma_g(2)\alpha(2)\right) \\ \Phi_3 = \left|\overline{\sigma}_g \sigma_u\right| = \frac{1}{\sqrt{2}}\left(\sigma_g(1)\beta(1)\sigma_u(2)\alpha(2) - \sigma_u(1)\alpha(1)\sigma_g(2)\beta(2)\right) \end{cases}$$

$$\sigma_u^{\,2}: \Phi_4 = \left|\sigma_u \overline{\sigma}_u\right| = \frac{1}{\sqrt{2}}\sigma_u(1)\sigma_u(2)\left(\alpha(1)\beta(2) - \beta(1)\alpha(2)\right)$$

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).

$$\sigma_g = \frac{1}{\sqrt{2}}\left(1s_A + 1s_B\right)$$

$$\sigma_u = \frac{1}{\sqrt{2}}\left(1s_A - 1s_B\right)$$

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.

```
Interatomic distance: 0.67663 Angström

     FINAL ONE-ELECTRON MATRIX
                H   1      H   2
 --------------------------------
    H   1   -22.395188
    H   2    -4.444041 -22.395188

ELECTRONIC ENERGY = -41.755076 eV
```

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

$$\begin{aligned}\int \sigma_g(\mathbf{r})\hat{h}\sigma_g(\mathbf{r})d\mathbf{r} &= \frac{1}{2}\int (1s_A + 1s_B)\hat{h}(1s_A + 1s_B)d\mathbf{r} \\ &= \frac{1}{2}\left(\int 1s_A\hat{h}1s_A d\mathbf{r} + \int 1s_B\hat{h}1s_B d\mathbf{r} + 2\int 1s_A\hat{h}1s_B d\mathbf{r}\right) \\ &= \int 1s_A\hat{h}1s_A d\mathbf{r} + \int 1s_A\hat{h}1s_B d\mathbf{r} \\ &= -22.395188 - 4.444041 \\ &= -26.839229 \text{ eV}\end{aligned}$$

$$\begin{aligned}\int \sigma_u(\mathbf{r})\hat{h}\sigma_u(\mathbf{r})d\mathbf{r} &= \frac{1}{2}\int (1s_A - 1s_B)\hat{h}(1s_A - 1s_B)d\mathbf{r} \\ &= \frac{1}{2}\left(\int 1s_A\hat{h}1s_A d\mathbf{r} + \int 1s_B\hat{h}1s_B d\mathbf{r} - 2\int 1s_A\hat{h}1s_B d\mathbf{r}\right) \\ &= \int 1s_A\hat{h}1s_A d\mathbf{r} - \int 1s_A\hat{h}1s_B d\mathbf{r} \\ &= -22.395188 + 4.444041 \\ &= -17.951147 \text{ eV}\end{aligned}$$

$$\begin{aligned}\int \sigma_g(\mathbf{r})\hat{h}\sigma_u(\mathbf{r})d\mathbf{r} &= \frac{1}{2}\int (1s_A + 1s_B)\hat{h}(1s_A - 1s_B)d\mathbf{r} \\ &= \frac{1}{2}\left(\int 1s_A\hat{h}1s_A d\mathbf{r} - \int 1s_B\hat{h}1s_B d\mathbf{r} - \int 1s_A\hat{h}1s_B d\mathbf{r} + \int 1s_B\hat{h}1s_A d\mathbf{r}\right) \\ &= 0\end{aligned}$$

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

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

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

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

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

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

The CI matrix (lower triangle) is of the form:

C.I. MATRIX (eV)

	1	2	3	4
1	H11			
2	H21	H22		
3	H31	H32	H33	
4	H41	H42	H43	H44

where the numbering of the Slater determinants (1-4) correspond to that defined in Step 1.
By symmetry:

$H_{21}=H_{31}$
$H_{22}=H_{33}$
$H_{42}=H_{43}$

The elements H_{11}, H_{22}, H_{44}, H_{21}, H_{41}, H_{32}, H_{42} are independent.

Calculation of the diagonal elements:

H_{11} is the energy of the reference HF configuration. From step 3,
H_{11} = `-41.755076 eV`

$$H_{22} = \int \Phi_2 \hat{H} \Phi_2 d\mathbf{r}$$
$$= \frac{1}{2}\left\langle g\bar{u} - \bar{u}g \middle| \hat{h}_1 \middle| g\bar{u} - \bar{u}g \right\rangle + \frac{1}{2}\left\langle g\bar{u} - \bar{u}g \middle| \hat{h}_2 \middle| g\bar{u} - \bar{u}g \right\rangle + \frac{1}{2}\left\langle g\bar{u} - \bar{u}g \middle| \frac{1}{r_{12}} \middle| g\bar{u} - \bar{u}g \right\rangle$$

where the following notation is used for simplicity:

$$\Phi_2 = \frac{1}{\sqrt{2}}\left(\sigma_g(1)\alpha(1)\sigma_u(2)\beta(2) - \sigma_u(1)\beta(1)\sigma_g(2)\alpha(2)\right) = \frac{1}{\sqrt{2}}\left(g\bar{u} - \bar{u}g\right)$$

Due to the orthogonality of spin functions:

$$H_{22} = \frac{1}{2}\left[\left\langle g\middle|\hat{h}_1\middle|g\right\rangle + \left\langle u\middle|\hat{h}_1\middle|u\right\rangle + \left\langle g\middle|\hat{h}_2\middle|g\right\rangle + \left\langle u\middle|\hat{h}_2\middle|u\right\rangle + \langle gu|gu\rangle + \langle ug|ug\rangle\right]$$
$$= \left(g\middle|\hat{h}\middle|g\right) + \left(u\middle|\hat{h}\middle|u\right) + (gg|uu)$$
$$= -26.839229 - 17.951147 + 11.923 = -32.867376$$

Similarly,

$$H_{44} = \int \Phi_4 \hat{H} \Phi_4 d\mathbf{r}$$
$$= \frac{1}{2}\left\langle u\bar{u} - \bar{u}u \middle| \hat{h}_1 \middle| u\bar{u} - \bar{u}u \right\rangle + \frac{1}{2}\left\langle u\bar{u} - \bar{u}u \middle| \hat{h}_2 \middle| u\bar{u} - \bar{u}u \right\rangle + \frac{1}{2}\left\langle u\bar{u} - \bar{u}u \middle| \frac{1}{r_{12}} \middle| u\bar{u} - \bar{u}u \right\rangle$$
$$= 2\left(u\middle|\hat{h}\middle|u\right) + (uu|uu)$$
$$= 2 \times -17.951147 + 11.923 = -23.979294$$

Calculation of the off-diagonal elements:

In virtue of the Brilouin's theorem, $H_{21} = 0$. This can be easily demonstrated:

$$H_{21} = \int \Phi_1 \hat{H} \Phi_2 d\mathbf{r}$$

$$= \frac{1}{2}\left\langle g\bar{g} - \bar{g}g \middle| \hat{h}_1 \middle| g\bar{u} - \bar{u}g \right\rangle + \frac{1}{2}\left\langle g\bar{g} - \bar{g}g \middle| \hat{h}_2 \middle| g\bar{u} - \bar{u}g \right\rangle + \frac{1}{2}\left\langle g\bar{g} - \bar{g}g \middle| \frac{1}{r_{12}} \middle| g\bar{u} - \bar{u}g \right\rangle$$

$$= \frac{1}{2}\left\langle g \middle| \hat{h}_1 \middle| u \right\rangle + \frac{1}{2}\left\langle g \middle| \hat{h}_2 \middle| u \right\rangle + \left\langle gg \middle| \frac{1}{r_{12}} \middle| ug \right\rangle$$

$$= \left(g \middle| \hat{h} \middle| u \right) + \left(gg \middle| gu \right) = \left(g \middle| \hat{F} \middle| u \right)$$

with:

$$\hat{F} = \hat{h} + \hat{J} = \hat{h} + \int \sigma_g(\mathbf{r}) \left| \frac{1}{r_{12}} \right| \sigma_g(\mathbf{r}) d\mathbf{r}$$

By definition, the Fock matrix is diagonal in the MOs basis. Thus, $H_{21} = 0$.

$$H_{32} = \int \Phi_2 \hat{H} \Phi_3 d\mathbf{r}$$

$$= \frac{1}{2}\left\langle g\bar{u} - \bar{u}g \middle| \hat{h}_1 \middle| \bar{g}u - u\bar{g} \right\rangle + \frac{1}{2}\left\langle g\bar{u} - \bar{u}g \middle| \hat{h}_2 \middle| \bar{g}u - u\bar{g} \right\rangle + \frac{1}{2}\left\langle g\bar{u} - \bar{u}g \middle| \frac{1}{r_{12}} \middle| \bar{g}u - u\bar{g} \right\rangle$$

$$= -\left\langle gu \middle| ug \right\rangle = -\left(gu \middle| gu \right) = -0.92462$$

$$H_{42} = \int \Phi_2 \hat{H} \Phi_4 d\mathbf{r}$$

$$= \frac{1}{2}\left\langle g\bar{u} - \bar{u}g \middle| \hat{h}_1 \middle| u\bar{u} - \bar{u}u \right\rangle + \frac{1}{2}\left\langle g\bar{u} - \bar{u}g \middle| \hat{h}_2 \middle| u\bar{u} - \bar{u}u \right\rangle + \frac{1}{2}\left\langle g\bar{u} - \bar{u}g \middle| \frac{1}{r_{12}} \middle| u\bar{u} - \bar{u}u \right\rangle$$

$$= \left(g \middle| \hat{h} \middle| u \right) + \left(gu \middle| uu \right) = 0$$

$$H_{41} = \int \Phi_1 \hat{H} \Phi_4 d\mathbf{r}$$

$$= \frac{1}{2}\left\langle g\bar{g} - \bar{g}g \middle| \hat{h}_1 \middle| u\bar{u} - \bar{u}u \right\rangle + \frac{1}{2}\left\langle g\bar{g} - \bar{g}g \middle| \hat{h}_2 \middle| u\bar{u} - \bar{u}u \right\rangle + \frac{1}{2}\left\langle g\bar{g} - \bar{g}g \middle| \frac{1}{r_{12}} \middle| u\bar{u} - \bar{u}u \right\rangle$$

$$= \left\langle gg \middle| uu \right\rangle = \left(gu \middle| gu \right) = 0.92462$$

Finally, we obtain the CI matrix:

	1	2	3	4
1	-41,755076	0,0000	0,0000	0,92462
2	0,0000	-32,867376	-0,92462	0,0000
3	0,0000	-0,92462	-32,867376	0,0000
4	0,92462	0,0000	0,0000	-23,979294

By taking the energy of the HF configuration as the reference energy, the CI matrix can be written alternatively:

	1	2	3	4
1	0,0000	0,0000	0,0000	0,92462
2	0,0000	8,8877	-0,92462	0,0000
3	0,0000	-0,92462	8,8877	0,0000
4	0,92462	0,0000	0,0000	17,775782

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
```

The calculated CI matrix is given as follows.

```
C.I. MATRIX (eV)
                    1          2          3          4
-------------------------------------------------------
         1   0.000000
         2   0.000000   8.888081
         3   0.000000  -0.924620   8.888081
         4   0.924620   0.000000   0.000000  17.776162
```

7) Show that the CI matrix can be written in a block-diagonal form, the first block involving the reference and doubly excited configurations (RD-block), the second one involving elements related to singly excited Slater determinants (S-block).

The ordering of the electron configurations Φ_1-Φ_4 in the CI matrix is arbitrary. By sorting the electron configurations in the following order: Φ_1, Φ_4, Φ_2, Φ_3, the matrix has a block diagonal form:

	1	2	3	4
1	0,0000	0,92462	0,0000	0,0000
2	0,92462	17,775782	0,0000	0,0000
3	0,0000	0,0000	8,8877	-0,92462
4	0,0000	0,0000	-0,92462	8,8877

RD-block

	1	2
1	0,0000	0,92462
2	0,92462	17,775782

S-block

	3	4
3	8,8877	-0,92462
4	-0,92462	8,8877

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.

The energies are obtained by solving the 2x2 secular determinant:

$$\begin{vmatrix} H_{11} - \varepsilon & H_{14} \\ H_{14} & H_{44} - \varepsilon \end{vmatrix} = 0$$

which leads to:
$\varepsilon_1 = -41,80304134$
$\varepsilon_2 = -23,93132866$

The CI expansion coefficients of state 1 (2) are obtained by replacing ε by ε_1 (ε_2) in the RD-block Schrödinger equation:

$$\mathbf{HC} = \mathbf{SC}\varepsilon$$

where the **C** matrix contains the CI expansion coefficients. Since the Φ_i functions are normalized and orthogonal one to each other, the overlap matrix can be replaced by the identity matrix **I**, so that:

$$(\mathbf{H} - \varepsilon\mathbf{I})\mathbf{C} = 0$$

For state 1, the $\mathbf{H}-\boldsymbol{\varepsilon}\mathbf{I}$ matrix is equal to

	1	**2**
1	0,047965342	0,92462
2	0,92462	17,82374734

Which leads to the following relationship between the expansion coefficients C_1 and C_2:
$C_2 = -0.051876\ C_1$

Then, using the normalization property of Ψ_1 allows extracting C_1 and C_2:

$$\Psi_1 = 0.9987\Phi_1 - 0.0518\Phi_4$$

Similarly, for state 2, the $\mathbf{H}-\boldsymbol{\varepsilon}\mathbf{I}$ matrix is equal to:

	1	**2**
1	-17,82374734	0,92462
2	0,92462	-0,047965342

which leads to:

$$\Psi_2 = -0.0518\Phi_1 - 0.9987\Phi_4$$

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.

Using similar developments as in Step 8, one obtains:

$\varepsilon_1 = -33{,}791996$
$\varepsilon_2 = -31{,}942756$

and:

$$\Psi_1 = \frac{1}{\sqrt{2}}\left(\Phi_2 + \Phi_3\right)$$
$$\Psi_2 = \frac{1}{\sqrt{2}}\left(\Phi_2 - \Phi_3\right)$$

From Step 1,

$$\Phi_2 = \frac{1}{\sqrt{2}}\left(\sigma_g(1)\alpha(1)\sigma_u(2)\beta(2) - \sigma_u(1)\beta(1)\sigma_g(2)\alpha(2)\right)$$
$$\Phi_3 = \frac{1}{\sqrt{2}}\left(\sigma_g(1)\beta(1)\sigma_u(2)\alpha(2) - \sigma_u(1)\alpha(1)\sigma_g(2)\beta(2)\right)$$

By replacing in Ψ_1 and Ψ_2:

$$\Psi_1 = \frac{1}{\sqrt{2}}\left(\sigma_g(1)\sigma_u(2) - \sigma_u(1)\sigma_g(2)\right)\left(\alpha(1)\beta(2) + \beta(1)\alpha(2)\right)$$
$$\Psi_2 = \frac{1}{\sqrt{2}}\left(\sigma_g(1)\sigma_u(2) + \sigma_u(1)\sigma_g(2)\right)\left(\alpha(1)\beta(2) - \beta(1)\alpha(2)\right)$$

Thus, state 1 is a triplet and state 2 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.

The four eigenstates of H_2 are listed below, in the order of increasing energy:

```
#1 SINGLET     E = -41.803041
#2 TRIPLET     E = -33.791996
#3 SINGLET     E = -31.942756
#4 SINGLET     E = -23.931329
```

By taking state #1 as the reference of energy:

```
#1 SINGLET     E =  0.0000
#2 TRIPLET     E =  8.0114
#3 SINGLET     E =  9.8607
#4 SINGLET     E = 17.8721
```

From AMPAC:

```
 MO: 00  1:SINGLET  2:TRIPLET  3:SINGLET  4:SINGLET
   : 12 eV: 0.0000     8.0114     9.8607    17.8721
   1 20        100%         0%         0%         0%
         ( 0.9987)  ( 0.0000)  ( 0.0000)  (-0.0518)
   2 +-          0%        50%        50%         0%
         ( 0.0000)  ( 0.7071)  (-0.7071)  ( 0.0000)
   3 -+          0%        50%        50%         0%
         ( 0.0000)  ( 0.7071)  ( 0.7071)  ( 0.0000)
   4 02          0%         0%         0%       100%
         (-0.0518)  ( 0.0000)  ( 0.0000)  (-0.9987)
```

Everything is fine, in the best possible world.

Correlation energy: $E = |E_{CI} - E_{HF}|$ = `-41.803041 + 41.755076 = 0.04796 eV`

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.

$$\Phi^{\alpha} = \left|\sigma_g \sigma_u\right| = \frac{1}{\sqrt{2}}\left(\sigma_g(1)\sigma_u(2) - \sigma_u(1)\sigma_g(2)\right)\alpha(1)\alpha(2)$$

$$\Phi^{\beta} = \left|\overline{\sigma}_g \overline{\sigma}_u\right| = \frac{1}{\sqrt{2}}\left(\sigma_g(1)\sigma_u(2) - \sigma_u(1)\sigma_g(2)\right)\beta(1)\beta(2)$$

For obvious reason, these two configurations have the same energy. Let's calculate the energy of Φ^{α}:

$$E^{\alpha} = \int \Phi^{\alpha}\hat{H}\Phi^{\alpha} d\mathbf{r}$$

$$= \frac{1}{2}\left\langle gu - ug\middle|\hat{h}_1\middle|gu - ug\right\rangle + \frac{1}{2}\left\langle gu - ug\middle|\hat{h}_2\middle|gu - ug\right\rangle + \frac{1}{2}\left\langle gu - ug\middle|\frac{1}{r_{12}}\middle|gu - ug\right\rangle$$

$$= \left\langle g\middle|\hat{h}\middle|g\right\rangle + \left\langle u\middle|\hat{h}\middle|u\right\rangle + \left\langle gu|gu\right\rangle - \left\langle gu|ug\right\rangle$$

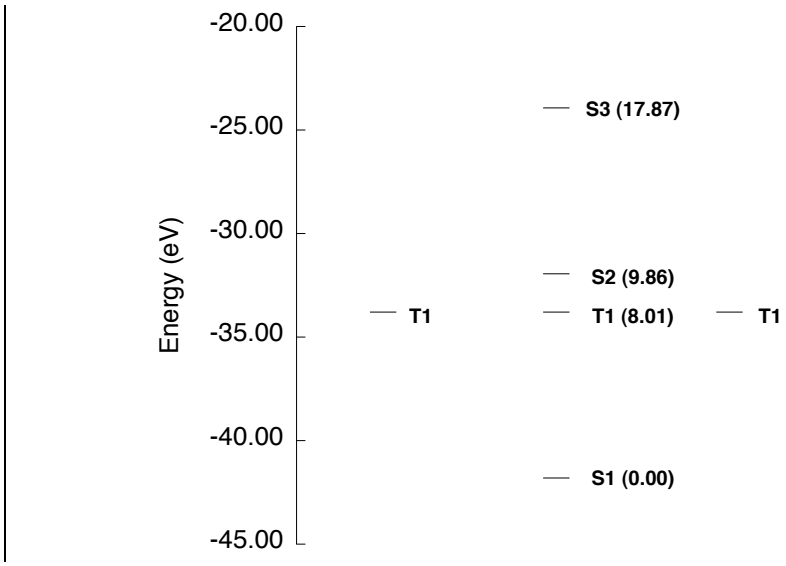
$$= \left(g\middle|\hat{h}\middle|g\right) + \left(u\middle|\hat{h}\middle|u\right) + \left(gg|uu\right) - \left(gu|gu\right)$$

$$= -26.839229 - 17.951147 + 11.923 - 0.92462$$

$$= -33.791996$$

This state has the same energy than state #2 calculated in Step 10.

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.


-20.00
-25.00
-30.00
-35.00
-40.00
-45.00
Energy (eV)
S3 (17.87)
S2 (9.86)
T1
T1 (8.01)
T1
S1 (0.00)