Chem 542 Problem Set 4

1. For this problem we will work a simple integral identity that you need for question 5. Can you show that the left integral is the same as on the right?

$$\int_{y=0}^{y=a}\left\{\int_{x=0}^{x=y} f(x,y)\partial x\right\}\partial y = \int_{x=0}^{x=a}\left\{\int_{y=x}^{y=a} f(x,y)\partial y\right\}\partial x$$

To make it easy just use a simple function such as $f(x,y) = 1$.

Answer: First solve the left-hand one:

$$\int_{y=0}^{y=a}\left\{\int_{x=0}^{x=y} f(x,y)\partial x\right\}\partial y = \int_{y=0}^{y=a}\left\{\int_{x=0}^{x=y} \partial x\right\}\partial y = \int_{y=0}^{y=a}\{x|_0^y\}\partial y = \int_{y=0}^{y=a} y\cdot\partial y = \frac{a^2}{2}$$

Likewise:

$$\int_{x=0}^{x=a}\left\{\int_{y=x}^{y=a} f(x,y)\partial y\right\}\partial x = \int_{x=0}^{x=a}\{y|_x^a\}\partial x = \int_{x=0}^{x=a}(a-x)\partial x = ax - \frac{x^2}{2}\bigg|_0^a = \frac{a^2}{2}$$

Atomic Structure: Optimizing the Wavefunction of He

2. For this problem we will examine the electronic structure of the He atom in the $1s^2$ configuration. The hydrogenic wavefunction for the 1s state is:

$$\psi_{1s}(r,\theta,\phi) = N\cdot R(r)\cdot Y_{0,0}(\theta)\cdot Y_{0,0}(\phi) = 2\cdot\left(\frac{Z^3}{a_0^3}\right)^{\frac{1}{2}} e^{-Z\cdot r/a_0}\cdot\frac{1}{2}\cdot\frac{1}{\sqrt{\pi}}$$

where Z is the nuclear charge (2 for He), and a_0 is a Bohr (5.29×10^{-11} m).

a. We need to check to see if it is normalized properly. I can think of two ways to demonstrate, but I am afraid one of them is incorrect! Please use Mathematica to determine which of the two expressions below is correct.

(1) $N^2\int_{r=0}^{r=\infty}\int_{\theta=0}^{\theta=\pi}\int_{\phi=0}^{\phi=2\pi}\psi_{1s}{}^*\psi_{1s}\cdot\partial\phi\cdot\partial\theta\cdot\partial r$

or

(2) $N^2\int_{r=0}^{r=\infty}\int_{\theta=0}^{\theta=\pi}\int_{\phi=0}^{\phi=2\pi}\psi_{1s}{}^*\psi_{1s}\cdot\partial\phi\cdot sin(\theta)\partial\theta\cdot r^2\partial r$

b. What does the factor $r^2\cdot sin(\theta)$ represent and why is it necessary?

Answer: a. Plug this into Mathematica and show that this is normalized.

$$\int_{\phi=0}^{\phi=2\pi} \frac{1}{\sqrt{\pi}}^* \frac{1}{\sqrt{\pi}} \cdot \partial\phi = \frac{1}{\pi}(2\pi - 0) = 2$$

$$\int_{\theta=0}^{\theta=\pi} \frac{1}{2}^* \frac{1}{2} \cdot \partial\theta = \frac{1}{4}(\pi - 0) = \frac{\pi}{4}$$

and

$$N^2 \int_{r_1=0}^{\infty} \psi(r)^* \psi(r) \cdot \partial r = 4\frac{Z^3}{a_0^3} \int_{r_1=0}^{\infty} e^{-2Z \cdot r/a_0} \cdot \partial r = 4\frac{Z^3}{a_0^3} 2\frac{Z^2}{a_0^2}$$

The whole thing is $2 \cdot \frac{\pi}{4} \cdot 4\frac{Z^3}{a_0^3} 2\frac{Z^2}{a_0^2} = 4\pi\frac{Z^5}{a_0^5}$. This isn't 1, so this isn't correct.

As for 2, we repeat the analysis:

$$\int_{\phi=0}^{\phi=2\pi} \frac{1}{\sqrt{\pi}}^* \frac{1}{\sqrt{\pi}} \cdot \partial\phi = \frac{1}{\pi}(2\pi - 0) = 2$$

$$\int_{\theta=0}^{\theta=\pi} \frac{1}{2}^* \frac{1}{2} \cdot sin(\theta) \cdot \partial\theta = -\frac{1}{4}\left(cos(\pi) - cos(0)\right) = -\frac{1}{4} \cdot -2 = \frac{1}{2}$$

and

$$N^2 \int_{r_1=0}^{\infty} \psi(r)^* \psi(r) \cdot \partial r = 4\frac{Z^3}{a_0^3} \int_{r_1=0}^{\infty} e^{-2Z \cdot r/a_0} \cdot r^2 \partial r = 1$$

The whole thing is $2 \cdot \frac{1}{2} \cdot 1 = 1$. Hence the 2nd expression is the correct one.

b. That part is the Jacobian and is necessary for proper volume integration in spherical coordinates.

3. Now let's calculate the kinetic energy of the He 1s^2 state. First you must note that the wavefunction is:

$$\psi = \left\{\frac{\psi_1(r_1,\theta_1,\phi_1) \cdot \psi_2(r_2,\theta_2,\phi_2) + \psi_1(r_2,\theta_2,\phi_2) \cdot \psi_2(r_1,\theta_1,\phi_1)}{\sqrt{2}}\right\}\left\{\frac{\alpha(1)\beta(2) - \alpha(2)\beta(1)}{\sqrt{2}}\right\}$$

Since both ψ_1 and ψ_2 are 1s orbitals, the wavefunction simplifies to:

$$\psi = \{\psi(r_1,\theta_1,\phi_1) \cdot \psi(r_2,\theta_2,\phi_2)\}\{\alpha(1)\beta(2) - \alpha(2)\beta(1)\}$$

Now when you apply this to the Hamiltonian:

$$\int \psi^* \hat{H} \psi \cdot \partial\tau = \int \psi^* \left\{ \frac{-\hbar^2}{2m} \nabla_1^2 + \frac{-\hbar^2}{2m} \nabla_1^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 |r_1 - r_2|} \right\} \psi \cdot \partial\tau$$

it is a bloody mess (looks like 20 terms!). However, the spin integrals:

$$\int \alpha(1)\beta(1) = 0, \;\; \int \alpha(1)\alpha(1) = 1, \;\; \int \beta(1)\beta(1) = 1$$

(likewise for electron 2) cause most of the terms to vanish. As a result, I won't make you work through all that and will give you all the non-zero integrals to work on.

Given the above we are now ready to start calculating the kinetic energy. First, I will let you know that the angular parts integrate to 1 since there is no rotational energy for 1s electrons. This leaves just two radial equations for the two electrons:

$$\frac{-\hbar^2}{2m} \int_{r_1=0}^{\infty} \psi(r_1)^* \frac{1}{r_1^2} \frac{\partial}{\partial r_1} r_1^2 \frac{\partial}{\partial r_1} \psi(r_1) \cdot r_1^2 \partial r_1 + \frac{-\hbar^2}{2m} \int_{r_2=0}^{\infty} \psi(r_2)^* \frac{1}{r_2^2} \frac{\partial}{\partial r_2} r_2^2 \frac{\partial}{\partial r_2} \psi(r_2) \cdot r_2^2 \partial r_2$$

Using $\psi(r) = 2\left(\frac{Z^3}{a_0^3}\right)^{\frac{1}{2}} e^{-Z \cdot r / a_0}$, can you calculate the kinetic energy? Hint: the integrals are equal so just calculate one then double it.

Answer: Using Mathematica:

$$\frac{-\hbar^2}{2m} 4 \frac{Z^3}{a_0^3} \int_{r_1=0}^{\infty} \psi(r_1)^* \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} \psi(r_1) \cdot r_1^2 \partial r_1$$

The result from Mathematica is $\frac{-Z^2}{a_0^2}$, giving us a total of $\frac{-\hbar^2}{2m} \frac{-Z^2}{a_0^2} = Z^2 \frac{\hbar^2}{2ma_0^2}$. Since there are two electrons the total kinetic energy is $2Z^2 \frac{\hbar^2}{2ma_0^2}$.

4. Now let's evaluate the (negative) Coulomb energy of each electron with the single nucleus. Since helium has two positive charges the Coulomb term has a 2 in it, $\frac{-2e^2}{4\pi\epsilon_0}$ as below:

$$\frac{-2e^2}{4\pi\epsilon_0} \int_{r_1=0}^{\infty} \psi(r_1)^* \frac{1}{r_1} \psi(r_1) \cdot r_1^2 \partial r_1 + \frac{-2e^2}{4\pi\epsilon_0} \int_{r_1=0}^{\infty} \psi(r_2)^* \frac{1}{r_2} \psi(r_2) \cdot r_2^2 \partial r_2$$

Note each integral will of course be exactly the same, so just do one and then double it.

Answer: The result from Mathematica is $\frac{2Z}{a_0}$, giving us a total of $\frac{-e^2}{4\pi\epsilon_0} \frac{2Z}{a_0} = -2Z \frac{e^2}{4\pi\epsilon_0 a_0}$. Since there are two electrons the total electron-nuclear energy is $-4Z \frac{e^2}{4\pi\epsilon_0 a_0}$.

5. Now let's try to solve the (positive) Coulomb interaction between two electrons of the helium atom. This part looks a bit different than the earlier ones due to the fact that the electrons are not separable, so the expectation value is:

$$\int\int |\psi(r_1)|^2 \frac{e^2}{4\pi\epsilon_0 |r_1 - r_2|} |\psi(r_2)|^2 \cdot \partial\tau_1 \cdot \partial\tau_2$$

The absolute value of the wavefunctions including the normalization constants are:

$$|\psi(r_1)|^2 = \frac{4Z^3}{a_0^3} e^{-2Z\cdot r_1/a_0} \cdot \left|Y_{0,0}(\theta_1, \phi_1)\right|^2 \text{ and } |\psi(r_2)|^2 = \frac{4Z^3}{a_0^3} e^{-2Z\cdot r_2/a_0} \cdot \left|Y_{0,0}(\theta_2, \phi_2)\right|^2$$

Including this info, and integrating over all the dimensions yields:

$$\int_{r_1=0}^{\infty}\int_{r_2=0}^{\infty} |\psi(r_1)|^2 \frac{e^2}{4\pi\epsilon_0 |r_1 - r_2|} |\psi(r_2)|^2 \cdot r_2^2 \partial r_2 \cdot r_1^2 \partial r_1$$
$$\cdot \int_{\theta_1=0}^{\pi}\int_{\phi_1=0}^{2\pi}\int_{\theta_2=0}^{\pi}\int_{\phi_2=0}^{2\pi} \left|Y_{0,0}(\theta_1, \phi_1)\right|^2 \cdot \left|Y_{0,0}(\theta_2, \phi_2)\right|^2 sin(\theta_2) sin(\theta_1) \partial\phi_2 \partial\theta_2 \partial\phi_1 \partial\theta_1$$

Here, the angular parts are easy to solve since $\left|Y_{0,0}(\theta, \phi)\right|^2 = \frac{1}{4\pi}$, and thus:

$$\int_{\theta_1=0}^{\pi}\int_{\phi_1=0}^{2\pi}\int_{\theta_2=0}^{\pi}\int_{\phi_2=0}^{2\pi} \left|Y_{0,0}(\theta_1, \phi_1)\right|^2 \cdot \left|Y_{0,0}(\theta_2, \phi_2)\right|^2 sin(\theta_2) sin(\theta_1) \partial\phi_2 \partial\theta_2 \partial\phi_1 \partial\theta_1$$
$$= \frac{1}{16\pi^2}\left(\int_{\theta_1=0}^{\pi}\int_{\phi_1=0}^{2\pi} sin(\theta_1)\partial\phi_1\partial\theta_1\right)\cdot\left(\int_{\theta_1=0}^{\pi}\int_{\phi_2=0}^{2\pi} sin(\theta_2)\partial\phi_2\partial\theta_2\right) = \frac{1}{16\pi^2}\cdot 4\pi \cdot 4\pi = 1$$

Of course, because the wavefunctions are normalized and the operator doesn't have any angles in it! Now you are left with the radial integral:

$$\frac{e^2}{4\pi\epsilon_0}\int_{r_1=0}^{\infty}\int_{r_2=0}^{\infty} |\psi(r_1)|^2 \frac{1}{|r_1 - r_2|} |\psi(r_2)|^2 \cdot r_2^2 \partial r_2 \cdot r_1^2 \partial r_1$$

…and this ***can't be solved*** as it is written. Bummer! Regardless of our math ability, there must be a way to do this calculation! In fact, the resolution is to use the "addition theorem for Legendre polynomials" to replace the $\frac{1}{|r_1 - r_2|}$ operator as shown below:

$$\frac{1}{|r_1 - r_2|} = \frac{1}{r_{12}} = \sum_{l=0}^{\infty} \frac{{r_{12}}_<^{l}}{{r_{12}}_>^{l+1}} \cdot \frac{4\pi}{2l+1} \sum_{m=-l}^{l} Y_{l,m}(\theta_1, \phi_1) \cdot Y_{l,m}(\theta_2, \phi_2)^*$$

where $r_{12<}$ and $r_{12>}$ have the following meaning: if $r_1 > r_2$ then $r_{12>} = r_1$ and likewise $r_{12<} = r_2$. However, if $r_2 > r_1$, then $r_{12>} = r_2$ and $r_{12<} = r_1$. Also, the addition theorem includes spherical harmonics, so we can't just integrate those away anymore. To this end, we will deal with the spherical harmonics first:

$$\sum_{l=0}^{\infty}\frac{4\pi}{2l+1}\sum_{m=-l}^{l}Y_{l,m}(\theta_1,\phi_1)\cdot Y_{l,m}(\theta_2,\phi_2)^*$$

This expression is integrated within the angular part, which yields:

$$\sum_{l=0}^{\infty}\frac{4\pi}{2l+1}\sum_{m=-l}^{l}\int_{\theta_1=0}^{\pi}\int_{\phi_1=0}^{2\pi}\int_{\theta_2=0}^{\pi}\int_{\phi_2=0}^{2\pi}\left|Y_{0,0}(\theta_1,\phi_1)\right|^2\cdot\left|Y_{0,0}(\theta_2,\phi_2)\right|^2\cdot Y_{l,m}(\theta_1,\phi_1)\cdot Y_{l,m}(\theta_2,\phi_2)^*$$
$$\cdot sin(\theta_1)\cdot sin(\theta_2)\cdot\partial\phi_2\partial\theta_2\partial\phi_1\partial\theta_1$$

This divvies up into two integrals:

$$\sum_{l=0}^{\infty}\frac{4\pi}{2l+1}\sum_{m=-l}^{l}\left(\int_{\theta_1=0}^{\pi}\int_{\phi_1=0}^{2\pi}Y_{0,0}(\theta_1,\phi_1)^*Y_{0,0}(\theta_1,\phi_1)Y_{l,m}(\theta_1,\phi_1)\cdot sin(\theta_1)\cdot\partial\phi_1\partial\theta_1\right)$$
$$\cdot\left(\int_{\theta_2=0}^{\pi}\int_{\phi_2=0}^{2\pi}Y_{0,0}(\theta_2,\phi_2)^*Y_{0,0}(\theta_2,\phi_2)Y_{l,m}(\theta_2,\phi_2)^*\cdot sin(\theta_2)\cdot\partial\phi_2\partial\theta_2\right)$$

To go about this, we can simplify the triple product of functions into two. However, in this problem there is a simple hack due to the fact that $Y_{0,0}(\theta_1,\phi_1)=Y_{0,0}(\theta_1,\phi_1)^*=\frac{1}{\sqrt{4\pi}}$. Specifically, we can simply factor out $Y_{0,0}(\theta_1,\phi_1)$ in the 1st integral and $Y_{0,0}(\theta_2,\phi_2)^*$ in the 2nd leaving:

$$\sum_{l=0}^{\infty}\frac{4\pi}{2l+1}\sum_{m=-l}^{l}\left(Y_{0,0}(\theta_1,\phi_1)\int_{\theta_1=0}^{\pi}\int_{\phi_1=0}^{2\pi}Y_{0,0}(\theta_1,\phi_1)^*\cdot Y_{l,m}(\theta_1,\phi_1)\cdot sin(\theta_1)\cdot\partial\phi_1\partial\theta_1\right)$$
$$\cdot\left(Y_{0,0}(\theta_2,\phi_2)^*\int_{\theta_2=0}^{\pi}\int_{\phi_2=0}^{2\pi}Y_{l,m}(\theta_2,\phi_2)^*\cdot Y_{0,0}(\theta_2,\phi_2)\cdot sin(\theta_2)\cdot\partial\phi_2\partial\theta_2\right)$$

a. Given that the spherical harmonics are actually orthonormal wavefunctions, the following can be used:

$$\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}Y_{l,m}{}^*\cdot Y_{l',m'}sin(\theta)\cdot\partial\phi\partial\theta=\delta_{l,l'}\delta_{m,m'}$$

where δ is the Kroneker delta function and has the following properties:

$$\delta_{l,l'}=1\text{ if }l=l',\delta_{l,l'}=0\text{ if }l\neq l'$$

Now, here is the question, can you explain why the whole thing above is just equal to 1? This is actually a very simple derivation that can mostly be explained in words.

b. Now that the angular parts integrate to just 1, we are left with the radial part:

$$\frac{e^2}{4\pi\epsilon_0}\int_{r_1=0}^{r_1=\infty}\int_{r_2=0}^{r_2=\infty}|\psi(r_1)|^2\frac{r_{12<}^{\ l}}{r_{12>}^{\ l+1}}|\psi(r_2)|^2\cdot r_2^2\partial r_2\cdot r_1^2\partial r_1$$

We must deal with the r greater or lesser than operators. To this end, we will break up the r_2 integral into parts using the fact that integrals are additive:

$$\int_a^c f(x)\cdot\partial x=\int_a^b f(x)\cdot\partial x+\int_b^c f(x)\cdot\partial x$$

where b is in between a and c. This allows us to do the following:

$$\frac{e^2}{4\pi\epsilon_0}\int_{r_1=0}^{r_1=\infty}\int_{r_2=0}^{r_2=\infty}|\psi(r_1)|^2\frac{r_{12<}^{\ l}}{r_{12>}^{\ l+1}}|\psi(r_2)|^2\cdot r_2^2\partial r_2\cdot r_1^2\partial r_1=$$

$$\frac{e^2}{4\pi\epsilon_0}\int_{r_1=0}^{r_1=\infty}\int_{\mathbf{r_2=0}}^{\mathbf{r_2=r_1}}|\psi(r_1)|^2\frac{r_{12<}^{\ l}}{r_{12>}^{\ l+1}}|\psi(r_2)|^2\cdot r_2^2\partial r_2\cdot r_1^2\partial r_1+\frac{e^2}{4\pi\epsilon_0}\int_{r_1=0}^{r_1=\infty}\int_{\mathbf{r_2=r_1}}^{\mathbf{r_2=\infty}}|\psi(r_1)|^2\frac{r_{12<}^{\ l}}{r_{12>}^{\ l+1}}|\psi(r_2)|^2\cdot r_2^2\partial r_2\cdot r_1^2\partial r_1$$

In the first term it is always true that $r_1>r_2$, hence $r_{12>}=r_1$ and likewise $r_{12<}=r_2$. The opposite is true on the 2nd term:

$$\frac{e^2}{4\pi\epsilon_0}\int_{r_1=0}^{r_1=\infty}\int_{r_2=0}^{r_2=r_1}|\psi(r_1)|^2\frac{r_2^l}{r_1^{l+1}}|\psi(r_2)|^2\cdot r_2^2\partial r_2\cdot r_1^2\partial r_1+\frac{e^2}{4\pi\epsilon_0}\int_{r_1=0}^{r_1=\infty}\int_{r_2=r_1}^{r_2=\infty}|\psi(r_1)|^2\frac{r_1^l}{r_2^{l+1}}|\psi(r_2)|^2\cdot r_2^2\partial r_2\cdot r_1^2\partial r_1$$

Next, to make this easier we apply the identity from question 1 for the 1st term above:

$$\frac{e^2}{4\pi\epsilon_0}\int_{r_1=0}^{r_1=\infty}\int_{r_2=0}^{r_2=r_1}|\psi(r_1)|^2\frac{r_2^l}{r_1^{l+1}}|\psi(r_2)|^2\cdot r_2^2\partial r_2\cdot r_1^2\partial r_1=\frac{e^2}{4\pi\epsilon_0}\int_{r_2=0}^{r_2=\infty}\int_{r_1=r_2}^{r_1=\infty}|\psi(r_1)|^2\frac{r_2^l}{r_1^{l+1}}|\psi(r_2)|^2\cdot r_1^2\partial r_1\cdot r_2^2\partial r_2$$

Note how the above identity allows us to switch from integrating: $\int_{r_2=0}^{r_2=r_1}\ldots\partial r_2$ to: $\int_{r_1=r_2}^{r_1=\infty}\ldots\partial r_1$. So the Coulomb integral is:

$$\frac{e^2}{4\pi\epsilon_0}\int_{r_2=0}^{r_2=\infty}\int_{r_1=r_2}^{r_1=\infty}|\psi(r_1)|^2\frac{r_2^l}{r_1^{l+1}}|\psi(r_2)|^2\cdot r_1^2\partial r_1\cdot r_2^2\partial r_2+\frac{e^2}{4\pi\epsilon_0}\int_{r_1=0}^{r_1=\infty}\int_{r_2=r_1}^{r_2=\infty}|\psi(r_1)|^2\frac{r_1^l}{r_2^{l+1}}|\psi(r_2)|^2\cdot r_2^2\partial r_2\cdot r_1^2\partial r_1$$

Please use Mathematica to evaluate it. Hint: oddly both integrals are equal.

Answer: a. According to the identity, each integral:

$$\int_{\theta_1=0}^{\pi}\int_{\phi_1=0}^{2\pi} Y_{0,0}(\theta_1,\phi_1)^* \cdot Y_{l,m}(\theta_1,\phi_1)\cdot sin(\theta_1)\cdot \partial\phi_1\partial\theta_1$$

and

$$\int_{\theta_2=0}^{\pi}\int_{\phi_2=0}^{2\pi} Y_{l,m}(\theta_2,\phi_2)^* \cdot Y_{0,0}(\theta_2,\phi_2)\cdot sin(\theta_2)\cdot \partial\phi_2\partial\theta_2$$

is 0 only if $Y_{l,m}(\theta_{1,2},\phi_{1,2}) = Y_{0,0}(\theta_{1,2},\phi_{1,2})$. Since there is a restriction on l and m, then the sums $\sum_{l=0}^{\infty}\frac{4\pi}{2l+1}$ and $\sum_{m=-l}^{l}$ ... simply disappear except for $l = 0$ and $m = 0$, meaning that they only leave behind $\frac{4\pi}{2l+1} = 4\pi$ (since $l = 0$). And even this gets canceled out by the wavefunctions that were substituted out of the integrals in the first step:

$$\sum_{l=0}^{\infty}\frac{4\pi}{2l+1}\sum_{m=-l}^{l} \ldots = 4\pi \cdot Y_{0,0}(\theta_1,\phi_1)\cdot 1\cdot Y_{0,0}(\theta_1,\phi_1)^*\cdot 1 = 4\pi\cdot\frac{1}{\sqrt{4\pi}}\cdot\frac{1}{\sqrt{4\pi}} = 1$$

b. We are now trying to solve:

$$\frac{e^2}{4\pi\epsilon_0}\frac{16Z^6}{a_0^6}\int_{r_2=0}^{r_2=\infty}\int_{r_1=r_2}^{r_1=\infty} e^{-2Z\cdot r_1/a_0}\cdot e^{-2Z\cdot r_2/a_0}\cdot r_1\partial r_1\cdot r_2^2\partial r_2$$
$$= \frac{e^2}{4\pi\epsilon_0}\frac{16Z^6}{a_0^6}\int_{r_2=0}^{r_2=\infty} e^{-2Z\cdot r_2/a_0}\left\{\int_{r_1=r_2}^{r_1=\infty} e^{-2Z\cdot r_1/a_0}\cdot r_1\partial r_1\right\}\cdot r_2^2\partial r_2$$

Using Mathematica the inner integral is $\frac{a_0}{4Z^2}e^{-2Z\cdot r_2/a_0}(a_0 + 2Zr_2)$. We find:

$$\frac{e^2}{4\pi\epsilon_0}\frac{16Z^6}{a_0^6}\int_{r_2=0}^{r_2=\infty} e^{-2\cdot Zr_2/a_0}\cdot\frac{a_0}{4Z^2}e^{-2\cdot Zr_2/a_0}(a_0+2Zr_2)\cdot r_2^2\partial r_2 = \frac{e^2}{4\pi\epsilon_0}\frac{16Z^6}{a_0^6}\frac{5a_0^5}{256Z^5}$$

Next one:

$$\frac{e^2}{4\pi\epsilon_0}\frac{256}{a_0^6}\int_{r_1=0}^{r_1=\infty}\int_{r_2=r_1}^{r_2=\infty} e^{-2Z\cdot r_1/a_0}\cdot e^{-2Z\cdot r_2/a_0}\cdot r_2\partial r_2\cdot r_1^2\partial r_1$$
$$= \frac{e^2}{4\pi\epsilon_0}\frac{256}{a_0^6}\int_{r_1=0}^{r_1=\infty} e^{-2Z\cdot r_1/a_0}\left\{\int_{r_2=r_1}^{r_2=\infty} e^{-2Z\cdot r_2/a_0}\cdot r_2\partial r_2\right\}\cdot r_1^2\partial r_1$$

The integration comes out identically: $\frac{e^2}{4\pi\epsilon_0}\frac{16Z^6}{a_0^6}\frac{5a_0^5}{256Z^5} = \frac{e^2}{4\pi\epsilon_0}\frac{5}{16}\frac{Z}{a_0}$. The sum of the two is: $\frac{e^2}{4\pi\epsilon_0}\frac{5}{8}\frac{Z}{a_0}$. This energy is Z×2.7252×10^{-18} J, which is Z×17 eV or Z×0.625 Hartrees.

6. a. There is a unit called a Hartree, which is:

$$\frac{\hbar^2}{ma_0^2} = \frac{e^2}{4\pi\epsilon_0 a_0} = 4.36 \times 10^{-18}\,J = 1\,Hartree$$

Thus, in units of Hartrees, the energy of a helium atom is (kinetic + nuclear potential + electron repulsion):

$$Z^2 - 4Z + Z\frac{5}{8} = Z^2 + Z\left(\frac{5}{8} - 4\right) = Z^2 - \frac{27}{8}Z$$

As stated in class, the use of a hydrogenic wavefunction helium isn't correct, and the energy we calculate for the helium atom will be too high. However, using the equation above we can empirically use a different atomic number "Z_{opt}" in the wavefunction:

$$\psi_{1s}(r) = 2 \cdot \left(\frac{Z_{opt}^3}{a_0^3}\right)^{\frac{1}{2}} e^{-Z_{opt}\cdot r_1/a_0} \cdot Y_{0,0}(\theta_1, \phi_1)$$

to get the lowest energy. What would that Z_{opt} be?

b. The optimum nuclear charge in the wavefunction (which is akin to the nuclear charge experienced by the electrons) is less than 2, the actual value. What physical phenomenon can this be attributed to? Hint: you often discuss this in Freshman Chem when explaining why the energies of orbitals are 1s < 2s < 2p <3s <3p <4s <3d etc.

Answer: a. Set the derivative to 0:

$$\frac{\partial}{\partial Z}\left(Z_{opt}^2 - \frac{27}{8}Z_{opt}\right) = 0$$

Therefore $2Z_{opt} - \frac{27}{8} = 0$ and thus $Z_{opt} = \frac{27}{16}$.

b. Shielding.

Mathematica Example Codes

Here I will do various calculations with a 3d hydrogenic orbital (n=3, l=2, m=+2) wavefunction.

$$\psi = \psi_{2,2}(r)Y_{2,2}(\theta,\phi) = \left\{\frac{4}{81\sqrt{30\cdot a_0^3}}\frac{r^2}{a_0^2}e^{-r/3a_0}\right\}\cdot\left\{\frac{\sqrt{15}}{4}sin^2(\theta)\right\}\cdot\left\{\frac{1}{\sqrt{2\pi}}e^{2i\cdot\phi}\right\}$$

First, define the radial orbital and then integrate it. This makes subsequent work easier. In the second line, the {r, 0, Infinity} represent the limits of integration and tell it that r is the integrand. The "assumptions" assist the software with converging to a reasonable answer, especially as it doesn't know what a0 is:

```
f[r] = 4/(81*Sqrt[30*a0^3])*(r^2/a0^2)*Exp[-r/3/a0]
```

Out[∘]= $\frac{2\sqrt{\frac{2}{15}}\,e^{-\frac{r}{3\,a0}}\,r^2}{81\,a0^2\,\sqrt{a0^3}}$

```
In[∘]:= Integrate[f[r]*r*r, {r, 0, Infinity}, Assumptions → {a0 > 0}]
```

Out[∘]= $48\sqrt{\frac{6}{5}}\,a0^{3/2}$

Well, I must be a monkey's uncle! Its not normalized! No wait, I integrated $\int_0^\infty \psi\cdot r^2\cdot\partial r$ and I should have integrated $\int_0^\infty |\psi|^2\cdot r^2\cdot\partial r$!

```
In[∘]:= Integrate[f[r]*f[r]*r*r, {r, 0, Infinity}, Assumptions → {a0 > 0}]
```

Out[∘]= 1

Here I used the fact that the radial function is real, so I could just square it rather than multiply by the complex conjugate.

Now let's do a more complex calculation, that being the kinetic energy:

$$\frac{-\hbar^2}{2m}\int_0^\infty \psi^*\cdot\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\psi\cdot r^2\partial r$$

Here: D[f[r],r] says take the derivative of the pre-defined function f[r] with respect to r. You can do a double derivative using: D[D[f[r],r],r], which looks like an onion, or solve a more complex expression such as the above using:

```
In[∘]:= Integrate[f[r]*(1/r^2)*D[r^2 D[f[r], r], r]*r*r, {r, 0, Infinity}, Assumptions → {a0 > 0}]
```

Out[∘]= $-\frac{1}{45\,a0^2}$

Don't forget your constants! The real result is: $\frac{\hbar^2}{90m\cdot a_0^2}$.

Now let's see about the angular. First define the functions:

```
In[•]:= f2[theta] = Sqrt[15] / 4 * Sin[theta] ^2
```

Out[•]= $\frac{1}{4}\sqrt{15}\,\mathrm{Sin}[\mathrm{theta}]^2$

```
In[•]:= f3[phi] = 1 / Sqrt[2 * Pi] * Exp[i * 2 * phi]
```

Out[•]= $\frac{e^{2\,i\,\mathrm{phi}}}{\sqrt{2\pi}}$

Next we will see if they are normalized:

```
In[•]:= Integrate[f2[theta] * Integrate[f3[phi], {phi, 0, 2 * Pi}], {theta, 0, Pi}]
Out[•]= 0
```

Whups, should have 1, not 0! You know what, it looks like I forgot the Jacobian sin(θ)! I incorporated it below:

```
In[•]:= Integrate[f2[theta] * Integrate[f3[phi] * Sin[theta], {phi, 0, 2 * Pi}], {theta, 0, Pi}]
Out[•]= 0
```

Whups! I forgot to square the wavefunctions! Try again!

```
In[•]:= Integrate[f2[theta] ^2 * Integrate[f3[phi] ^2 * Sin[theta], {phi, 0, 2 * Pi}], {theta, 0, Pi}]
Out[•]= 0
```

Whups! The $Y_{2,2}(\phi)$ is complex, and the square is really the function times its conjugate!

```
In[•]:= Integrate[f2[theta] ^2 * Integrate[f3[phi] * Conjugate[f3[phi]], {phi, 0, 2 * Pi}] * Sin[theta],
         {theta, 0, Pi}]
Out[•]= 1
```

Finally! You see you need to be careful with these!