8	Fri.10/24	4.2 Hydrogen Atom (Q9.1)	**Daily 8.F**
9	Mon., 10/27 Tues. 10/28 Wed., 10/29 Fri., 10/31	**4.3** Angular Momentum 6pm More Math/Physics Research Talks – AHoN 116 **4.4.1-.2** Spin ½ & Magnetic Fields (Q5.5,6.1-.2, 8.5) **4.4.3** Addition of Angular Momenta	**Daily 9.M** **Weekly 9** **Daily 9.W** **Daily 9.F**

Equipment

- Griffith's text
- Printout of roster with what pictures I have
- Spherical Schrodinger handout
- P plot.py

Check dailies

4.2 The Hydrogen Atom

Having found the radial factors of the wavefunction for anything in a central potential, and tackled the comparatively easy infinite spherical well, we're ready to go after the 1/r potential. More specifically, the electric potential shared by an electron and a proton defining a hydrogen atom.

4.2.1 The Radial Wave Function

Where we left off with the general radial equation was

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)-r^2\frac{2m}{\hbar^2}\left[V(r)-E\right]\equiv l(l+1)$$

Where that constant *l(l+1)* connects it to the spherical equation to form the full Shrodinger equation.

We'd rephrased this in terms of a new function, $u \equiv rR$

So we could get the markedly-simpler

$$Eu=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2}u+\left(V(r)+\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right)u$$

Now, to specify that

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

So,

$$Eu=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2}u+\left(-\frac{e^2}{4\pi\varepsilon_o}\frac{1}{r}+\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right)u$$

As Griffiths says, we want to tidy this up so we can see the forest for the trees and begin solving this differential equation.

The first step is motivated by a factor that has appeared time and time again:

$$\kappa \equiv \sqrt{-2mE}/\hbar$$

In the event that the energy is itself negative, this is real, and in the event that energy is positive this is imaginary.

In any event, if we divide our equation by E, we can rewrite our expression as

$$u = \frac{1}{\kappa^2}\frac{\partial^2}{\partial r^2}u + \left(-\frac{e^2}{4\pi\varepsilon_o E}\frac{1}{r} - \frac{1}{\kappa^2}\frac{l(l+1)}{r^2}\right)u$$

For that middle term, we kind of have to force it, but multiplying and dividing by $2m/\hbar^2$

$$u = \frac{1}{\kappa^2}\frac{\partial^2}{\partial r^2}u + \left(\frac{me^2}{2\pi\varepsilon_o\hbar^2\kappa^2}\frac{1}{r} - \frac{1}{\kappa^2}\frac{l(l+1)}{r^2}\right)u$$

Or defining

$\rho \equiv \kappa r$, Note: this is unitless

This cleans up a tad:

$$u = \frac{\partial^2}{\partial \rho^2}u + \left(\frac{me^2}{2\pi\varepsilon_o\hbar^2\kappa}\frac{1}{\rho} - \frac{l(l+1)}{\rho^2}\right)u$$

Now, there's just one lone clump of constants; calling that $\rho_o \equiv \frac{me^2}{2\pi\varepsilon_o\hbar^2\kappa}$, we have something that looks considerably simpler:

$$u = \frac{\partial^2}{\partial \rho^2}u + \left(\frac{\rho_o}{\rho} - \frac{l(l+1)}{\rho^2}\right)u$$

$$\left(1 - \frac{\rho_o}{\rho} + \frac{l(l+1)}{\rho^2}\right)u = \frac{\partial^2 u}{\partial \rho^2}$$

1. *Conceptual*: What do ρ and ρ_0 stand for? Don't just give an equation. What are they, physically? What units do they have?

   "After finding the units for p and p0 in eq. 4.55 I stil am not sure what they measn physically." Kyle B

   Yes! I have no idea either... Spencer

   Is p the hydrogen radius from the electron to its proton but normalized to some quantized Bohr radius (and p0 accords to the ground state energy)....? I'm confused. Gigja

   Yeah, the p0 units are pretty odd to conceptualize. Mark T, Aside from just plain looking less daunting, this simplified form lets us recognize a few things about the solutions.

First, if we divide both sides by u to have

$$\left(1-\frac{\rho_o}{\rho}+\frac{l(l+1)}{\rho^2}\right)=\frac{\partial^2 u}{\partial\rho^2}\frac{1}{u}$$

And think about the meaning of that ratio: concavity of a function divided by the function. If this is positive, then whenever the function is positive, above the axis, the concavity is positive too – which either means its bending away from the axis – either blowing up or as part of an exponential-ish decay. If this is negative, then whenever the function is positive, the concavity is negative, so its arching back toward the axis, and it oscillates sine-like. So, what determines whether it's positive or negative?

$$\frac{\rho_o}{\rho}>\left(1+\frac{l(l+1)}{\rho^2}\right)\Rightarrow\frac{\partial^2 u}{\partial\rho^2}\frac{1}{u}<0 \text{ oscillates.}$$

$$\frac{\rho_o}{\rho}<\left(1+\frac{l(l+1)}{\rho^2}\right)\Rightarrow\frac{\partial^2 u}{\partial\rho^2}\frac{1}{u}>0 \text{ exponentially decays}$$

In the simple, $l=0$ case, it's quite straight forward

$$\rho_o>\rho\Rightarrow\frac{\partial^2 u}{\partial\rho^2}\frac{1}{u}<0 \text{ oscillates}$$

$$\rho_o<\rho\Rightarrow\frac{\partial^2 u}{\partial\rho^2}\frac{1}{u}>0 \text{ decays}$$

So $\rho_o\equiv\frac{me^2}{2\pi\varepsilon_o\hbar^2\kappa}$ is the like the boundary of a potential well – the wavefunction is significant and oscillating inside this range and decays away outside it. (That's assuming that E<0 so k is real and ρ is positive.) Translating that over to an actual distance,

$$r_o\equiv\frac{\rho_o}{\kappa}\equiv\frac{me^2}{2\pi\varepsilon_o\hbar^2\kappa^2}=\frac{me^2\hbar^2}{2\pi\varepsilon_o\hbar^2 2m|E|}=\frac{e^2}{4\pi\varepsilon_o(-E)}\Rightarrow E=-\frac{e^2}{4\pi\varepsilon_o r_o}=V(r_o)$$

This, of course, is the classical turning point, where the Energy equals the potential energy, i.e. there's no kinetic energy because the particle has stopped.

If l isn't 0, the boundary shifts a bit, but this still gives us a length scale for the radial wavefunction.

Speaking of length scales, in the oscillatory region, something sine-ish in $\rho\equiv\kappa r$, then the scale of the oscillating is $1/\kappa=\hbar/\sqrt{-2mE}$. In fact, if we had an actual sine wave, then

$\lambda = 2\pi/\kappa = 2\pi\hbar/\sqrt{-2mE}$, and so the number of waves lengths before it decays, out at ρ_o, would be

$$\frac{r_o}{\lambda} \equiv \frac{me^2\kappa}{2\pi\varepsilon_o\hbar^2\kappa^2 2\pi} = \frac{me^2}{4\pi^2\varepsilon_o\hbar^2\kappa} = \frac{me^2}{4\pi^2\varepsilon_o\hbar\sqrt{-2mE}}$$

Out in the decaying region, exponential-ish, the scale of the decay is $1/\kappa = \hbar/\sqrt{-2mE}$.

So, these constants tell us a lot about the function; we already have a great qualitative picture of everything but what the allowed energies are anyway.

Solving the Radial Equation

Alright, on to solving this equation. Griffiths takes an approach that's *very* similar to what he took with hermite polynomials for the harmonic oscillator.

Identify and factor out limiting behavior

$\rho \to \infty$

$$\frac{\partial^2 u}{\partial \rho^2} = \left(1 - \frac{\rho_o}{\rho} + \frac{l(l+1)}{\rho^2}\right)u \to u_\infty$$

For which the solution is simply

$u_\infty = Ae^{-\rho} + Be^{\rho}$ or throwing out the term that blows up in this limit,

$u_\infty = Ae^{-\rho}$

$\rho \to 0$

$$\frac{\partial^2 u}{\partial \rho^2} = \left(1 - \frac{\rho_o}{\rho} + \frac{l(l+1)}{\rho^2}\right)u \to u_o\frac{l(l+1)}{\rho^2}$$

And he points out that this has a general solution of

$u_o = C\rho^{l+1} + D\rho^{-l}$

which is kind of obvious when you look at the equation for a moment.

2. *Math*: Show that $u(\rho) = C\rho^{l+1} + D\rho^{-l}$ satisfies $\frac{d^2u}{d\rho^2} = \frac{l(l+1)}{\rho^2}u$.

Again, we toss the solution that blows up in this limit, so

$u_o = C\rho^{l+1}$

So, the solution should have a form $u(\rho) = v(\rho)u_o(\rho)u_\infty(\rho) = Av(\rho)\rho^{l+1}e^{-\rho}$

Plug this factored expression into the equation to get new equation for remaining mystery factor.

Without going through the steps, I'll just quote that doing that gets us

$$\rho\frac{\partial^2 v}{\partial\rho^2}+2(l+1-\rho)\frac{\partial v}{\partial\rho}+(\rho_o-2(l+1))v=0$$

Recognize as amenable to series solution and find Recursion Relation

Like we had for the harmonic oscillator at this point, we have an expression that involves the second order derivative with respect to the variable, the first order derivative, the function, and the variable itself. This suggests we could get somewhere with a series solution:

$$v=c_o+c_1\rho+c_2\rho^2+c_3\rho^3+\ldots=\sum_{j=0}^{\infty}c_j\rho^j$$

$$\frac{d}{d\rho}v=\frac{d}{d\rho}\left(c_o+c_1\rho+c_2\rho^2+c_3\rho^3\ldots\right)=c_1+c_2 2\rho^1+c_3 3\rho^2\ldots=\sum_{j=0}^{\infty}c_{j+1}(j+1)\rho^j$$

Similarly, $\rho\frac{d}{d\rho}v==c_1\rho+c_2 2\rho^2+c_3 3\rho^3\ldots=\sum_{j=0}^{\infty}c_j j\rho^j$

and

$$\rho\frac{d^2}{d\rho^2}v=\rho\frac{d}{d\rho}\left(c_1+c_2 2\rho^1+c_3 3\rho^2\ldots\right)=c_2 2\rho+c_3 3\cdot 2\rho^2\ldots=\sum_{j=0}^{\infty}c_{j+1}(j+1)j\rho^j$$

So,

$$\rho\frac{\partial^2 v}{\partial\rho^2}+2(l+1-\rho)\frac{\partial v}{\partial\rho}+(\rho_o-2(l+1))v=0$$

Becomes

$$\sum_{j=0}^{\infty}c_{j+1}(j+1)j\rho^j+2(l+1)\sum_{j=0}^{\infty}c_{j+1}(j+1)\rho^j-2\sum_{j=0}^{\infty}c_j j\rho^j+(\rho_o-2(l+1))\sum_{j=0}^{\infty}c_j\rho^j=0$$

Or

$$\sum_{j=0}^{\infty}\left(c_{j+1}(j+1)j+2(l+1)(j+1)c_{j+1}-2c_j j+(\rho_o-2(l+1))c_j\right)\rho^j=0$$

Defining $g_j\equiv\left(c_{j+1}(j+1)(j+2(l+1))-2c_j j+(\rho_o-2(l+1))c_j\right)$, our differential equation has morphed into the requirement that

$$\sum_{j=0}^{\infty}g_j\rho^j=0 \text{ for all } \rho.$$

The only way that can be is if each coefficient is 0.

$$g_j\equiv\left(c_{j+1}(j+1)(j+2l+2)-2c_j j+(\rho_o-2(l+1))c_j\right)=0$$

Which gives us a recursion relation:

$$c_{j+1}((j+1)(j+2l+2))=-(\rho_o-2(l+1)-2j)c_j$$

$$c_{j+1}=\left(\frac{2(l+1+j)-\rho_o}{(j+1)(j+2l+2)}\right)c_j$$

First, notice that *this* recursions relation *doesn't* skip every-other term as does the one for hermite polynomials, so we'll get even *and* odd terms.

Ball park sum's convergence and its behavior – deduce need to terminate sum

If we want to see what a sum of terms that are thus related adds up to, we can expect that eventually the terms get to large enough j that we have $j>>$ anything it's added to or subtracted from.

For $j >> 1$

$$c_{j+1} \approx \left(\frac{2(j)}{(j+1)(j)}\right)c_j = \left(\frac{2}{(j+1)}\right)c_j \text{ so where, of course, } c_j \approx \left(\frac{2}{j}\right)c_{j-1} \text{ so}$$

$$c_{j+1} \approx \left(\frac{2(j)}{(j+1)(j)}\right)c_j = \left(\frac{2}{(j+1)}\right)\left(\frac{2}{j}\right)c_{j-1}\ldots = \frac{2^{j+1}}{(j+1)!}c_o \text{ or } c_j \approx \frac{2^j}{j!}c_o$$

So

$$v = \sum_{j=0}^{\infty} c_j \rho^j \approx c_o \sum_{j=0}^{\infty} \frac{(2\rho)^j}{j!} = c_o e^{2\rho}$$

Which blows up as ρ goes to infinity – not the behavior we want.

The only way this catastrophe can be averted is if the sum terminates. That is, there's a maximum j_{max}, beyond which $c_{jmax+1} = 0$, and thus all others do to.

$$c_{j\max+1} = \left(\frac{2(l+1+j_{\max}) - \rho_o}{(j+1)(j+2l+2)}\right)c_{j\max} = 0 \Rightarrow 2(l+1+j_{\max}) - \rho_o = 0 \Rightarrow \rho_o = 2(l+1+j_{\max}) \equiv 2n$$

Where $(l+1+j_{max}) = n = 1, 2, 3, \ldots$

Or

$j_{max} = n-1-l$

So

$$c_{j+1} = \left(\frac{2(l+1+j-n)}{(j+1)(j+2l+2)}\right)c_j$$

note that, for a given n, the largest l can be is when $j_{max} = 0$. And then it's $l_{max} = n-1$

So, we've just tied our limit on l to that on n.

$l = 0, 1, 2, \ldots n-1.$

Extract energy quantization requirement from limit to sum.

Going back to the definition of ρ_o in terms of constants and E, we now have an expression for the allowed energies:

$$2n = \rho_o \equiv \frac{me^2}{2\pi\varepsilon_o\hbar^2\kappa} = \frac{me^2\hbar}{2\pi\varepsilon_o\hbar^2\sqrt{-2mE}} \Rightarrow E = -\frac{m}{2\hbar^2}\left(\frac{e^2\hbar}{4\pi\varepsilon_o}\right)^2\frac{1}{n^2} = \frac{E_1}{n^2} \text{ for } n = 1, 2, 3, 4, \ldots$$

For that matter, we can now go back and nail down expressions for a few things:

$$\kappa \equiv \sqrt{-2mE}/\hbar = \frac{m}{\hbar^2}\frac{e^2}{4\pi\varepsilon_o}\frac{1}{n}$$ so the 'wavelength' of oscillations is about 2π over this.

$$r_o \equiv \frac{\rho_o}{\kappa} = \frac{2n^2 4\pi\varepsilon_o\hbar^2}{me^2}$$ is the distance beyond which the wavefunction starts decaying (for l = 0) and it's the classical 'turning point.'

Not going through the classical argument, but I'll remind you from Phys 231 that the radius of a stable circular orbit is half this. For n = 1, this distance goes by the name of *Bohr's* radius:

$$a_o \equiv \frac{4\pi\varepsilon_o\hbar^2}{me^2}$$

3. *Math*: Explicitly plug in constants to derive numbers in equations 4.72 and 4.77. Show explicitly that the units work.

Assemble Solutions

And we have

$$R_{n,l}(r) = \frac{u(r)}{r} = \frac{u_o(r)u_\infty(r)v(r)}{r} = \frac{(\kappa r)^{l+1}e^{-\kappa r}}{r}\sum_{j=0}^{j_{\max}=n-1-l} c_j(\kappa r)^j$$

$$R_{n,l}(r) = \kappa r^l e^{-\kappa r}\sum_{j=0}^{j_{\max}=n-(1+l)} c_j(\kappa r)^j$$

"Can we talk about the Laguerre polynomial because I'm still confused where they come from in the derivation of 4.89." Jessica

Griffiths rephrases the sum in terms of Laguerre polynomials. He doesn't *derive* the relation, just presents it:

Note: while he didn't *derive* this representation, by analogy with the simple harmonic oscillator, we shouldn't be surprised that it can be represented this way – there were the two ways of coming up with the solutions: one was creating a generating operator (the creation operator) and the other was coming up with a recursion relation in the power-series expansion.

I suspect there's something wrong with his expression, or I'm putting it together wrong, because I get only a few terms when I put it all together.

$$v(\rho)=\sum_{j=0}^{j_{\max}=n-1-l} c_j\rho^j=(-1)^{2l+1}\frac{d^{2l+1}}{d(2\rho)^{2l+1}}\left(e^{2\rho}\left(\frac{d^{n+l}}{d(2\rho)^{n+l}}\left(e^{-2\rho}(2\rho)^{n+l}\right)\right)\right)$$

4. *Starting Weekly HW*: Griffiths 4.11
5. *Starting Weekly HW*: Griffiths: 4.13

Putting together the *whole* wavefunction

$$\psi_{nlm}=\ldots$$

4.2.2 The Spectrum of Hydrogen

This subsection should be familiar from Phys 233. While it's some of the pay-off for doing all this hard work, it's familiar enough to not be worth going over.

1. *Math*: Calculate the Rydberg constant. Be explicit, especially with units.
2. *Conceptual*: What is the wavelength of Hydrogen-alpha? What is the transition that produces this wavelength?