February 9, 2015

PHY 752 – Problem Set #11

Read Chapter 9 in **Marder**

1. This problem is concerned with variationally estimating the ground state electronic energy of a two-electron atom with nuclear charge Ze in the Hartree-Fock approximation. The Hamiltonian for the two-electron system is

$$H(\mathbf{r}_1, \mathbf{r}_2) = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - Ze^2\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}.$$

Assume that the spatial part of the two-electron wavefunction can be written in the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \phi(r_1)\phi(r_2),$$

where

$$\phi(r) = \mathcal{N}\mathrm{e}^{-\alpha r/a},$$

where $\mathcal{N}$ is the normalization factor, $a = \hbar^2/(me^2)$ is the Bohr radius, and α is a variational parameter.

(a) Show that

$$E(\alpha) \equiv \frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \frac{\hbar^2}{2ma^2}\left(\alpha^2 - 2\alpha\left(Z - \frac{5}{8}\right)\right).$$

Hint: Show that the two electron term involves the integral

$$\int_0^\infty dr r^2 \mathrm{e}^{-2\alpha r/a}\left(\frac{1}{r}\int_0^r dr' r'^2 \mathrm{e}^{-2\alpha r'/a} + \int_r^\infty dr' r' \mathrm{e}^{-2\alpha r'/a}\right) = 2\int_0^\infty dr r \mathrm{e}^{-2\alpha r/a}\int_0^r dr' r'^2 \mathrm{e}^{-2\alpha r'/a}.$$

(b) Find the value of α that minimizes the Hartree Fock energy $E(\alpha)$ and the corresponding estimate of the ground state energy of the two-electron system.