Chemistry 651

Problem set 4

Due: 8 June 2006

1. A variational wavefunction of the helium atom is

$$\psi(1,2) = \frac{1}{\pi}\xi^3 e^{-\xi(r_1+r_2)} \qquad E = -(Z - \tfrac{5}{16})^2 \tag{1}$$

   Using the virial theorem, calculate $\langle T\rangle, \langle V\rangle$, the kinetic and potential energies, respectively.

2. From perturbation theory, we have the result that if

$$H = H^{(0)} + \lambda H^{(1)} \tag{2}$$

   then

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots \tag{3}$$

   Use the Hellmann-Feynman theorem in the $\lambda = 0$ limit to show that

$$E_n^{(1)} = \langle \psi_n^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle \tag{4}$$

3. Suggest a derivation of the second order Moller-Plesset energy correction,

$$E_0^{(2)} = \sum_{b=a+1}^{\infty} \sum_{a=n+1}^{\infty} \sum_{i=j+1}^{n} \sum_{j=1}^{n-1} \frac{|\langle ab|r_{12}^{-1}|ij\rangle - \langle ab|r_{12}^{-1}|ji\rangle|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \tag{5}$$

$$\langle ab|r_{12}^{-1}|ij\rangle = \int d1d2\phi_a^*(1)\phi_b^*(2)r_{12}^{-1}\phi_i(1)\phi_j(2) \tag{6}$$

   noting the limits in the sums, the energy denominator and the overlap numerator. Is n the number of electrons or orbitals?

Problem set 4

1. By the virial theorem,

$$\langle T\rangle = nE/(n+2)$$
$$\langle U\rangle = 2E/(n+2)$$

For the He - atom $V(r) = 1/r \Rightarrow$ homogeneous of degree -1.

$$\therefore \quad \langle T\rangle = -E$$
$$\langle U\rangle = 2E \qquad \text{where} \quad E = -(Z-5/16)^2$$

2. $$H = H^{(0)} + \lambda H^{(1)}$$

$$E_n = E_n^{(0)} + E_n^{(1)}\lambda + \cdots \qquad E_n(\lambda)$$

$$E_n(\lambda) = \langle \psi_n^*(\lambda) | H(\lambda) | \psi_n(\lambda)\rangle$$

$$\frac{\partial E_n(\lambda)}{\partial \lambda} = E_n^{(1)} + 2\lambda E_n^{(2)} + 3\lambda^2 E_n^{(3)}$$

$$= \langle \psi_n^*(\lambda) \underbrace{\frac{\partial H(\lambda)}{\partial \lambda}}_{H_1} \psi_n(\lambda)\rangle$$

$$\therefore \quad E_n^{(1)} + 2\lambda E_n^{(2)} + \cdots = \langle \psi_n^*(\lambda) | H_1 | \psi_n(\lambda)\rangle$$

$$\lim_{\lambda\to 0} \frac{\partial E}{\partial \lambda} = E_n^{(1)} = \langle \psi_n(\lambda=0) | H_1 | \psi_n(\lambda=0)\rangle$$

same as 1st order pert. theory

3. In MP2, we wish to calculate

$$\cancel{E}_k = \sum_l \frac{\langle k | H' | l \rangle \langle l | H' | k \rangle}{E_k^0 - E_l^0}$$

The l-states correspond to double exatations from the $n/2$ occupied Fock orbitals

Since $E_k^0 = \epsilon_i + \epsilon_j$ + other bits (occupied states)

and $E_l^0 = \underbrace{\epsilon_a + \epsilon_b}_{\text{unoccupied}}$ + same other bits

then

$$E_k^0 - E_l^0 = \epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b$$

Next,

$$\langle k | H' | l \rangle = \langle \phi_i(1) \phi_j(2) | H' | [\phi_a(1) \phi_b(2) + (1 \rightleftharpoons 2)] \rangle$$

$$\sim \langle \phi_i(1) \phi_j(2) | \frac{1}{r_{12}} | [\phi_a(1) \phi_b(2) - \phi_a(2) \phi_b(1)] \rangle$$

when we insert this into the standard pert. theory result, we obtain MP2.