HW problem week 9

A Helium atom is the second simplest atom after hydrogen: it has two electrons surrounding a nucleus of two protons and two neutrons. Unfortunately, the second simplest atom is impossible to solve exactly! Therefore we will study a model which makes some approximations, yet obtains very good agreement with experiment.

1. What is the Hamiltonian for the helium atom? You can leave it in terms of $\hat{p}_1$ and $\hat{p}_2$, i.e. dont write out the whole spherical laplacian expressions.

   $$\hat{H} = \frac{\hat{p}_1^2}{2m_e} + \frac{\hat{p}_2^2}{2m_e} - kZe^2\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{ke^2}{|r_1 - r_2|} \equiv H_0 + H_{e-e}$$

   with $Z = 2$. The first two terms are the kinetic energy of electrons 1 and 2, the second term are the coulomb interaction of the electrons with the nucleus, and the last term H_{e-e} is the coulomb energy between the two electrons.

2. Neglecting the coulomb energy between the two electrons, what is the ground state energy of this system? How does it compare with the experimental value of -78.98 eV?

   In this case, the problem is reduced to a hydrogen-like atom for each electron. The electrons occupy the two (spin up and spin down) $n = 1$ states which have energy $-4E_0$ each for a ground state energy of -108.8 eV. This is significantly different from the experimental value.

3. We can obtain a better estimate for the ground state energy by assuming that the wavefunctions for each electron are of the hydrogen type - $\psi = C_{100}e^{-rZ/a_0}$ - and calculating the expectation value of the energy now including the coulomb energy between the two electrons. Show that the potential energy due to the electron-electron interaction makes a contribution $5ke^2/4a_0$ to the energy. What is the new ground state energy?

   Hint: the following integral may be useful :

   $$\int dr_1 d\theta d\phi \, \frac{r_1^2 \sin\theta e^{-2r_1}}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta}} = \frac{\pi}{r_2}\left(1 - e^{-2r_2}(1 + r_2)\right)$$

   Hint: it will be helpful for part 4 to leave your answer in terms of Z until the end. The two-electron wave function is $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \phi(\boldsymbol{r}_1)\phi(\boldsymbol{r}_2)$ where $\phi(r) = \sqrt{\frac{Z^3}{\pi a_0^3}}e^{-Zr/a_0}$. We already found $\langle H_0 \rangle = -8E_0$ so we just need to calculate

$$\langle H_{e-e}\rangle = ke^2 \int d^3\boldsymbol{r}_1 d^3\boldsymbol{r}_2 \,\frac{|\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2)|^2}{|\boldsymbol{r}_1-\boldsymbol{r}_2|} = \frac{Z^6 ke^2}{\pi^2 a_0^6}\int d^3\boldsymbol{r}_1 d^3\boldsymbol{r}_2 \frac{e^{-2Z(|r_1|+|r_2|)/a_0}}{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta_{12}}}$$

where $d^3\boldsymbol{r}_1$ means integrate coordinate 1 over all space (i.e. $dx_1dy_1dz_1$). Define the dimensionless lengths $l = Zr/a_0$

$$\frac{Zke^2}{\pi^2 a_0}\int d\boldsymbol{l}_1 d\boldsymbol{l}_2 \,\frac{e^{-2(|l_1|+|l_2|)}}{\sqrt{l_1^2+l_2^2-2l_1l_2\cos\theta_{12}}}$$

Using the hint, we can do the integral over $\boldsymbol{l}_2$

$$\int dl_2 d\theta d\phi \frac{l_2^2 \sin\theta e^{-2l_2}}{\sqrt{l_1^2+l_2^2-2l_1l_2\cos\theta_{12}}} = \frac{\pi}{l_1^2}\left(1-e^{-2l_1}(1+l_1)\right).$$

Plugging this into the line above, we have

$$\frac{Zke^2}{a_0\pi}\int dl_1 d\theta d\phi \,(1-e^{-2l_1}(1+l_1))\sin\theta e^{-2l_1}$$

The integral over θ and ϕ gives 4π and what remains is $\int_0^\infty dl_1 \;\left(l_1e^{-2l_1}-l_1e^{-4l_1}-l_1^2e^{-4l_1}\right) = \frac{5}{32}$

So altogether we get $\frac{5}{4}\frac{ke^2}{a_0}$ for $Z=2$. The total energy then is $-8E_0+5/2E_0 = -74.8eV$. Getting pretty close now.

4. In the previous part, we calculated the energy using the unperturbed hydrogenic wave functions. In reality, there are two electrons, and each electron partially 'screens' the nuclear charge from the other electron. We can take this into account by using modifying the wavefunction to e^{-rZ_{eff}/a_0} for some $Z_{eff} < 2$. Calculate the expectation value of the energy in this state, as a function of Z_{eff}.

   Hint: by writing the Hamiltonian as

   $$p_1^2/2m + p_2^2/2m - kZ_{eff}e^2(1/r_1+1/r_2) - (Z-Z_{eff})ke^2(1/r_1+1/r_2) + V_{e-e}$$

   you can maximize your ability to use previous results and only need to do one integral.

   Following the hint: the first couple terms are the single electron hamiltonians for a hydrogen like atom with charge Z_{eff}, so these terms combine to contribute an energy $-2 * Z_{eff}^2 * E_0$. In part 3 we calculated the expectation value $\langle V_{e-e}\rangle = 5Z_{eff}/4E_0$. What's left is to calculate

   $$\langle V_{e-n}\rangle = 2(Z-Z_{eff})ke^2\langle\frac{1}{r}\rangle = (Z-Z_{eff})ke^2\frac{\int dr\; r^2\frac{1}{r}e^{-2rZ_{eff}/a_0}}{\int dr\; r^2 e^{-2rZ_{eff}/a_0}}$$

Using the formula $\int dx\ x^s e^{-\lambda x} = s!/\lambda^{s+1}$ we can evaluate the integrals in the numerator and denominator (and plugging in Z=2) to get a final answer

$$\langle V_{e-n} \rangle = 2(2 - Z_{eff}) ke^2 \left(\frac{2Z_{eff}}{a_0} \right) \frac{1}{2} = 4E_0 Z_{eff}(2 - Z_{eff})$$

So the total energy is:

$$E/E_0 = -2Z_{eff}^2 - 4Z_{eff}(2 - Z_{eff}) + \frac{5}{4} Z_{eff}$$

5. Find the value of Z_{eff} which minimizes the total energy. How does your final result for the ground state energy compare with the correct value? Describe qualitatively the effect of this modification on the electron wave function, and how the kinetic and potential energies of this new trial wavefunction compare to those with $Z = 2$.

   Find $Z_{eff} = 27/16$ for a ground state energy of -77.5 eV, which is now quite close to the correct answer. The electron wave function spreads out, recall $r \sim 1/Z$. So the potential energy between the electrons and the nucleus increases. This is balanced by a decrease in the electron-electron coulomb energy as the electrons are now farther apart on average. The kinetic and potential energies between the electrons and the nucleus are related by $-2\langle KE \rangle = \langle V \rangle$ so the kinetic energy also decreases.