LAB. EXERCISE 6
PERTURBATIVE CALCULATION OF THE CORRELATION ENERGY IN THE HYDROGEN MOLECULE

PART 1: EXACT CORRELATION ENERGY IN THE MINIMAL BASIS SET

1) Write the general expression of the Hartree-Fock total energy for a closed-shell system, using the physicists' and chemists' notations for the two electron integrals.

2) Write the expression of the Hartree-Fock total energy for the ground state of the hydrogen molecule, and calculate the numerical value using the integral values obtained in LAB-EX5. We will use the notation:

$$h_{gg} = \int \sigma_g(\mathbf{r})\hat{h}\sigma_g(\mathbf{r})d\mathbf{r}$$
$$h_{uu} = \int \sigma_u(\mathbf{r})\hat{h}\sigma_u(\mathbf{r})d\mathbf{r}$$
$$J_{gg} = (gg|gg)$$
$$J_{uu} = (uu|uu)$$
$$J_{gu} = (gg|uu)$$
$$K_{gu} = (gu|gu)$$

3) Give the expression of the energy ε_g and ε_u of the molecular orbitals σ_g and σ_u as a function of the integrals h, J and K. Deduce the expression of the Hartree-Fock total energy as a function of ε_g and J_{gg}.

4) Using results of LAB-EX5 (Step 8), write the expression of the *exact* ground state energy of the hydrogen molecule obtained from a full SDCI calculation in the minimal basis set.

5) Deduce the expression of the *exact* correlation energy E_{corr} as a function of the orbital energies ε_g and ε_u, and of the J and K integrals. Compute the numerical value of E_{corr} using the integral values given in LAB-EX5.

PART 2: MP2 CORRELATION ENERGY

6) Derive the standard expressions of Rayleigh-Schrödinger Perturbation Theory for different order terms (0,1,2) in the power series expansion of the perturbed energies and wavefunctions.

7) Derive the 0^{th}-, 1^{th}- and 2^{th}-order electron correlation energy ($E^{(0)}$, $E^{(1)}$ and $E^{(2)}$) within the Moller-Plesset partition scheme.

8) Evaluate $E^{(0)}$, $E^{(1)}$ and $E^{(2)}$ for the hydrogen molecule.

9) Deduce the expression of the correlation energy obtained at the second-order of the Moller-Plesset theory (MP2), and compare to the exact correlation energy.