Today

I. Last Time

II. Completing Our Discussion of the Radial Equation

III. The 'Old' Quantum Theory of Hydrogen

I. Last time

* Separation of variables to arrive at the radial and angular Schrodinger equations in 3D.
* Found the eigenstates of L^2 and L_z, which turned out to be the spherical harmonics $Y_\ell^m(\theta, \phi)$.
* One intuition behind these functions is that they provide a basis for all functions on the sphere. We can also think of them as describing the quantum states of definite magnitude of angular momentum and definite z-component of ang. mom. These are made up of $e^{im\phi}$ and solutions to Legendre's equation.

I. Derivation of angular momentum eigenfunctions.

Let's focus on (1) at first

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -m^2 \quad (1)$$

It has solutions

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

Boundary conditions tell us the allowed values for m, in the present case they are

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

Let's impose this

$$e^{im(\phi+2\pi)} = e^{im\phi} \quad \Longrightarrow \quad e^{im2\pi} = 1,$$

The last condition is satisfied when

$$m = 0, \pm 1, \pm 2, \ldots, \pm \ell\,.$$

I. Derivation of angular momentum eigenfunctions.

Let's focus on (2) at first

$$\left\{ \frac{1}{\Theta} \left[s\theta \frac{d}{d\theta} \left(s\theta \frac{d\Theta}{d\theta} \right) \right] + \ell(\ell+1) s^2\theta \right\} = m^2 \quad (2)$$

It has solutions

$$\Theta(\theta) = A P_\ell^m(\cos\theta),$$

where P_ℓ^m is the associated Legendre polynomial (or function),

$$P_\ell^m(x) = (1 - x^2)^{|m|/2} \left(\frac{d}{dx} \right)^{|m|} P_\ell(x),$$

which in turn is defined in terms of the Legendre polynomial

$$P_\ell(x) = \frac{1}{2^\ell \ell!} \left(\frac{d}{dx} \right)^\ell (x^2 - 1)^\ell.$$

This last formula is called the Rodrigues formula.

I. Derivation of angular momentum eigenfunctions.

This all amounts to having found the "spherical harmonics"

$$Y_\ell^m(\theta,\phi) = \Phi(\phi)\Theta(\theta) = \sqrt{\frac{(2\ell+1)(\ell-|m|)!}{4\pi(\ell+|m|)!}} e^{im\phi} P_\ell^m(\cos\theta).$$

These are also orthogonal (why?). So,

$\int_0^{2\pi}\int_{\theta=0}^{\pi}\left[Y_\ell^m(\theta,\phi)\right]^*\left[Y_{\ell'}^{m'}(\theta,\phi)\right]\sin\theta d\theta d\phi = \delta_{\ell\ell'}\delta_{mm'}$. (Beware the Condon-Shortley phase. Also the Geodesy convention, which is a real basis for spherical harmonics.)

Our first example of a basis for functions were sin and cos in the context of Fourier analysis. The intuition for spherical harmonics is exactly the same—they provide a basis of functions for the sphere.

I. The Radial Equation

In these spherical coordinates

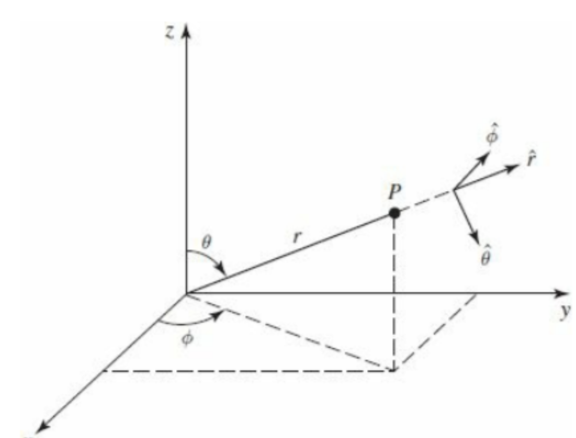
$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2 s\theta}\frac{\partial}{\partial\theta}\left(s\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2 s^2\theta}\frac{\partial^2}{\partial\phi^2}$$

Notice that part of this (the last two terms) is exactly

$$-\frac{1}{\hbar^2 r^2}L^2.$$

Once again we're tempted to try and use separation of variables

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi).$$



Then

$$-\frac{\hbar^2}{2m}\nabla^2(RY) + V(RY) = E(RY)$$

$$\implies -\frac{\hbar^2}{2mr^2}Y\frac{\partial}{\partial r}\left(r^2\frac{dR}{dr}\right) + \frac{\hbar^2}{\hbar^2 2mr^2}RL^2Y + VRY = ERY$$

I. The Radial Equation

$$-\frac{\hbar^2}{2mr^2}Y\frac{\partial}{\partial r}\left(r^2\frac{dR}{dr}\right)+\frac{\hbar^2}{\hbar^2 2mr^2}RL^2Y+VRY=ERY$$

Dividing by RY and multiplying by $-2mr^2/\hbar^2$:

$$\left\{\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{2mr^2}{\hbar^2}\left[V(r)-E\right]\right\}+\frac{1}{Y}\left\{\frac{1}{s\theta}\frac{\partial}{\partial\theta}\left(s\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{s^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right\}=0$$

II. Completing Our Discussion of the Radial Equation

Notice that the second operator is ang. mom. squared roughly,

$$-\frac{1}{\hbar^2 Y}L^2Y=-\ell(\ell+1),$$

So the solutions to the angular equation are the spherical harmonics.

This means that

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{2mr^2}{\hbar^2}[V(r)-E]=\ell(\ell+1)$$

II. Completing Our Discussion of the Radial Equation

This means that

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}[V(r) - E] = \ell(\ell + 1);$$

let's study this equation. Let's change variables to

$u(r) = rR(r)$ or $R(r) = u/r$. Let's compute derivatives

$$\frac{dR}{dr} = \frac{r\frac{du}{dr} - u}{r^2},$$

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) = r^2\frac{d^2u}{dr^2}.$$

Then our differential equation in terms of u becomes

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V(r) + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]u = Eu$$

Or

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + V_{\text{eff}}u = Eu, \quad \text{where} \quad V_{\text{eff}}(r) = V(r) + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}$$

II. Completing Our Discussion of the Radial Equation

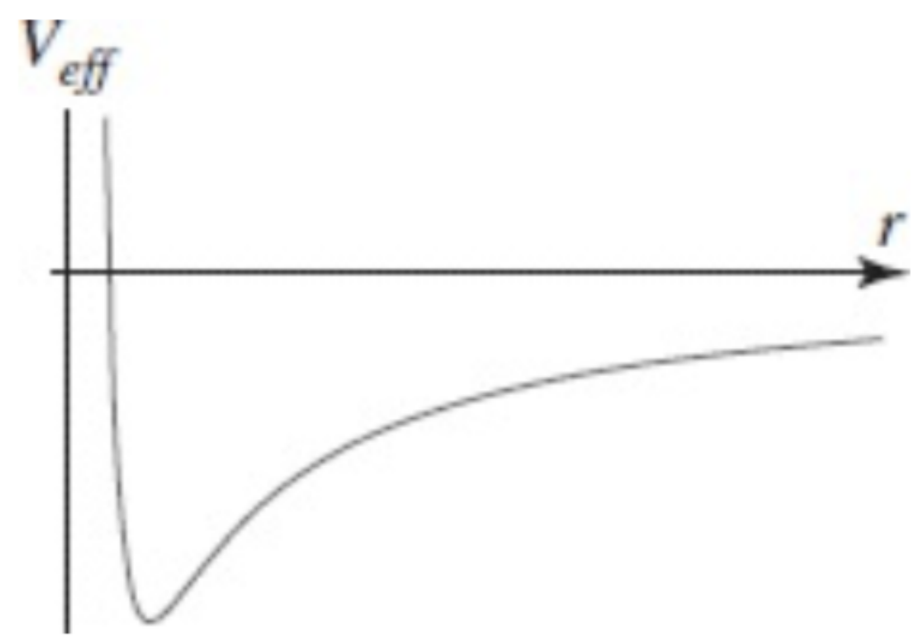
$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + V_{\text{eff}}u = Eu, \quad \text{where} \quad V_{\text{eff}}(r) = V(r) + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}$$

Let's consider a particular potential, just to get a feel for what this looks like. The hydrogen atom potential is

$$V(r) = -\frac{1}{4\pi\epsilon_0}\frac{e^2}{r} = -\frac{k_e e^2}{r},$$

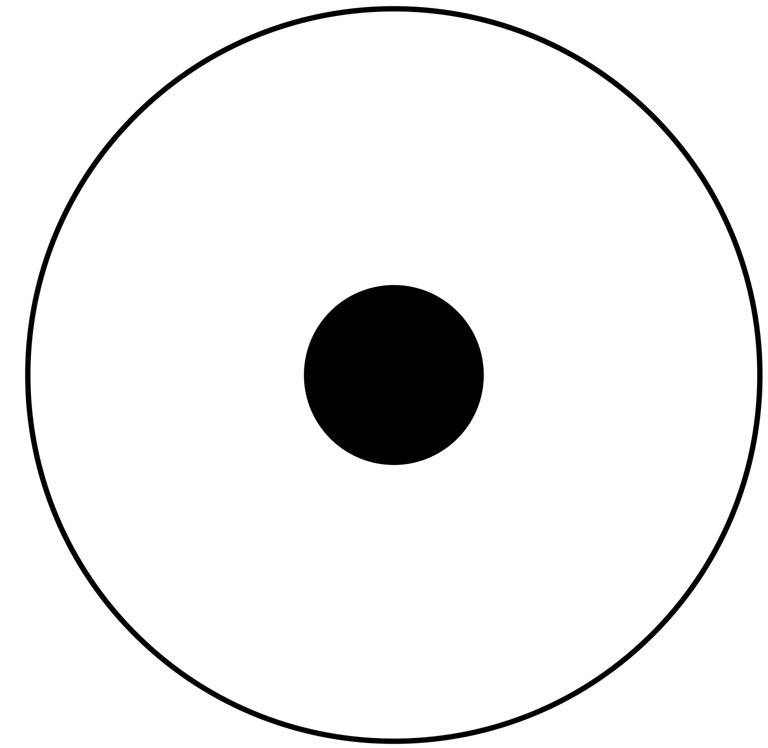
then the effective potential is

$$V_{\text{eff}} = -\frac{k_e e^2}{r} + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}$$



III. The 'Old' Quantum Theory of Hydrogen (The Bohr Model)

Classical Circular Orbit



$$\frac{mv^2}{r} = \frac{k_e e^2}{r^2}$$ centripetal force for a circular orbit

This gives

$$\frac{k_e e^2}{r} = mv^2.$$

The total energy in the system (KE+PE),

$$E = \left(\frac{1}{2}mv^2 - \frac{k_e e^2}{r}\right) = -\frac{1}{2}mv^2 = -\frac{1}{2}\frac{k_e e^2}{r}$$

The angular momentum of this circular orbit is

$$|\overrightarrow{L}| = |\vec{r} \times \overrightarrow{p}| = rmv,$$

And

$$E = \left(-\frac{L^2}{2mr^2}\right) = -\frac{1}{2}\frac{k_e e^2}{r}.$$