

TD 2: Post-Hartree-Fock calculations

1 Helium atom

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.

1.1 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.

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. The Epstein-Nesbet (EN) perturbation theory can be defined by choosing a different zeroth order Hamiltonian. It also corresponds to the infinite summation of a certain class of terms (or diagrams) appearing in MP perturbation theory. At second order, the EN energy correction can be obtained from the MP energy correction by replacing the orbital energy differences in the denominator by $\langle \Psi_{ab}^{rs} | \hat{H} | \Psi_{ab}^{rs} \rangle - \langle \Psi_0 | \hat{H} | \Psi_0 \rangle$, where Ψ_0 is the HF determinant wave function and Ψ_{ab}^{rs} is a doubly-excited determinant wave function. Calculate the second-order EN energy of the He atom.

1.3 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 and EN perturbation theories.
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)?

- 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).
- Repeat the calculations of the first ionization energy using now the exact ground-state energy of the He^+ ion. Comment.

2 C_2 molecule

The C_2 molecule is not very stable. Yet, it is formed in flames (being partly responsible for the emission of blue light), and it has been detected in comets and in interstellar clouds. We want to calculate its dissociation energy. We will perform *ab initio* calculations with the standard Gaussian basis cc-pVTZ. The experimental equilibrium internuclear distance is $R_e = 2.3481$ bohr.

- Predict the molecular orbital energy diagram of this molecule. What is the spin multiplicity of the ground state?
- A restricted Hartree-Fock (RHF) calculation performed at the equilibrium distance in D_{2h} symmetry gives for the first 12 orbitals the following irreducible representations (IRs), energies and occupation numbers:

IRs of orbitals	AG	B1U	AG	B1U	B2U	B3U	AG	B2G	B3G	B1U
energies (a.u.)	-11.360	-11.357	-1.061	-0.517	-0.457	-0.457	-0.111	0.152	0.152	0.273
occupations	2	2	2	2	2	2	0	0	0	0

The total RHF energy is $E_{\text{RHF}}(R_e) = -75.401446$ a.u..

Establish the correspondence between these IRs and the IRs of the true $D_{\infty h}$ symmetry group (for character tables of symmetry groups, see www.webqc.org). Verify whether your prediction for the ground state was correct.

- We also perform a RHF calculation (with the same orbital occupations) at a very large internuclear distance ($R = 1000$ bohr) which gives $E_{\text{RHF}}(R = 1000) = -74.802480$ a.u., and a restricted open-shell Hartree-Fock (ROHF) calculation of the 3P ground state of the C atom which gives $E_{\text{ROHF}}(\text{C}) = -37.686708$ a.u.. Using these calculations, give two estimates of the dissociation energy (in eV) of the C_2 molecule. Why are they different?
- We now perform a CISD (configuration interaction single doubles) calculation of the molecule at the equilibrium distance, with the core orbitals being frozen. It gives $E_{\text{CISD}}(R_e) = -75.711300$ a.u.. The occupation numbers of the associated natural orbitals are

IRs of orbitals	AG	B1U	AG	B1U	B2U	B3U	AG	B2G	B3G	B1U
occupations	2.00	2.00	1.98	1.85	1.93	1.93	0.14	0.05	0.05	0.01

What does this tell us about the ground-state wave function of the C_2 molecule?

- We decide to perform multiconfiguration self-consistent field (MCSCF) calculations, using complete active spaces (CAS) of orbitals. What is the smallest CAS, containing only 2 configuration state functions (CSF), that you would choose for the description of the ground state of this molecule at the equilibrium distance? Is this CAS appropriate to calculate the dissociation energy?
- We now perform larger MCSCF calculations, distributing the 8 valence electrons in the 8 valence orbitals, i.e. CAS(8,8), at equilibrium and large distance. They give $E_{\text{CAS}(8,8)}(R_e) = -75.638411$ a.u. and $E_{\text{CAS}(8,8)}(R = 1000) = -75.411691$ a.u.. What would be the corresponding atomic calculation ensuring size consistency? Calculate the dissociation energy. Compare to the experimental value of the dissociation energy, 6.2 eV, after remembering to correct for the vibrational zero-point energy of 927.4 cm^{-1} .
- We continue by performing MRCISD (multireference CISD) calculations on top of the MCSCF CAS(8,8) calculations at equilibrium and large distance. They give $E_{\text{MRCISD}}(R_e) = -75.779961$ a.u. and $E_{\text{MRCISD}}(R = 1000) = -75.554055$ a.u.. Calculate the corresponding dissociation energy. What is the main deficiency of MRCISD calculations?
- It would be nice to have a size-consistent multireference coupled cluster (MRCC) method. Many variants of such a method have been proposed these recent years. Each variant has some advantages and drawbacks, and there is still no consensus in the quantum chemistry community on the best way to construct a MRCC method. Design your own MRCC method, implement it in a computer program and apply it to the C_2 molecule.