Fall 2011 CHEM 760: Introductory Quantum Chemistry

Homework 8 Due: Not to be turned in for a grade. For practice only

1. In the simplest treatment of helium, we used a trial function of the form

$$\phi(1,2) = 1s(1)1s(2)\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

By varying the 1s function in all ways consistent with the form

$$1s(r,\theta,\phi) = [c_0 + c_1r + c_2r^2 + c_3r^3 + \dots]\exp[-\frac{z_{eff}r}{a}]$$

We found that the variational integral predicted a ground state energy of -77.9 eV, while the ground state energy is experimentally measured to be -78.99 eV.

- a) Describe why the uncertainty is big for this variational approach. What phenomenon is neglected in this treatment?
- b) Describe, in as much detail as possible, an approach that can be used to overcome this problem.
- 2. textbook 8.1, 8.4, 8.6, 8.7, 8.8, 8.14
- 3. textbook 9.11, 9.12, 9.15