Mardi 12 janvier 2015

Examen
UE 5C208 Chimie quantique de l'UPMC
Master spécialité CAPT Chimie Paris Centre
Durée de l'épreuve : une heure

Documents et calculatrices sont autorisés. Le sujet comporte cinq questions et il est sur une feuille recto-verso.

Part 1: Helium atom with quantum chemical approaches

Q1: Write down a Slater determinant for the ground electronic state of He (^1S).

Q2: Write down a Slater determinant for the excited electronic state of He (^3S).

Q3: Within HF-SCF theory, write down the electronic energy for He (^1S) and for He (^3S) states.

Q4: Explain why the electronic energy is different from the sum of occupied orbital energies?

Q5: The energetic results of HF/TZVP and CCSD(T)/TZVP are gathered in Table 1.

	^1S: ground state	^3S: excited state
HF/TZVP	-2.8598954	-1.7910023
CCSD(T)/TZVP	-2.8929575	-1.7910023

- Explain the most important difference between two methods
- For the ground electronic state of He, why the HF energy is different from the CCSD(T) one?
- Explain why we obtain the same energy with two approaches for the excited state?

Part 2: Density functional theory

The Kohn and Sham (KS) approach allows the application of Density Functional Theory to chemical problems. Please give details about the KS approach, including the definition of the different terms in the total energy functional, and underlie differences and similitudes with the Hartree-Fock model

Part 3: Spectrocopie

Décrire les méthodes utilisées pour calculer un spectre d'absorption électronique UV/Vis d'un composé moléculaire

Part 4:

Molecular properties

For a closed-shell system, the *spin-singlet* excitations can be calculated by the *spin-adapted time-dependent Hartree-Fock* generalized eigenvalue equation

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{X}_n \\ \mathbf{Y}_n \end{pmatrix} = \omega_n \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \mathbf{X}_n \\ \mathbf{Y}_n \end{pmatrix},$$

where $A_{ar,bs} = (\varepsilon_r - \varepsilon_a)\,\delta_{ab}\delta_{rs} + 2\langle rb|as\rangle - \langle rb|sa\rangle$ and $B_{ar,bs} = 2\langle rs|ab\rangle - \langle rs|ba\rangle$, where a, b are occupied HF *spatial* orbitals and r, s are unoccupied HF *spatial* orbitals. The orbitals are assumed to be real-valued.

We consider the H_2 molecule in a minimal basis with two spatial HF orbitals: one doubly occupied σ_g orbital which will be called "1" and one unoccupied σ_u orbital which will be called "2".

1. In this case, what is the dimension of each matrix **A** and **B**?
2. Write the expressions of **A** and **B** in terms of the orbital eigenvalues ε_1 and ε_2, and the two-electron integrals $J_{12} = \langle 21|21\rangle$ and $K_{12} = \langle 21|12\rangle = \langle 22|11\rangle$.
3. What is the Tamm-Dancoff approximation?
4. In the Tamm-Dancoff approximation, write the expressions of the eigenvalues ω_n and eigenvectors $(\mathbf{X}_n, \mathbf{Y}_n)$. What does each eigenvalue ω_n represent?

Part 5:

Post-Hartree-Fock

We consider second-order Møller–Plesset perturbation theory (MP2). The second-order energy contribution is

$$E_{\mathrm{MP}}^{(2)} = \sum_I \frac{\langle \Phi_{\mathrm{HF}}|\hat{V}|\Phi_I\rangle^2}{E_0^{(0)} - E_I^{(0)}}$$

with the Hartree-Fock determinant Φ_{HF} and the excited determinants Φ_I.

1. Explain what is understood by $\hat{V}$, $E_0^{(0)}$, $E_I^{(0)}$.
2. Show that $\langle \Phi_{\mathrm{HF}}|\hat{V}|\Phi_I\rangle = \langle \Phi_{\mathrm{HF}}|\hat{H}|\Phi_I\rangle$.
3. Is the MP2 total energy always an upper bound of the exact ground-state energy? Why or why not?
4. Give at least two arguments for motivating why MP2 is a widely used method in quantum chemistry.