Physics 685 – Electronic Structure

Homework 15

Please read Martin, Electronic Structure, Chapter 7, especially sections 3-5. Read handout by Tomás Arias. Come prepared to answer questions based on reading.

Correlation Kinetic and Potential Energy in He

A simple model for a correlated wavefunction for the He atom, and thus a much better approximation to the true ground state than the independent particle picture is

$$\psi_{He}(\mathbf{r}_1, \mathbf{r}_2) = (C_0)^2 \exp(-\zeta r_1/a_B) \exp(-\zeta r_2/a_B)(1 + br_{12}) \tag{1}$$

Here C_0 is the normalization of the single particle orbital, ζ is the shielded nuclear charge (around 1.65) and b is a variational parameter, usually a fair bit less than 1.0. The variables r_1 and r_2 are the distances of each particle from the nucleus, and r_{12} is the distance between particles. The first two terms in the wavefunction are of course, independent particle orbitals; the third describes the correlation between the two. It enhances the wavefunction for configurations in which r_{12} is large as compared to when it is zero, and thus increases the probability that the two electrons are spatially separated. This spatial separation reduces the Coulomb potential energy stored in the system. One minor last issue is that this wavefunction is not exactly normalized since the extra should change the normalization factor from the single particle case. We will ignore this effect, which will be ok if b is small.

1. Calculate an expression for the kinetic energy integral $-\frac{1}{2} < \psi| \sum_i \nabla_i^2 |\psi >$ and compare to the non-correlated case $b = 0$. Do not try to evaluate it! Don't even try to evaluate the derivatives yet! The difference between the two is the correlation kinetic energy T_c. Is it likely to be negligible?

2. Let's try to answer the "is it likely to be negligible" issue. Evaluate the following expression that occurs in the kinetic energy above:

$$-\frac{1}{2}(\nabla_1^2 + \nabla_2^2)(1 + br_{12}). \tag{2}$$

   You may wish to review some results for gradient of "cursive-r" from Griffiths' Electricity and Magnetism to do so. What happens to this term as r_{12} goes to zero? Why would this be a useful, in fact necessary, feature of the true Helium ground state? (Hint: think of what happens to the Coulomb potential energy (for the true many-body Hamiltonian, not for the Kohn-Sham equation!) as r_{12} goes to zero.)

3. Assume the two particles are both 1 a_B from the nucleus. Put particle 1 on the z-axis and let particle 2 be oriented at an azimuthal angle θ from the z-axis. Plot the

probability $P(\theta)$ that particle 2 will be at an angle θ with respect to the first particle, for θ from 0 to π and for $b = 0.2$, 0.5 and 1.0. It is easiest to plot this in units of $C_0^2 \exp(-4\zeta)$, i.e., only plotting the dependence of θ on the correlation term. This function shows the correlation hole formed around the first particle because of the Coulomb repulsion of the second one. This lowers the Coulomb potential energy of the system.

4. At what value of $\mathbf{r}_1$ and $\mathbf{r}_2$ does this wavefunction take on its highest value? Compare to that of the independent particle case, $b = 0$.