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?