Chemistry 651

Final exam

12 June 2006

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1. Explain why we should not use the function

$$\psi(1,2) = \mathcal{N}e^{-a(r_1+r_2)}(r_1 - r_2) \qquad (1)$$

for the helium atom ground state.

2. A particle exists in a box of length L ($0 \le x \le L$) and is subject to a small potential island in the box center such that,

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$$U(x) = k, \qquad \frac{L}{4} \le x \le \frac{3L}{4} \qquad (2)$$

   (a) Calculate the first order shift in energy and the first order change in wavefunction.
   (b) We know that the system will exhibit tunnelling when k is very large. Accordingly, when is our perturbation theory valid?
   (c) Are any exact results obtainable from the application of the Hellmann-Feynman theorem independent of the size of k?

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3. A new particle is found to have a spin of unity (a Boson) and a charge of -1. A Hartree SCF calculation is performed on a three particle system which has a wavefunction $\psi(1,2,3) = a(1)b(2)c(3)$ where a, b and c are distinct orthonormal spin orbitals.
   (a) Write the symmetrized and normalized Boson wavefunction.
   (b) What is the Hamiltonian of this system?
   (c) What is the ground state energy, as expressed in terms of ϵ_0, J and K.

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4. Suppose we perform a MO calculation on a fixed geometry with a single degree of freedom as expressed by the coordinate R, and that we could calculate the first and second derivative of the energy with respect to R. Implement the Newton-Raphson algorithm to optimize the geometry and thereby arrive at the potential minimum.

5. Define these:

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   - 6-31 G
   - contracted Gaussian
   - correlation energy
   - configuration interaction
   - MP2

6. Write the DFT expression for the energy of a many electron atom. Define all terms.

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Final Exam

1. $\psi(1,2)$ is antisymmetric wrt space $\Rightarrow$ symmetric wrt spin

$\alpha\alpha$
$\beta\beta$
$\frac{1}{\sqrt{2}}(\alpha\beta + \beta\alpha)$

The ground state of He is not a triplet.

2. a)

$$E_n^{(1)} = \int_{L/4}^{3L/4} dx \, \sin^2(n\pi x/L) \left(\frac{2}{L}\right)$$

$$\psi_n^{(1)} = \psi_n^{(0)} + \sum_{m \neq n}^{\infty} \left[\frac{\int_{L/4}^{3L/4} \psi_n(x)\psi_m(x)\,dx}{E_n^0 - E_m^0} \right] \psi_m^0(x)$$

b) Perturbation theory valid when

$E_n^0 - E_m^0 \gg k$ energy below barrier

c) Hellmann-Feynman theorem

$$\left(\frac{\partial E}{\partial k}\right) = \int_0^L dx \, \psi_n^*(x) \underbrace{\left(\frac{\partial H}{\partial k}\right)}_{\xi} \psi_n(x) = \int_{L/4}^{3L/4} dx \, \psi_n^2(x, k)$$

rhs is a function of k. Can't see that HF theorem gave us much in this application.

3 a) $\psi = \frac{1}{\sqrt{6}} \{ a(1)\, b(2)\, c(3) + a(1)\, b(3)\, c(2) +$
$a(2)\, b(1)\, c(3) + a(2)\, b(3)\, c(1) +$
$a(3)\, b(1)\, c(2) + a(3)\, b(2)\, c(1) \}$

b) $H = -\frac{1}{2m_p}(\nabla_1^2 + \nabla_2^2 + \nabla_3^2) + z^2 \{ \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}} \}$

m_p = mass of the particle

c) Ground state energy

$E = \epsilon_a + \epsilon_b + \epsilon_c + J_{ab} + J_{ac} + J_{bc}$

where $\epsilon_a = -\frac{1}{2}\langle a(1)\, \nabla_1^2\, a(1) \rangle$

$J_{ab} = \int d1\, d2\, a^2(1)\, b^2(2) / r_{12}$

4) Newton-Raphson

$U(R) = U(R_0) + U'(R_0)(R-R_0) + \frac{1}{2}U''(R_0)(R-R_0)^2 + \cdots$
require, at equilibrium, that the force vanishes

$-F(R) = \frac{\partial U}{\partial R} = U'(R_0) + (R-R_0)\, U''(R_0) \Rightarrow$
$= 0$

$R - R_0 = -\frac{U'(R_0)}{U''(R_0)}$, $\quad R = R_0 - \frac{U'(R_0)}{U''(R_0)}$

5. a) 6-31G

6 - inner shell contracted Gaussian

3 - valence shell " "

1 - diffuse (long range) " "

in a HF basis set

b) contracted Gaussian $= \sum_{i=1}^{N} a_i \exp(-r^2/\alpha_i)$

c) correlation energy $\equiv E_{exact} - E_{HF}$

d) CI corresponds to a HF approach in which we have included extra Slater determinants in which double excitation states are used in addition to the usual set of ground state orbitals. multi-determinantal wf.

e) MP2 a perturbation theory using double excitation states, perturbation

$$H^{(1)} = \frac{1}{r_{12}} - \text{HF}$$ representation of the Coulomb int

6) DFT $\Rightarrow$ $E[\rho]$

ρ = electron density

$$E[\rho] = T[\rho] + V[\rho] + \int dr\, \rho(r)\, V(r) + E_{xc}[\rho]$$

$T[\rho] \equiv$ kinetic energy $= -\frac{1}{2}\sum_i \langle \phi_i(1) | \nabla_1^2 | \phi_i(1) \rangle$

Kohn-Sham orbitals

$V[\rho] \equiv$ classical coulomb $e^- - e^-$ repulsion $= \int d1\,d2\ \rho(1)\rho(2)/r_{12}$

$V(r) \equiv -\sum_\alpha Z_\alpha / r_\alpha$

distance of an e^- from the nucleus

$E_{xc}[\rho] \equiv$ exchange-correlation energy

$\sim \rho^{1/3}(r) \Leftarrow$ weak link