Mardi 9 décembre 2014

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

Les documents sont interdits. Les calculatrices sont autorisées. Le sujet comporte quatre parties et il est sur une feuille recto-verso.

Part 1: Hartree-Fock method

A Hartree-Fock calculation on the ground state of the H_2 molecule was carried out at a fixed internuclear distance of 1.40 a.u. The energetic results are gathered in Table 1:

MO energies	$\varepsilon_1 = -0.619$ *a.u.* $\varepsilon_2 = -0.401$ *a.u.*
The two-electron integrals φ_1 and φ_1 : the molecular orbitals	$\langle\varphi_1(1)\varphi_1(2)\|1/r_{12}\|\varphi_1(1)\varphi_1(2)\rangle = 0.566$ *a.u.* $\langle\varphi_1(1)\varphi_2(2)\|1/r_{12}\|\varphi_1(1)\varphi_2(2)\rangle = 0.558$ *a.u.* $\langle\varphi_1(1)\varphi_2(2)\|1/r_{12}\|\varphi_2(1)\varphi_1(2)\rangle = 0.140$ *a.u.* $\langle\varphi_2(1)\varphi_2(2)\|1/r_{12}\|\varphi_2(1)\varphi_2(2)\rangle = 0.582$ *a.u.*

Q1: Write down a Slater determinant for the ground electronic state of H_2.

Q2: Give the general expression of the electronic energy of a system containing 2n electrons.

Q3: Using the molecular orbital energies and the two-electron integrals given above, compute the electronic energy of H_2 at an internuclear separation of 1.40 a.u.

Q4: Determine the total energy from the SCF calculation for H_2 at an internuclear separation of 1.40 a.u.

Part 2: Density functional theory

1) Give a definition of the exchange correlation energy.

2) What is the difference between Hartree-Fock and Kohn-Sham orbitals?

3) Define a double hybrid functional

Part 3: Solid

Explain the electronic structure of crystal titanium dioxide with the help of use Density of States. Establish a link with the oxidation number of oxygen and titanium.

Part 4: Molecular properties

1) Give the advantages and drawbacks of numerical differentiation and analytical differentiation for calculating derivatives of the energy.

2) Explain why it is easier to calculate molecular properties with quantum chemistry methods that are *variational* such as Hartree-Fock.

3) Explain what the exponential parametrization of the Hartree-Fock wave function is and why it is useful.

4) Write down the definition of the quasi-energy. Explain why it is useful to introduce this quantity.

5) Write down, in matrix form, the equations for calculating excitation energies in time-dependent Hartree-Fock and define each term.