F2008

Problem 6: Hydrogen Atom (10 Points)

The spatial component of the ground state wavefunction for the hydrogen atom is

$$\phi(r,\theta,\phi) = Ae^{-\left(\frac{r}{a_o}\right)}$$

where A and a_o (the Bohr radius) are constants.

a) Find A by normalizing the wavefunction. Express your answer in terms of a_o. **(2 Points)**

b) Calculate the expectation value of the potential energy. **(2 Points)**

c) Calculate the expectation value of r and the most probable value for r. **(2 Points)**

? d) What is the expectation value for L, the magnitude of the angular momentum? How does this value compare to the prediction of the Bohr model? **(2 Points)**

e) Many solutions to the Schrodinger equation for the hydrogen atom are related to a z-axis despite the fact that the potential energy is spherically symmetric. What defines the z-axis? Explain your answer. **(2 Points)**

(a)

We have

$$\phi(r,\theta,\phi) = Ae^{-\left(\frac{r}{a_0}\right)},$$

so normalizing gives us

$$\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} A^2 e^{-\frac{2r}{a_0}} r^2 dr \sin\theta \, d\theta \, d\phi = 1$$

$$4\pi A^2 \int_0^{\infty} r^2 e^{-\frac{2r}{a_0}} dr = 1$$

In general,

$$\int_0^{\infty} x^n e^{-ax} dx = \frac{n!}{a^{n+1}},$$

so if $n=2$ and $a = 2/a_0$,

$$4\pi A^2 \left(\frac{2!}{(2/a_0)^3} \right) = 1$$

$$\frac{8\pi A^2 a_0^3}{8} = 1$$

$$A^2 = \frac{1}{\pi a_0^3}$$

$$A = \left(\frac{1}{\pi a_0^3}\right)^{1/2}$$

and thus,

$$\boxed{\phi(r,\theta,\phi) = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}}.$$

(b)

The potential for the hydrogen atom is

$$V(r) = -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}$$

or

$$V(r) = -\frac{ke^2}{r}.$$

So

$$\langle V \rangle = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0} \left(-\frac{ke^2}{r}\right) \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}\, r^2\, dr \sin\theta\, d\theta\, d\phi$$

$$= -\frac{4\pi k e^2}{\pi a_0^3}\int_0^{\infty} r e^{-2r/a_0}\, dr$$

$$= -\frac{4\pi k e^2}{\pi a_0^3}\left(\frac{1!}{(2/a_0)^2}\right)$$

$$= -\frac{\cancel{4\pi} k e^2 a_0^2}{\cancel{4\pi} a_0^3}$$

$$\boxed{\langle V \rangle = -\frac{ke^2}{a_0}}$$

This is just the potential at the Bohr radius.

(c)

The expectation value of the radius is

$$\langle r \rangle = \int_0^{2\pi}\int_0^{\pi}\int_0^{r} \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}\, r \left(\frac{1}{\pi a_0^3}\right) e^{-r/a_0}\, r^2 dr \sin\theta\, d\theta\, d\phi$$

$$= \frac{4\pi}{\pi a_0^3}\int_0^{r} r^3 e^{-2r/a_0}\, dr$$

$$= \frac{4\pi}{\pi a_0^3}\left(\frac{3!}{(2/a_0)^4}\right)$$

$$= \frac{4}{a_0^3}\left(\frac{6a_0^4}{16}\right)$$

$$\boxed{\langle r \rangle = \frac{3a_0}{2}}$$

We know the radial probability density is found by noting

$$dP = |\psi_r|^2\, 4\pi r^2 dr.$$

So

$$dP = \frac{1}{\pi a_0^3} e^{-2r/a_0}\, 4\pi r^2 dr$$

$$= \frac{4r^2}{a_0^3} e^{-2r/a_0}\, dr$$

Then maximizing,

$$\frac{d\rho}{dr} = \frac{d}{dr}\left(\frac{4r^2}{a_0^3} e^{-2r/a_0}\right) = 0$$

where $\rho = dP/dr$. Then

$$-\frac{8r^2}{a_0^4} e^{-2r/a_0} + \frac{8r}{a_0^3} e^{-2r/a_0} = 0$$

(c), cont'd...

$$\frac{8r}{a_0^3} e^{-2r/a_0} = \frac{8r^2}{a_0^4} e^{-2r/a_0}$$

$$\frac{8r}{a_0^3} = \frac{8r^2}{a_0^4}$$

$$1 = \frac{r}{a_0}$$

and the most probable radius is the Bohr radius,

$$\boxed{r = a_0}\ .$$

(d)

In general,

$$\vec{L} = \vec{r} \times \vec{p},$$

so

$$\hat{L} = \hat{r}\hat{p}\sin\theta$$

or

$$L = -i\hbar\, r\nabla\sin\theta$$

$$= -i\hbar\, r\left(\frac{\partial}{\partial r} + \frac{1}{r}\frac{\partial}{\partial\theta} + \frac{1}{r\sin\theta}\frac{\partial}{\partial\phi}\right)\sin\theta .$$

Then

$$\langle L\rangle = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \frac{1}{\pi a_0^3} e^{-r/a_0}(-i\hbar r)\left(\frac{\partial}{\partial r} + \frac{1}{r}\frac{\partial}{\partial\theta} + \frac{1}{r\sin\theta}\frac{\partial}{\partial\phi}\right)\left(\sin\theta\, e^{-r/a_0}\right) d^3r$$

$$= \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \frac{-i\hbar}{\pi a_0^3} r e^{-r/a_0}\left[-\frac{\sin\theta}{a_0}e^{-r/a_0} + \frac{1}{r}\cos\theta\, e^{-r/a_0}\right] r^2 dr \sin\theta\, d\theta\, d\phi$$

$$= \frac{-i\hbar}{\pi a_0^3}\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}\left[-\frac{\sin^2\theta}{a_0} r^3 e^{-2r/a_0} + \sin\theta\cos\theta\, r^2 e^{-2r/a_0}\right] dr\, d\theta\, d\phi$$

$$= -\frac{2i\hbar}{a_0^3}\int_0^{\pi}\int_0^{\infty}\left[-\frac{\sin^2\theta}{a_0} r^3 e^{-2r/a_0} + \sin\theta\cos\theta\, r^2 e^{-2r/a_0}\right] dr\, d\theta$$

$$= -\frac{2i\hbar}{a_0^3}\int_0^{\infty}\left[-\frac{\pi}{2a_0} r^3 e^{-2r/a_0}\right] dr$$

$$= \frac{2i\pi\hbar}{2a_0^4}\left[\frac{3!}{(2/a_0)^4}\right]$$

$$= \frac{i\pi\hbar}{a_0^4}\left[\frac{6a_0^4}{16}\right]$$

$$\boxed{\langle L\rangle = i\frac{3\pi\hbar}{8}}$$

(c), cont'd...

This value honestly doesn't seem right to me, but I'm not sure where I went wrong. The Bohr model predicts that

$$L = n\hbar .$$

In the ground state, we have $n=1$, so we have

$$L = \hbar .$$

If we use Dirac notation to represent our state, we can say

$$\phi(r,\theta,\phi) = |n\,l\,m\rangle$$
$$= |1\,0\,0\rangle$$

since $n=1$ and $l=n-1$, with $m=-l,\dots,+l$. Then

$$\hat{L}^2|1\,0\,0\rangle = \hbar^2 l(l+1)|1\,0\,0\rangle$$

which implies

$$L = \hbar\sqrt{l(l+1)}$$

$$L = 0 .$$

I don't think this helps us, though.