8	Mon.10/20 Wed.10/22 Thurs 10/23 Fri.10/24	**4.1.1 -.2** Schrodinger in Spherical: Separation & Angular (Q9.1) **4.1.2-.3** Schrodinger in Spherical: Angular & Radial(Q9.1) Computational: Spherical Schrodinger's 4.2 Hydrogen Atom (Q9.1)	**Daily 8.M** **Daily 8.W** **Weekly 8** **Daily 8.F**
9	Mon., 10/27 Tues. 10/28 Wed., 10/29 Fri., 10/31	**4.3** Angular Momentum **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
- Whiteboards and pens
- Spherical Schrodinger handout
- Computer cued up with http://www.falstad.com/wavebox/

Check dailies

Announcements:
Plotting assignment for next time – Alan's plotting tutorial

Daily 8.M Monday 10/20 Griffiths **4.1.1-4.1.2** Schrödinger in Spherical: Separation & Angular (Q9.1)

4.1 Schrödinger Equation in Spherical Coordinates

Going to 3-D in Cartesian is exactly as you'd expect it to be. Rather than having just one component of momentum, there are three; along with that, rather than just taking the derivative with respect to x, you take it with respect to y and z too.

Classically,

$$E = \frac{p^2}{2m} + V = \frac{p_x^2 + p_y^2 + p_z^2}{2m} + V$$

So, translating this into Schrodinger's equation,

$$i\hbar \frac{\partial}{\partial t}\Psi(x,y,z,t) = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\Psi(x,y,z,t) + V(x,y,z)\Psi(x,y,z,t)$$

Of course, this combo of derivatives should look familiar as

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

And thus

$$i\hbar\frac{\partial}{\partial t}\Psi = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi$$

Along with moving our equation to 3-D; obviously the waves now live in 3-D.

1. *Conceptual*: Write the momentum operator in 3 dimensions in terms of unit vectors xhat, yhat, and zhat.

Example: 3-D Infinite Square Well

1. *Prep for in class:* Read problem 4.2; we will do this problem in class.
   a. *Conceptual*: Set up the problem. Where do you start?
   b. *Math*: How would the solution change if the box is not cubical? Say the particle is confined to: 0 < x < a and 0 < y < b and 0 < z < c.

For example, think of the 3-D infinite square well, of width *a*, depth *b*, and height *c*. Would anyone be truly surprised if it was solved by

$$\Psi = A\sin\left(\frac{n_x\pi}{a}x\right)\sin\left(\frac{n_y\pi}{b}y\right)\sin\left(\frac{n_z\pi}{c}z\right)e^{-i\frac{E}{\hbar}t}\ ?$$

Heck, let's plug it in and see that it works and see what the energy expression is

$$i\hbar\frac{\partial}{\partial t}\Psi = -\frac{\hbar^2}{2m}\nabla^2\Psi$$

$$E = \frac{1}{2m}\left(\left(\hbar\frac{n_x\pi}{a}\right)^2 + \left(\hbar\frac{n_y\pi}{b}\right)^2 + \left(\hbar\frac{n_z\pi}{c}\right)^2\right)$$

How could we represent such a wavefunction? With color intensity playing the role of the fourth dimension, red positive, green negative, something like this:

http://www.falstad.com/wavebox/

Normalization:

Again, the square of this thing relates to the probability of finding the particle somewhere, but now "somewhere" is throughout a 3-D volume rather than just along a 1-D line. So summing over all possibilities to get a probability of 1 means doing a *volume* integral.

$$1 = \int_{all.space} |\Psi|^2 dVol = \int_{all.space} A^2 \sin^2\left(\tfrac{n_x\pi}{a}x\right)\sin^2\left(\tfrac{n_y\pi}{b}y\right)\sin^2\left(\tfrac{n_z\pi}{c}z\right)dxdydz$$

$$1 = \int_{z=-\infty}^{\infty}\int_{y=-\infty}^{\infty}\int_{x=-\infty}^{\infty} A^2 \sin^2\left(\tfrac{n_x\pi}{a}x\right)\sin^2\left(\tfrac{n_y\pi}{b}y\right)\sin^2\left(\tfrac{n_z\pi}{c}z\right)dxdydz$$

Of course, in our case the wavefunction is simply 0 outside the box, so that effectively shrinks the limits of integration to

$$1 = \int_{z=0}^{c}\int_{y=0}^{b}\int_{x=0}^{a} A^2 \sin^2\left(\tfrac{n_x\pi}{a}x\right)\sin^2\left(\tfrac{n_y\pi}{b}y\right)\sin^2\left(\tfrac{n_z\pi}{c}z\right)dxdydz$$

$$1 = A^2 \int_{x=0}^{a}\sin^2\left(\tfrac{n_x\pi}{a}x\right)dx \int_{y=0}^{b}\sin^2\left(\tfrac{n_y\pi}{b}y\right)dy \int_{z=0}^{c}\sin^2\left(\tfrac{n_z\pi}{c}z\right)dz$$

Just focusing on one of these three integrals first,

$$\int_{z=0}^{c}\sin^2\left(\tfrac{n_z\pi}{c}z\right)dz = \int_{z=0}^{c}\tfrac{1}{2} - \tfrac{1}{2}\cos\left(\tfrac{2n_z\pi}{c}z\right)dz = \tfrac{c}{2} - \tfrac{c}{4n_z\pi}\sin\left(\tfrac{2n_z\pi}{c}z\right)\Big|_0^c = \tfrac{c}{2}$$

Similarly for the other two integrals, so

$$1 = A^2\frac{abc}{8} \Rightarrow A = \sqrt{\frac{8}{abc}} = \sqrt{\frac{8}{Vol}}$$

So,

$$\Psi = \sqrt{\frac{8}{abc}}\sin\left(\frac{n_x\pi}{a}x\right)\sin\left(\frac{n_y\pi}{b}y\right)\sin\left(\frac{n_z\pi}{c}z\right)e^{-i\frac{E}{\hbar}t}$$

Perhaps this looks familiar from Statistical Mechanics: treating an air particle in a room as a particle in a 3-D infinite square well.

4.1.1 Separation of Variables

Now, in this case I just slipped in, without saying anything about it, that our solution would likely be separable; in fact, this solution has the form of

$$\Psi = \psi_x(x)\psi_y(y)\psi_z(z)\phi(t)$$

where each factor in the solution is simply the solution to a 1-D problem,

$$\psi_x(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n_x\pi}{a}x\right), \text{ etc.}$$

though they're all linked in that

$$E = \frac{1}{2m}\left(\left(\hbar\frac{n_x\pi}{a}\right)^2 + \left(\hbar\frac{n_y\pi}{b}\right)^2 + \left(\hbar\frac{n_z\pi}{c}\right)^2\right)$$

Other Coordinate Systems.

Now, as I'm sure you're familiar, Cartesian coordinates are handy if your problem has rectangular symmetry (or lack thereof), while cylindrical coordinates are handy if you have cylindrical symmetry (like the electric field of a charged rod or the magnetic field of a line current), and spherical coordinates hare handy if you have spherical symmetry (like the electric field of a point charge.)

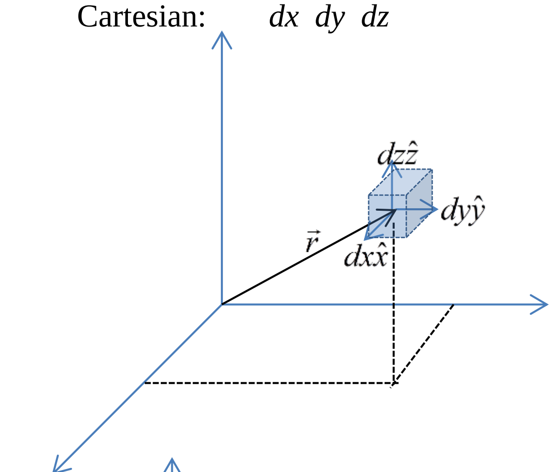
Now, we're going to get pretty interested in "central" potentials. That is, potential energies that depend on how far apart two objects are, *r,* but not the direction of their separation. More mathematically, $V(|r|)$. So this potential has spherical symmetry, and we'll want to use spherical coordinates.

Notice that whether we're looking to integrate over a space or differentiate a function as it varies through space, it's the same basic differential blocks: an infinitesimal step in each orthogonal coordinate direction; call them dr_1 , dr_2 , and dr_3:

$$dVol = dr_1 dr_2 dr_3 \quad \text{and} \quad \nabla = \frac{\partial}{\partial r_1}\hat{r}_1 + \frac{\partial}{\partial r_2}\hat{r}_2 + \frac{\partial}{\partial r_3}\hat{r}_3$$

(where the hat denotes a unit vector rather than an operator – sorry)

Cartesian: $dx \;\; dy \;\; dz$



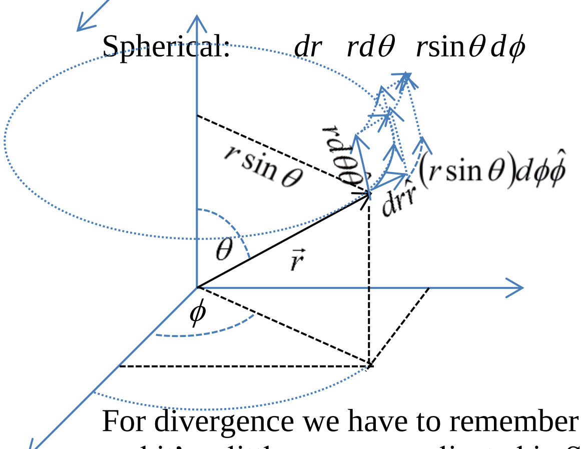
$$dVol = dxdydz$$

$$\vec{\nabla} = \frac{\partial}{\partial x}\hat{x} + \frac{\partial}{\partial y}\hat{y} + \frac{\partial}{\partial z}\hat{z} \quad \text{for gradient and divergance}$$

$$\nabla^2 = \vec{\nabla}\cdot\vec{\nabla} = \left(\frac{\partial}{\partial x}\hat{x} + \frac{\partial}{\partial y}\hat{y} + \frac{\partial}{\partial z}\hat{z}\right)\cdot\left(\frac{\partial}{\partial x}\hat{x} + \frac{\partial}{\partial y}\hat{y} + \frac{\partial}{\partial z}\hat{z}\right)$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Spherical: $dr \;\; rd\theta \;\; r\sin\theta\, d\phi$



$$dVol = r^2 dr\,\sin\theta\, d\theta\, d\phi$$

Double check; is there something about subtracting off a curl?

1. *Conceptual*: What the limits of integration when you integrate over all space in spherical coordinates? Why?

$$\vec{\nabla} = \frac{\partial}{\partial r}\hat{r} + \frac{1}{r}\frac{\partial}{\partial\theta}\hat{\theta} + \frac{1}{r\sin\theta}\frac{\partial}{\partial\phi}\hat{\phi} \quad \text{for gradient}$$

For divergence we have to remember exactly what we *mean* by "divergence" in the first place, and it's a little more complicated in Spherical:

$$\vec{\nabla}\cdot\vec{f} = \lim_{Vol\to 0}\frac{\sum_{sides}\Phi_{flix}}{Vol} = \frac{\partial\left(f_r r\sin\theta\partial\phi r\partial\theta\right)+\partial\left(f_\theta r\sin\theta\partial\phi\partial r\right)+\partial\left(f_\phi r\partial\theta\partial r\right)}{r\sin\theta\partial\phi r\partial\theta\partial r}$$

$$\vec{\nabla}\cdot\vec{f} = \frac{\partial\left(r^2 f_r\right)}{r^2\partial r}+\frac{\partial\left(f_\theta\sin\theta\right)}{r\sin\theta\partial\theta}+\frac{\partial\left(f_\phi\right)}{r\sin\theta\partial\phi}$$

$$\vec{\nabla}\cdot\vec{f} = \frac{1}{r^2}\frac{\partial\left(r^2 f_r\right)}{\partial r}+\frac{1}{r\sin\theta}\frac{\partial\left(\sin\theta f_\theta\right)}{\partial\theta}+\frac{1}{r\sin\theta}\frac{\partial\left(f_\phi\right)}{\partial\phi}$$

(note: this could be derived by doing change of variables from Cartesian to spherical, but it's a pain and, while possibly reassuring, not terribly enlightening.)

Then the Laplacian is still the divergence of the gradient, but it's a little more complicated than in Cartesian. Then it's straight forward to dot this into the gradient.

$$\nabla^2 = \vec{\nabla}\cdot\vec{\nabla} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

So, the Schrodinger Equation in Spherical (and with a central potential) looks like

$$i\hbar\frac{\partial}{\partial t}\Psi = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi$$

$$i\hbar\frac{\partial}{\partial t}\Psi = -\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\Psi}{\partial\phi^2}\right)+V(r)\Psi$$

2. *Math*: Fill in any missing steps in the derivation of equations 4.16 and 4.17. Any questions?

Now, if just like we crossed our fingers and hoped that the *time* and *position* dependence of the wavefunction could be separated into separate factors, and like the x, y, and z dependence could be separated for the 3-D infinite potential, we should look for the possibility of separating r, θ and ϕ. First off, we'll focus on separating off r, so we guess a form

$$\Psi(r,\theta,\phi,t) = R(r)Y(\theta,\phi)\phi(t)$$

Plugging in and treating the different factors as constant for the *other* derivatives,

$$ERY = -\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)Y+\frac{1}{r\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)R+\frac{1}{r^2\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}R\right)+VRY$$

Dividing by RY, and cleaning up a little,

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)-r^2\frac{2m}{\hbar^2}\left[V(r)-E\right] = -\frac{1}{Y}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right)$$

Like this, at most the right depends on r but not on θ or ϕ; at most the left depends at most on θ and ϕ but not on r. But since these two sides are equal to each other; as a whole, the left can't depend on *any* of the variables; ditto for the right. So, they must equal a common constant.

With some foresight, Griffiths writes that constant in the form $l(l+1)$.

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

1. *Conceptual*: What variables can the potential energy in the Schrödinger equation depend on (in other words, V in eq. 4.8 is generally a function of what)? Is equation 4.8 valid if V is a function of time? Why? Is equation 4.4 valid if V is a function of time? Why? In the derivation of equations 4.16 and 4.17 what is V a function of? What can't it be a function of?

4.1.2 The Angular Equation

Griffiths goes after the angular equation first.

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}=-l(l+1)Y$$

Just to bring all function up to the numerator,

$$\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{\partial^2 Y}{\partial\phi^2}=-l(l+1)\sin^2\theta Y$$

Heck, now that we've got a taste for separability, you probably recognize that the θ and ϕ dependence is separable.

$$Y=\Theta(\theta)\Phi(\phi)$$

Plugging this in and dividing by it, we have

$$\frac{1}{\Theta(\theta)}\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right)+l(l+1)\sin^2\theta=-\frac{1}{\Phi(\phi)}\frac{\partial^2\Phi(\phi)}{\partial\phi^2}$$

ϕ dependence

By the same kind of argument we just made when separating off the r dependence, the left of this, at most depends on θ and the right at most depends on ϕ, but the two sides equal each other so they must, as a whole, depend on neither, that is, equal a constant. Convention is to call that m^2 (the reason for the square will become evident shortly).

$$\frac{1}{\Theta(\theta)}\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right)+l(l+1)\sin^2\theta\equiv m^2\equiv-\frac{1}{\Phi(\phi)}\frac{\partial^2\Phi(\phi)}{\partial\phi^2}$$

So, focusing on the right-hand side first, this differential equation looks pretty darn familiar.

$$\frac{1}{\Phi(\phi)}\frac{\partial^2\Phi(\phi)}{\partial\phi^2}=-m^2 \text{ or } \frac{\partial^2\Phi(\phi)}{\partial\phi^2}=-m^2\Phi(\phi)$$

Since we don't have a reason to believe that the wavefunction is simply 0 at a particular angle, guessing cosines or sines may not be the best, so we'll go with exponentials.

$$\Phi(\phi)=e^{im\phi}$$

does the job, and it's already normalized!

If we require that the wavefunction be single valued in space, then this needs to have the property that

$$\Phi(\phi)=\Phi(\phi+2\pi)$$

You may remember from last week's homework that this is easily satisfied if

$$m=0,\pm1,\pm2,\ldots$$

θ Dependence

Now, the θ equation's not so simple. Griffiths doesn't even pretend to lead us through a *derivation* of that solution; instead he names it and gets us familiar with it.

I'll back up at least one step to motivate it a little. The equation is

$$\frac{1}{\Theta(\theta)}\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right)+l(l+1)\sin^2\theta=m^2$$

At each location where there's a $d\theta$, let's multiply and divide by $\sin\theta$.

$$\frac{1}{\Theta(\theta)}\sin^2\theta\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin^2\theta\frac{1}{\sin\theta}\frac{\partial\Theta(\theta)}{\partial\theta}\right)+l(l+1)\sin^2\theta=m^2$$

Now, recall that $\sin\theta d\theta=d(\cos\theta)$

So we can write (bear with me)

$$\frac{1}{\Theta(\theta)}\sin^2\theta\frac{\partial}{\partial(\cos\theta)}\left(\sin^2\theta\frac{\partial\Theta(\theta)}{\partial(\cos\theta)}\right)+l(l+1)\sin^2\theta=m^2$$

For that matter, see all those sine squareds? We can rewrite them as cosines

$$\frac{1}{\Theta(\theta)}(1-\cos^2\theta)\frac{\partial}{\partial(\cos\theta)}\left((1-\cos^2\theta)\frac{\partial\Theta(\theta)}{\partial(\cos\theta)}\right)+l(l+1)(1-\cos^2\theta)=m^2$$

At this point, it's evident that we should rephrase the theta-dependent function as a *cosine of theta dependent function.* And for the sake of not making this look any worse, let's define

$$\xi \equiv \cos\theta$$

(Griffiths uses x, but I don't want any confusion with this being, oh, say, an *x* coordinate.)
So the differential equation that needs solving is

$$\frac{1}{\Theta(\xi)}\left(1-\xi^2\right)\frac{\partial}{\partial\xi}\left(\left(1-\xi^2\right)\frac{\partial\Theta(\xi)}{\partial\xi}\right)+l(l+1)\left(1-\xi^2\right)=m^2$$

$$\left(1-\xi^2\right)\frac{\partial}{\partial\xi}\left(\left(1-\xi^2\right)\frac{\partial\Theta(\xi)}{\partial\xi}\right)=\left(m^2+l(l+1)\left(\xi^2-1\right)\right)\Theta(\xi)$$

Putting together equations 4.27 and 4.28, we have

$$\Theta(\xi)=AP_l^m(\xi)=A\frac{\left(1-\xi^2\right)^{|m|/2}}{2^l\,l!}\frac{\partial^{l+|m|}}{\partial\xi^{l+|m|}}\left(\xi^2-1\right)^l$$

No, that wasn't self-evident, but looking at the form of the differential equation, it's certainly gets points for plausibility.

1. *Conceptual*: This time Griffith's simply gives you the solution to a differential equation (4.26 solves 4.25). List some of the properties of these solutions.

   Let's look at it (see Python program P.py)

2. *Conceptual*: What are the possible values of *m*? Why?

   Magnitude no bigger than *l* because $\left(\xi^2-1\right)^l=\xi^{2l}+a_{l-1}\xi^{2(l-1)}+a_{l-2}\xi^{2(l-2)}+\ldots+1$

   So $\dfrac{\partial^{l+|m|}}{\partial\xi^{l+|m|}}\left(\xi^2-1\right)^l$ is 0 for $l+|m| > 2l$.