Physics 342 Lecture 29

Ed 1

Welcome back, well, to this online version of quantum mechanics. Last lecture, we had discussed the hydrogen atom, its physics and Hamiltonian. We had found that the energy eigenstates satisfy:

$$\left(-\frac{\hbar^2}{2m_e}\frac{\partial^2}{\partial r^2}+\frac{\hbar^2}{2m_e r^2}\ell(\ell+1)-\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}\right)\psi = E\psi,$$

where we assumed that the proton is infinitely massive and so is at rest, and that the electron is traveling at non-relativistic velocities. At the end of last lecture, we had found the wavefunction of the ground state, ψ_0, and the ground state energy, E_0, to be:

$$\psi_0(r) = N r e^{-\frac{r}{a_0}}, \quad \text{where } a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2} \text{ is the } \underline{\text{Bohr radius}}$$

and N is a normalization factor, while the ground state energy is

$$E_0 = -\frac{m_e e^4}{2(4\pi\varepsilon_0)^2\hbar^2} = -\frac{\hbar^2}{2m_e a_0^2}$$

In SI units, $a_0 = 5.3\times10^{-11}\,m = .53$ Angstroms (Å) and $E_0 = -13.6$ electron-Volts, where $1\,eV = 1.6\times10^{-19}\,J$.

The first thing we will do this lecture is justify that our assumptions were valid. In particular, we will verify that the electron is moving non-relativistically, so our Schrödinger equation/potential formalism is valid. The first thing we will do is normalize the wavefunction:

$$\int_0^\infty dr\, \psi_0(r)^*\psi_0(r) = 1 = N^2\int_0^\infty dr\, r^2 e^{-\frac{2r}{a_0}}.$$

One can of course just do this integral in any number of ways, but I want to show you it has a rich body beneath a seemingly trivial venoer. Let's call

$$t = \frac{2r}{a_0}, \quad \text{so} \quad r = \frac{a_0 t}{2} \quad \text{and} \quad dr = \frac{a_0}{2} dt.$$

Then, the integral becomes:

$$\int_0^\infty dr\, r^2 e^{-\frac{2r}{a_0}} = \int_0^\infty dt\, \frac{a_0}{2}\left(\frac{a_0}{2}\right)^2 t^2 e^{-t} = \frac{a_0^3}{8}\int_0^\infty dt\, t^{3-1} e^{-t}.$$

I've written the final integral in the suggestive form of $2=3-1$. This is because the integral is special:

$$\int_0^\infty dt\, t^{n-1} e^{-t} = \Gamma(n),$$ called the Gamma function, one of the most important functions in mathematics, after elementary functions (powers, exp, ln, sin, cos). The Gamma function is a continuous generalization of the factorial, as you can show with integration-by-parts that it satisfies:

$$\Gamma(n+1) = n\Gamma(n), \quad \text{and} \quad \Gamma(1) = 1.$$

Thus, the integral we need to calculate is $\Gamma(3)$, which, by the recursion relation is:

$$\Gamma(3) = \Gamma(2+1) = 2\Gamma(2) = 2\Gamma(1+1) = 2\cdot 1\cdot \Gamma(1) = 2.$$

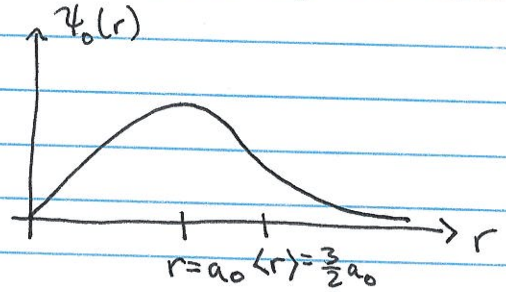
Then, we find the normalization constant to be:

$$N^2 = \frac{a_0^3}{4} \quad \text{so that} \quad \psi_0(r) = \frac{2}{\sqrt{a_0^3}}\, r e^{-r/a_0}.$$

What does this wave function look like? We can test for extrema by identifying r such that:

$$\frac{d}{dr}\psi_0(r) \stackrel{!}{=} 0 = \frac{2}{\sqrt{a_0^3}}\left(e^{-r/a_0} - \frac{r}{a_0}e^{-r/a_0}\right), \text{ or that}$$

$r = a_0$ is an extremum. As $\psi_0(r=0) = \psi_0(r\to\infty) = 0$ and $\psi_0(r)$ is non-negative for all $r>0$, this must be a maximum. Thus, $\psi_0(r)$ looks like:



That is, $r=a_0$ is the point of greatest probability, or the mode of the wave function. The mean, or expected value, of the radius of the electron is:

$$\langle r\rangle = \int_0^\infty dr\, \psi_0(r)^* r\, \psi_0(r) = \frac{4}{a_0^3}\int_0^\infty dr\, r^3 e^{-\frac{2r}{a_0}}$$

$$= \frac{4}{a_0^3}\frac{a_0^4}{16}\int_0^\infty dt\, t^{4-1}e^{-t} = \frac{a_0}{4}\Gamma(4) = \frac{3}{2}a_0;$$

which is 50% larger than the Bohr radius. Nevertheless, it is indeed a_0 that is the characteristic radius of the electron.

So, the task at hand is to determine the speed of the electron as it orbits the proton. We can identify the speed from the mean kinetic energy: $\langle\hat{K}\rangle = \frac{1}{2m}\langle\hat{p}^2\rangle$. Then, speed is just found by:

$$\frac{1}{2}m\langle v^2\rangle = \frac{\langle\hat{p}^2\rangle}{2m}.$$ This will technically be the "root-mean square" speed.

So, we calculate

$$\frac{\langle \hat{p}^2 \rangle}{2m} = \frac{1}{2m}\int_0^\infty dr\, \psi_0(r)^* \overbrace{\left(-i\hbar \frac{\partial}{\partial r}\right)^2}^{\hat{p}^2} \psi_0(r)$$

$$= -\frac{\hbar^2}{2m}\int_0^\infty dr\, \frac{4}{a_0^3}\, r e^{-\frac{r}{a_0}} \frac{d^2}{dr^2}\left(r e^{-r/a_0}\right)$$

$$= -\frac{2\hbar^2}{m a_0^3}\int_0^\infty dr \left(\frac{r^2}{a_0^2} - \frac{2r}{a_0}\right) e^{-2r/a_0}$$

$$= -\frac{\hbar^2}{4 m a_0^2}\left(\underbrace{\Gamma(3)}_{2} - \underbrace{4\Gamma(2)}_{4}\right) = \frac{\hbar^2}{2 m_e a_0^2}$$

This result is amazing, and we nearly could have guessed it! This is just the squared momentum/kinetic energy of a particle in an infinite square well with width $a = a_0/\pi$. It then follows that the root mean square speed of the electron is:

$$\langle \hat{v}^2 \rangle^{1/2} = v_{rms} = \frac{\langle \hat{p}^2 \rangle^{1/2}}{m_e} = \frac{\hbar}{m_e a_0} = \frac{e^2}{4\pi\varepsilon_0 \hbar}.$$

To justify our non-relativistic treatment of the hydrogen atom, we want this to be small with respect to the speed of light; or, we want the dimensionless ratio:

$$\frac{v_{rms}}{c} \equiv \alpha = \frac{e^2}{4\pi\varepsilon_0 \hbar c} \ll 1.$$

Indeed, if you plugin numbers, you find that $\alpha \sim \frac{1}{137}$, which is indeed quite small. Thus, our non-relativistic treatment of hydrogen is justified!

By the way, this dimensionless constant α is called the <u>fine-structure</u> <u>constant</u>. As it is dimensionless, it takes the same numerical value in <u>any</u> unit system. Also, it combines the fundamental electric charge e, the permittivity of free space ε_0, $\hbar$, <u>and</u> c, so it is a universal, dimensionless constant that quantifies the strength of the quantum, relativistic electromagnetic interaction. Its appearance here in the speed of the electron makes sense: If the strength of electromagnetism were larger, then the electron would be more tightly bound to the proton, and a_0 would be smaller. If a_0 decreases, then the effective wavelength of the electron's wavefunction must also decrease; or, its momentum/kinetic energy increases.

It's further interesting to ask about the contribution of the potential energy to the electron's total energy. We've already calculated the expected kinetic energy, and recall that the sum of the kinetic and potential is just the total energy:

$$\langle \hat{H} \rangle = E_0 = \langle \hat{K} \rangle + \langle \hat{V} \rangle.$$

So, while it might be a good integration exercise to explicitly calculate $\langle \hat{V} \rangle$ in this ground state, we can also just calculate it from:

$$\langle \hat{V} \rangle = E_0 - \langle \hat{K} \rangle = -\frac{\hbar^2}{2m_e a_0^2} - \frac{\hbar^2}{2m_e a_0^2} = -\frac{\hbar^2}{m_e a_0^2}.$$

That is, we find the fascinating relationship ~~the~~ between the kinetic and potential energies that:

$|\langle \hat{V} \rangle| = 2\langle \hat{K} \rangle$. This relationship is called the <u>virial</u> <u>theorem</u>. For $1/r$ potentials like electromagnetism or gravity considered here, the mean kinetic energy is <u>always</u> half of the absolute value of the potential energy. Thus, just by knowing the total energy E for the states of the hydrogen atom, we immediately know the corresponding mean kinetic and potential energies for that given state. That is,

$$E = \langle \hat{K} \rangle + \langle \hat{V} \rangle = \langle \hat{K} \rangle - 2\langle \hat{K} \rangle = -\langle \hat{K} \rangle$$

$$= -\frac{\langle \hat{V} \rangle}{2} + \langle \hat{V} \rangle = \frac{1}{2}\langle \hat{V} \rangle.$$

As a final thing for today, I want to find <u>all</u> energy eigenstates for $l=0$, not just the ground state. Griffiths and Schröeter does this in generality, so check that out for more details. We want to solve the differential equation:

$$\left(-\frac{\hbar^2}{2m_e}\frac{\partial^2}{\partial r^2} - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r}\right)\psi = E\psi,$$ well, really for E, the energy eigenvalues. We had already identified the behavior of ψ as $r \to 0$ and $r \to \infty$. Normalizability required that $\psi \sim e^{-r/a}$ as $r \to \infty$, and we can imagine that there is an infinite potential for $r<0$, which restricts $r>0$. Further, $\psi(0)=0$. This motivates the ansatz for the energy eigenstate wavefunction:

$$\psi(r) = f(r)\, r e^{-r/a}, \text{ where } a = \frac{\hbar}{\sqrt{2m|E|}}.$$

Now, we can ask what differential equation $f(r)$ must satisfy by inserting this into the above equation.

Note that the second derivative on this form of the wavefunction is:

$$\frac{d^2}{dr^2}\left(f(r)\, r e^{-r/a}\right) = \left[r f''(r) + 2\left(1 - \frac{r}{a}\right) f'(r) - \left(\frac{2}{a} - \frac{r}{a^2}\right) f(r) \right] e^{-r/a}$$

So the Hamiltonian eigenstate problem can be written as:

$$-\frac{\hbar^2}{2m_e}\left[r f''(r) + 2\left(1-\frac{r}{a}\right) f'(r) - \left(\frac{2}{a} - \frac{r}{a^2}\right) f(r) \right] - \frac{e^2}{4\pi\varepsilon_0} f(r)$$
$$= E r f(r),$$

where we have just eliminated the overall exponential factor. Now we want a strategy for solving this for E, which means we need another ~~strategy~~ assumption for $f(r)$. First, we can clean this up slightly by noting that:

$$E = -\frac{\hbar^2}{2ma^2},$$ so that ~~the~~ a couple terms cancel:

$$-\frac{\hbar^2}{2m_e}\left[r f''(r) + 2\left(1 - \frac{r}{a}\right) f'(r) - \left(\frac{2}{a} - \frac{2e^2 m_e}{4\pi\varepsilon_0 \hbar^2}\right) f(r) \right] = 0.$$

Now, note that the normalization must be enforced on the wave function, such that

$$\int_0^\infty dr\, \psi(r)^* \psi(r) = \int_0^\infty dr\, r^2 f(r)^2 e^{-2r/a} < \infty$$

This normalization isn't guaranteed to be satisfied if $f(r)$ is itself exponential. Further, the n'th eigenstate should have $n-1$ nodes; i.e., points where the wavefunction vanishes away from $r=0,\infty$. Compare this feature to the nodes in the harmonics of a standing wave from physics 102 loooooong ago. These features then suggest that $f(r)$ is an $(n-1)^{th}$ order polynomial in r, for the n^{th} eigenstate. Recall that an $(n-1)^{th}$ order polynomial has a ~~least~~ most $n-1$ roots at real values of r. These roots are precisely the nodes of the wavefunction!

Then, we can write $f(r)$ as:

$$f(r) = \sum_{i=0}^{n-1} \beta_i r^i \text{, for some coefficients } \beta_i.$$

We can then plug this into our differential equation and find a recursive formula for the β_i. This is done in gorey detail in Griffiths and Schroeter, so I will spare you here. However, note the equation that the r^{n-1} term must satisfy. We can find it by identifying the terms in the differential equation that scale like r^{n-1}. So, we are assuming that $f(r) \sim r^{n-1}$. Then, it follows that

$$\frac{d}{dr} f(r) \sim (n-1) r^{n-2},$$ which is one power lower, which you could have guessed because $\frac{d}{dr}$ has a power of r in the denominator. Now, we can determine the scaling in r of each term in the differential equation:

$$r f''(r) \sim r^{n-2}, \quad f'(r) \sim r^{n-2}, \quad r f'(r) \sim r^{n-1}, \quad f(r) \sim r^{n-1}.$$

This equation must be satisfied order-by-order in r, so this restricts to a simpler equation, ~~namely~~ focusing ~~the~~ on the r^{n-1} terms:

$$-2\frac{r}{a}f'(r) - \left(\frac{2}{a} - \frac{2m_e e^2}{4\pi\varepsilon_0\hbar^2}\right)f(r) = 0, \text{ or, as}$$

$r f'(r) \sim (n-1) f(r)$, we find

$$-\frac{2}{a}(n-1) - \frac{2}{a} + \frac{2m_e e^2}{4\pi\varepsilon_0\hbar^2} = 0 \Rightarrow n = \frac{a m_e e^2}{4\pi\varepsilon_0\hbar^2}$$

As $a = \frac{\hbar}{\sqrt{2m_e|E|}}$, the energy is then

$$\boxed{E_n = -\frac{m_e e^4}{2(4\pi\varepsilon_0)^2\hbar^2}\frac{1}{n^2}}$$

Here, because $f(r)$ was a polynomial, n is a natural number: $n = 1, 2, 3, \ldots$

Note the pre-factor is just the ground state energy,

$E_0 = -\frac{m_e e^4}{2(4\pi\varepsilon_0)^2\hbar^2}$, so this can also be expressed as

$E_n = \frac{E_0}{n^2}$. These energy levels of hydrogen were among the first quantitative predictions of quantum mechanics, and we'll discuss how it is tested next lecture.