

TD 2: Post-Hartree-Fock calculations

We continue our toy example of a ground-state calculation of the helium atom, with two s -type Gaussian basis functions of exponents $\alpha_1 = 3.8$ and $\alpha_2 = 0.5$. In TD 1, we performed a Hartree-Fock (HF) calculation and found the HF orbital coefficients: $\mathbf{c}_1 = (0.300859, 0.811650)$ for the occupied orbital, and $\mathbf{c}_2 = (1.125742, -0.836084)$ for the virtual orbital.

1 Transformation of the integrals

1. Give the expressions of the one-electron and two-electron integrals over the HF orbitals in terms of the orbital coefficients and the integrals over the basis functions. With the most naive algorithm, how do the computational costs of these integral transformations scale with the number of basis functions? Can you think of a better algorithm for reducing the scaling of the two-electron integral transformation?
2. Using the integrals calculated in TD 1, check that the one-electron integrals over the orbitals are

$$h_{11} = -1.880726 \text{ a.u.}, \quad h_{12} = -0.294242 \text{ a.u.}, \quad h_{22} = 1.527091 \text{ a.u.}$$

and the two-electron integrals over the orbitals are

$$\begin{aligned} (11|11) = J_{11} &= 1.015389 \text{ a.u.}, & (11|22) = J_{12} &= 1.133273 \text{ a.u.}, & (11|12) &= 0.294247 \text{ a.u.}, \\ (22|22) = J_{22} &= 1.393927 \text{ a.u.}, & (12|22) &= 0.462571 \text{ a.u.}, & (12|12) = K_{12} &= 0.284985 \text{ a.u.} \end{aligned}$$

3. Using these integrals over the orbitals:
 - (a) Verify that Brillouin's theorem is satisfied.
 - (b) Recalculate the energies of the two HF orbitals and the HF total energy, already obtained in TD 1.

2 Perturbation theory

1. Recall the expressions of the zeroth-, first- and second-order total energies, $E^{(0)}$, $E^{(1)}$ and $E^{(2)}$, in Møller-Plesset (MP) perturbation theory in terms of spin orbitals and spatial orbitals, and calculate them for the He atom.
2. Are there contributions of triple and quadruple excitations in the higher-order perturbation terms for this system?

3 Configuration interaction

1. Write down the form of the full configuration interaction (FCI) ground-state wave function of the He in terms of spin-adapted configurations (also called configuration state functions). What are the dimensions of the FCI Hamiltonian matrix?
2. Write down the expressions of the elements of the FCI Hamiltonian matrix in terms of the one- and two-electron integrals. Calculate them.
3. The ground-state FCI total energy is -2.757357 a.u.. Verify that it is indeed an eigenvalue of the Hamiltonian matrix. Calculate the FCI correlation energy. Compare with the correlation energies found in second-order MP perturbation theory.
4. What is the ground-state total energy in CISD (configuration interaction singles doubles) and CID (configuration interaction doubles)? Same question for CCSD (coupled cluster singles doubles) and CCD (coupled cluster doubles)?
5. Calculate the first ionization energy of the He atom by difference of total energies in HF and FCI (using for the He^+ ion the same HF orbitals than the neutral atom). Compare to the energy of the occupied HF orbital of the He atom and to the experimental value, 24.59 eV (1 a.u. = 27.21 eV).
6. Repeat the calculations of the first ionization energy using now the exact ground-state energy of the He^+ ion. Comment.