Hydrogen Atom

Now we're going to consider the hydrogen atom, the simplest bound state - an electron and proton bound by their electromagnetic interaction - found in nature. It's amazing that the simple Schrödinger Eq'n gives all the correct details of atomic spectra when we put~~s~~ in the Coulomb potential - the same $1/r$ behavior we see in classical E+M. We'll see that like the simple harmonic oscillator, the H atom potential is special because we can solve it exactly. But it's more complicated, because it involves two particles and it's 3-dimensional.

Aside: I say the H atom, but actually our result will apply to any atom with a single electron and a heavy, positively charged nucleus - we just have to make the appropriate adjustments to the mass and charge of the nucleus. The mathematical form of the potential is the same, so the form of the sol'n is the same as well.

S.E. for a two-particle system

We know how to deal w/ the 3-D aspect - we've already obtained the 3-D Schr. eq'n. Now we have to incorporate two particles, the proton (or more generally, the nucleus) and the electron, along with the interaction between them. So now the wave fn depends on positions of both particles. Let

M_2 = mass of proton (or nucleus)

m_1 = mass of electron

Similarly, $\vec{r}_1, \vec{r}_2$ are position of proton + electron, respectively.

The total wave function Ψ is $\Psi(\vec{r}_1, \vec{r}_2, t)$ and we have kinetic terms for both particles. The S.E. is

$$-\frac{\hbar^2}{2m_1}\nabla_1^2\,\Psi - \frac{\hbar^2}{2m}\nabla_2^2\,\Psi + V(\vec{r}_1 - \vec{r}_2)\,\Psi = i\hbar\frac{\partial}{\partial t}\Psi$$

where ∇_1^2 means $\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2}$ + similarly for ∇_2^2.

It turns out that we can separate this eq'n, not into eq'ns for functions of $\vec{r}_1$ + $\vec{r}_2$ (because of the form of the potential), but into eq'ns for functions of the center-of-mass and relative coordinates.

Aside This is like similar cases in classical mechanics. Same coordinates.

So we're separating the motion of the center of mass of the whole system and the motion of the electron relative to the proton.

The coordinates are

relative: $\boxed{\vec{r} = \vec{r}_1 - \vec{r}_2}$ $\qquad |\vec{r}| = r \qquad \vec{r} = (x, y, z)$

center - of - mass: $\boxed{\vec{r}_c = \frac{m_1 \vec{r}_1 + m_2 \vec{r}_2}{m_1 + m_2}} = \frac{m_1 \vec{r}_1 + m_2 \vec{r}_2}{M}$ $\quad \boxed{M = m_1 + m_2}$

Now to transform the S.E., we just need $\frac{\nabla_1^2}{m_1} + \frac{\nabla_2^2}{m_2}$ in terms of ∇_r^2 + ∇_c^2. Let's just look at the x coords.

$$x = x_1 - x_2$$

$$x_c = \frac{m_1 x_1 + m_2 x_2}{M}$$

That means

$$\frac{\partial}{\partial x_1} = \frac{\partial x}{\partial x_1} \frac{\partial}{\partial x} + \frac{\partial x_c}{\partial x_1} \frac{\partial}{\partial x_c} = \frac{\partial}{\partial x} + \frac{m_1}{M} \frac{\partial}{\partial x_c}$$

$$\frac{\partial^2}{\partial x_1^2} = \frac{\partial}{\partial x_1}\left(\frac{\partial}{\partial x_1}\right) = \left(\frac{\partial x}{\partial x_1}\right)^2 \frac{\partial^2}{\partial x^2} + \left(\frac{\partial x_c}{\partial x_1}\right)^2 \frac{\partial^2}{\partial x_c^2} = \frac{\partial^2}{\partial x^2} + \frac{m_1^2}{M^2} \frac{\partial^2}{\partial x_c^2}$$

+ cross term

$$+ 2 \frac{m_1}{M} \frac{\partial}{\partial x} \frac{\partial}{\partial x_c}$$

and similarly

$$\frac{\partial^2}{\partial x_2^2} = \frac{\partial^2}{\partial x^2} + \frac{m_2^2}{M^2} \frac{\partial^2}{\partial x_c^2} - 2 \frac{m_2}{M} \frac{\partial}{\partial x} \frac{\partial}{\partial x_c}$$

Then $\frac{1}{m_1}\frac{\partial^2}{\partial x_1^2} + \frac{1}{m_2}\frac{\partial^2}{\partial x_2^2} = \frac{1}{m_1}\frac{\partial^2}{\partial x} + \frac{m_1}{\underline{M}^2}\frac{\partial^2}{\partial x_c^2}$

$$+ \frac{1}{m_2}\frac{\partial^2}{\partial x^2} + \frac{m_2}{\underline{M}^2}\frac{\partial^2}{\partial x_c^2}$$

$$= \underbrace{\left(\frac{1}{m_1} + \frac{1}{m_2}\right)}\frac{\partial^2}{\partial x^2} + \frac{1}{\underline{M}}\frac{\partial^2}{\partial x_c^2}$$

$$\equiv \frac{m_1+m_2}{m_1 m_2} \equiv \frac{1}{\mu} \quad \text{where} \quad \boxed{\mu = \frac{m_1 m_2}{m_1+m_2} = \text{"reduced mass"}}$$

So $\frac{1}{m_1}\nabla_1^2 + \frac{1}{m_2}\nabla_2^2 = \frac{1}{\mu}\nabla^2 + \frac{1}{\underline{M}}\nabla_c^2$

+ this gives kinetic terms for the center of mass coord w/ the total mass, and the relative coord w/ the reduced mass.

Now separation of the time dependence works just as for a single particle, and we can write

$$\Psi(\vec{r}_1, \vec{r}_2, t) = \psi(\vec{r}_1, \vec{r}_2)\,\Phi(t)$$

and we find

$$\Psi(\vec{r}_1, \vec{r}_2, t) = \psi(\vec{r}_1, \vec{r}_2)\,e^{-iE_{tot}t/\hbar}$$

and E_{tot} is the <u>total</u> energy.

Now the time independent eq'n depends only on the variables $\vec{r}_c$ + $\vec{r}$, so $\psi(\vec{r}_1, \vec{r}_2) = \psi(\vec{r}, \vec{r}_c)$

The time-indep equation is

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi - \frac{\hbar^2}{2M}\nabla_c^2\psi + V(\vec{r})\psi = \underbrace{E_{tot}}\psi$$

Now we do the <u>separation</u>: write

$$\psi(\vec{r}_1,\vec{r}_2) = \psi(\vec{r},\vec{r}_c) = \psi_r(\vec{r})\,\psi_c(\vec{r}_c)$$

+ substitute into the S.E.. We get

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2\psi_r\right)\psi_c - \left(\frac{\hbar^2}{2M}\nabla_c^2\psi_c\right)\psi_r + V(r)\psi_r\psi_c = E_{tot}\psi_r\psi_c$$

Dividing by $\psi = \psi_r\psi_c$ + rearranging, we find

$$\underbrace{\frac{1}{\psi_r}\left[-\frac{\hbar^2}{2\mu}\nabla^2\psi_r(\vec{r}) + V(\vec{r})\psi_r(\vec{r})\right]} + \underbrace{\frac{1}{\psi_c}\left[-\frac{\hbar^2}{2M}\nabla_c^2\psi_c(\vec{r}_c)\right]} = E_{tot}$$

Now, the 1st term depends <u>only on</u> $\vec{r}$, and the 2nd term depends <u>only</u> on $\vec{r}_c$. They must add up to E, and to do so for any value of $\vec{r}$ and independently for any value of $\vec{r}_c$, each term must separately be equal to a constant, and the two constants must add up to E_{tot}.

So we're left with an equation for ψ_c and one for ψ_r. They are

$$-\frac{\hbar^2}{2M}\nabla_c^2\,\psi_c = E_c\,\psi_c$$

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi_r + V(\vec{r})\psi_r = E_r\,\psi_c \quad , \quad E_c + E_r = E_{TOT}$$

Now the eq'n for ψ_c that describes the center of mass motion is simply the equation of a free particle — we know how to solve it, so we don't need to think about it any more.

All the action is in the ψ_r equation, the one for the relative motion. That's because V only depends on $\vec{r}$. Notice that this separation & resulting eq'ns applies to any two-particle system whose potential depends only on the relative coordinate — we have not restricted ourselves to the hydrogen atom.

Now let's think about the hydrogen atom. Notice that the proton mass is much bigger than the electron mass, by a factor of about 2000, i.e. $m_1 >> m_2$.

That means $\underline{M} = m_1 + m_2 \simeq m_2 = m_p$

$$\mu = \frac{m_1 m_2}{M} \simeq \frac{m_1 m_2}{m_2} \simeq m_e$$

and
$$\vec{r}_c = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{M} \simeq \frac{m_1}{m_2}\vec{r}_1 + \frac{m_2}{m_2}\vec{r}_2 \simeq \vec{r}_2 = \vec{r}_p$$

So the center of mass motion is governed by $M \simeq m_p$ and $\vec{r}_c$ is approximately the position of the proton - the overall center of mass motion of the atom is pretty much that of the proton.

So the relative coordinate measures the position of the electron relative to that of the proton, and since the reduced mass is approximately the electron mass, the eq'n for ψ_r is basically the eq'n for the electron.

Now we're only going to deal with the ψ_r eq'n, and we're going to drop the r and just call it ψ.

Before we go specifically to the Coulomb potential, we're going to separate the equation again, in spherical coordinates. We will assume $V(\vec{r}) = V(|\vec{r}|)$ but we won't be more specific just yet.

Separation of S.E. in sph. coords.

Recall the 3-D Schrödinger eq'n:

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi(\vec{r}) + V(\vec{r})\,\psi(\vec{r}) = E\,\psi(\vec{r})$$

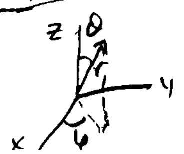
In the special case where V only depends on the magnitude of r, $V(|\vec{r}|)$, we can separate the S.E. like we separated the space and time dependence, only this time we can do it in spherical coordinates r, θ, φ, so that the wave function separates into a product of three functions, one each of $r, \theta, + \varphi$.

To do this we have to express the Laplacian, ∇^2, in terms of spherical coordinates. It is:

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

The derivation of this can be found in Appendix M of Eisberg and Resnick. It is worth working through, but we won't go through it here.

Recall



$z = r\cos\theta$

$x = r\sin\theta\cos\varphi$

$y = r\sin\theta\sin\varphi$

$r = \sqrt{x^2+y^2+z^2}$

$\theta = \cos^{-1}\left(\frac{z}{r}\right)$

$\varphi = \tan^{-1}\left(\frac{y}{x}\right)$

Now the trick is to write the wave fn as a product:

$$\psi(\vec{r}) = \psi(r,\theta,\varphi) = R(r)\Theta(\theta)\Phi(\varphi)$$

and the separation works as before: we plug this into the S.E. and get separate eq'ns for the functions R, Θ, Φ.

Plugging into S.E., we get

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}R\right)\Theta\Phi + \frac{1}{r^2\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\Theta\right)R\Phi + \frac{1}{r^2\sin^2\theta}\left(\frac{d^2\Phi}{d\varphi^2}\right)R\Theta\right] + V(r)R\Theta\Phi = ER\Phi\Theta$$

where the partial derivatives are now total derivatives.

Multiplying through by $\dfrac{-2\mu r^2\sin^2\theta}{\hbar^2\psi}$ and rearranging,

$$\underbrace{\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2}}_{\text{fn of } \varphi \text{ only}} = \underbrace{-\frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) - \frac{2\mu}{\hbar^2}r^2\sin^2\theta\big[E-V}_{\text{fn of } r, \theta \text{ only}}$$

As usual, the only way the left- and right-hand sides of these eq'ns can be equal for all r, θ, φ is for them to be equal to a constant. Call it ~~$-m_\ell^2$~~.

$-m_\ell^2$

We'll see the significance of $-m_\ell^2$ below. Now we have

$$\boxed{\frac{d^2\Phi}{d\varphi^2} = m_\ell^2\,\Phi}$$

and
$$-\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) - \frac{2\mu}{\hbar^2}r^2\left[E-V(r)\right] = -\frac{m_\ell^2}{\sin^2\theta}$$

We can do some more rearranging,

$$\underbrace{\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu}{\hbar^2}r^2\left[E-V(r)\right]}_{\text{fn of } r \text{ only}} = \underbrace{\frac{m_\ell^2}{\sin^2\theta} - \frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)}_{\text{fn of } \theta \text{ only}}$$

Again, the two sides must be separately equal to the same constant. Call it $\ell(\ell+1)$, + we'll see what ℓ is below. We've finally completed the separation, and the eq'ns for R + Θ are

$$\boxed{-\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{m_\ell^2}{\sin^2\theta}\Theta = \ell(\ell+1)\Theta}$$

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

Now we're down to three ordinary linear differential equations, which we can solve using the techniques we already have at our disposal.

Sol'n to φ eq'n

We have

$$\frac{d^2\Phi}{d\varphi^2} = -m_\ell^2\,\Phi$$

Where $-m_\ell^2$ is just some number w/ no special value, yet. It appears in both this eq'n for φ and in the eq'n for θ, so what it is and how it might be related to other quantities in the problem will be determined by solving this eq'n and the one for θ.

So the sol'n is

$$\Phi(\varphi) = e^{im_\ell\varphi}$$

and we still have no restrictions on m_ℓ. Now this function is finite and continuous so there's no problem there, but we finally get some useful info from the requirement that φ must be single-valued

This matters because $\varphi + 2\pi$ is the same physical angle as φ. So we must have

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

Now $\Phi(\varphi + 2\pi) = e^{im_\ell(\varphi + 2\pi)} = e^{im_\ell 2\pi} e^{im_\ell \varphi}$

$$= e^{im_\ell 2\pi} \Phi(\varphi)$$

So we must have

$$e^{im_\ell 2\pi} = 1$$

i.e. $m_\ell = \text{integer} = 0, \pm 1, \pm 2, \ldots$

We'll see the reason for the subscript ℓ when we solve the Θ equation

Sol'n to Θ eq'n

The eq'n for Θ is

$$-\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\,\frac{d\Theta}{d\theta}\right)+\frac{m_\ell^2}{\sin^2\theta}\Theta=\ell(\ell+1)\Theta$$

The sol'n to this eq'n is obtained using a similar approach to that for the ~~simple~~ harmonic oscillator. The main steps are given in Appendix N. I won't belabor them here, except to give an outline of how it goes, with the crucial step that gives quantization.

First we simplify by changing variables:

$$z\equiv\cos\theta \qquad (-1\le z\le +1)$$

The eq'n becomes one for $\Theta_{\ell m_\ell}(z)$, the "associated Legendre functions." It turns out we can write them as

$$\Theta_{\ell m_\ell}(z)=(1-z^2)^{|m_\ell|/2}\,\frac{d^{|m_\ell|}}{dz^{|m_\ell|}}\,P_\ell(z)\quad\nwarrow\text{"Legendre polynomials"}$$

Recall that the sol'n to the φ eq'n required that m_ℓ be an integer; this just involves its absolute value. We don't have a connection between ℓ + m_ℓ yet.)

Now all we have to do is find $P_\ell(z)$; we've taken care of the m_ℓ dependence $P_\ell(z)$ satisfies

$$(1-z^2)\frac{d^2P_\ell}{dz^2} - 2z\frac{dP_\ell}{dz} + \ell(\ell+1)P_\ell = 0$$

Now it's $P_\ell(z)$ that we find a power series sol'n for. With

$$P_\ell(z) = \sum_{j=0}^{\infty} a_k z^k$$

we find the recursion rel'n

$$a_{j+2} = \frac{j(j+1) - \ell(\ell+1)}{(j+2)(j+1)} a_j$$

Now, as we did for the harmonic oscillator, look at the behavior for large j:

$$\frac{a_{j+2}}{a_j} \to 1 \quad \text{as} \quad j \to \infty$$

That means all of the coefficients are equal at large j and at $z = \pm 1$ $P_\ell(z)$ blows up. As with the harmonic oscillator, we can either set $a_0 = 0$ or $a_1 = 0$, but not both; the series must cut off (and again we get only even or odd powers of z).

The cutoff condition is

$$\frac{a_{j+2}}{a_j} = 0 \quad \Rightarrow \quad j(j+1) = \ell(\ell+1)$$

i.e., $j = \ell$. $\boxed{\ell = 0, 1, 2, \ldots}$

So ℓ is a nonnegative integer, and $P_\ell(z)$ is a polynomial of order ℓ. The first few Legendre polynomials are, from the recursion relns,

$$P_0 = 1$$

$$P_1 = z$$

$$P_2 = 1 - 3z^2$$

$$P_3 = 3z - 5z^3$$

Now we can get the Θ functions, which also depend on m_ℓ. But the $\frac{d^{|m_\ell|}}{dz^{|m_\ell|}} P_\ell$ part

tells us that, because the P_ℓ are polynomials of order ℓ, you can only take up to ℓ derivatives. That means, for any given ℓ, you can only have

$$\boxed{m_\ell = -\ell, -\ell+1, \ldots, 0, \ldots, \ell-1, \ell}$$

You can then find the first few $\Theta_{\ell m_\ell}$, which are given at the bottom of p. N-2 in the book.

Now we go back and express things in terms of Θ again (cf p. 4.7). Note that

$$1-z^2 = 1-\cos^2\theta = \sin^2\theta$$

$$\Rightarrow (1-z^2)^{|m_\ell|/2} = (\sin\theta)^{|m_\ell|}$$

and we have

$$\boxed{\Theta_{\ell m}(\theta) = (\sin\theta)^{|m_\ell|}\frac{d^{|m_\ell|}}{(d\cos\theta)^{|m_\ell|}}P_\ell(\cos\theta)}$$

Sol'n to r eq'n

Recall that the eq'n for the r behavior is

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

Up until now, we haven't specified the potential; all we needed to know was that it only depends on the magnitude of $\vec{r}$, i.e., it only depends on r. [That means the angular sol'ns we just found are also the sol'ns for any central potential!]

Now let's put in the Coulomb potential, and rather than restrict ourselves to the hydrogen atom, let's keep the one electron but assume the nucleus has Z protons. Recall the Coulomb potential is

$$V = \frac{1}{4\pi\epsilon_0}\frac{q_1 q_2}{r}$$

and since $q_1 = q_{nucleus} = Ze$, and $q_2 = q_e = -e$, we have

$$V(r) = \frac{-Ze^2}{4\pi\epsilon_0 r}$$

and the r eq'n becomes

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu}{\hbar^2}\left[E + \frac{Ze^2}{4\pi\epsilon_0 r}\right]R = l(l+1)\frac{R}{r^2}$$

(and note that now we know that l must be a nonnegative integer.)

The approach here is very much like that for the harmonic oscillator. We will

1) Change variables + define constants
2) Solve for the asymptotic behavior at large r
3) Find a power series solution for what remains. Quantization of energy will follow from requiring that the wave fn be finite

In just a little more detail:

1) Let $\rho = 2\beta r$

Where $\beta^2 = \frac{-2\mu E}{\hbar^2}$

Note that β has units 1/dist : $[\beta] = \text{kg}\,\frac{\text{kg m}}{\text{sec}^2}\left(\frac{\text{sec}}{\text{kg m}}\right)^2 = \frac{1}{m}$

So ρ is dimensionless. ~~[Aside: β is usually called $1/a_0$, but we use a_0 as a coefficient in power series expansions.]~~

and let

$$\gamma = \frac{\mu Z_1 e^2}{4\pi\epsilon_0 \hbar^2 \beta}\,, \quad \text{dimensionless.}$$

This simplifies the eq'n for R (see eq'n N-19 in book).

2) By considering the asymptotic limit of the R eq'n (see eq'n N-21) we find

$$R(\rho) \rightarrow e^{-\rho/2} \quad \text{as} \quad \rho \rightarrow \infty$$

3) We now assume this behavior appears as an overall factor, and that the whole

sol'n is

$$R(\rho) = e^{-\rho/2} F(\rho)$$

and we'll try for a power series sol'n for $F(\rho)$.

In this case, we'll assume

$$F(\rho) = \rho^s \sum_{k=0}^{\infty} a_k \rho^k$$

where s is some integer ≥ 0 and $a_0 \neq 0$.

This is to make sure F stays finite as $\rho \to 0$, because there are some terms in the eq'n for F, which is

$$\frac{d^2F}{d\rho^2} + \left(\frac{2}{\rho} - 1\right)\frac{dF}{d\rho} + \left[\frac{\gamma - 1}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right]$$

that blow up as $\rho \to 0$. So in addition to the usual recursion rel'n (see below), we also get an eq'n for s:

$$s(s+1) - \ell(\ell+1) = 0$$

"indicial eq'n"

The sol'ns are

$$s = \frac{-1 \pm \sqrt{1 + 4\ell(\ell+1)}}{2} = -\frac{1}{2} \pm \frac{\sqrt{(2\ell+1)^2}}{2}$$

$$= -\frac{1}{2} \pm \left(\ell + \frac{1}{2}\right)$$

So $s = l$ or $s = -(l+1)$. The second one is no good because it gives a negative power of ρ, which blows up as $\rho \to 0$. So

$$s = l.$$

The recursion relation is

$$a_{j+1} = \frac{j+l+1-\gamma}{(j+l+1)(j+l+2)-l(l+1)}\, a_j$$

Now for large j, this gives

$$\frac{a_{j+1}}{a_j} = \frac{1}{j}$$

But notice that the expansion for e^{ρ}

$$e^{\rho} = \sum_{k=0}^{\infty} \frac{\rho^k}{k!}$$

has the same ratio of successive terms. But R already has $e^{-\rho/2}$; combining gives

$$R \sim \rho^{l} e^{+\rho/2} \quad \text{as} \quad \rho \to \infty$$

which blows up & hence is no good. As usual, we cut off the power series by setting the coefficients to 0 at some point. Notice that the recursion rel'n involves a_{j+1} and a_j — there's no skipping coefficients so we don't have two separate sets of power series with even and odd powers.

We need

$$\frac{a_{j+1}}{a_j} = 0 \quad \Rightarrow \quad j + \ell + 1 - \gamma = 0$$

or

$$\gamma = n$$

where $n = j + \ell + 1$, so n is an integer and $n \geq \ell + 1$. The maximum power of ℓ is $j_{max} = n - \ell - 1$, and combining with the overall ρ^{ℓ}, we get ρ^{n-1} as max power of $\rho \Rightarrow$ the $F(\rho)$ are <u>polynomials of order $n-1$.</u>

Now what does $\gamma = n$ mean? Going back to its def,

$$\gamma = \frac{\mu Z e^2}{4\pi\epsilon_0 \hbar^2 \beta},$$

and substituting for $\beta^2 = \frac{-2\mu E}{\hbar^2}$, We find that the energy is quantized:

$$E = \frac{-\beta^2 \hbar^2}{2\mu},$$

$$\Rightarrow \boxed{E_n = -\frac{\mu Z^2 e^4}{(4\pi\epsilon_0)^2 \, 2\hbar^2 n^2}}$$

same as for the Bohr atom! Schrödinger eq'n triumphs!

Now let's collect quantum numbers:

$$\boxed{\begin{aligned} n &= 1, 2, \ldots \\ \ell &= 0, 1, 2 \ldots n-1 \\ m_\ell &= -\ell, -\ell+1, \ldots 0, \ldots \ell-1, \ell \end{aligned}}$$

n = "principal quantum number" determin E

ℓ = "azimuthal quantum no." ↔ angular dependence

m_ℓ = "magnetic quantum no." determine energies in $\vec{B}$ fie

and putting things back in terms of r, and defining

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{\mu e^2} \quad \text{"Bohr radius"}$$

$$= 0.529\,\text{Å}$$

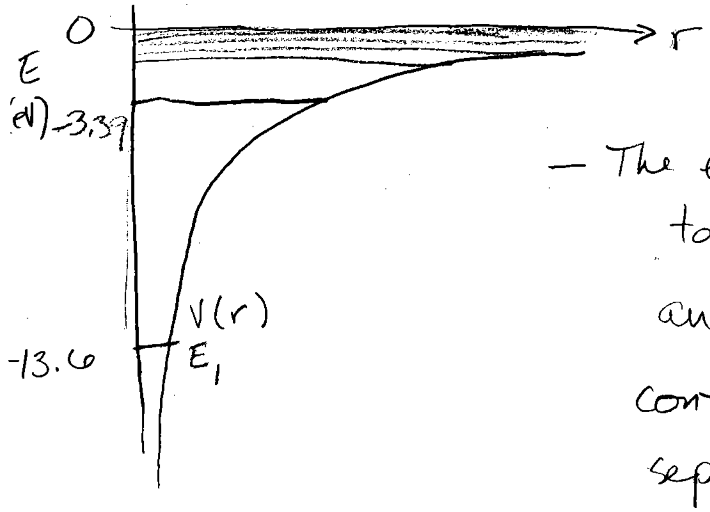
the radial wave fns are

$$R_{n\ell}(r) = e^{-Zr/na_0} \left(\frac{Zr}{a_0}\right)^{\ell} \underset{\uparrow \text{ polynomials}}{G_{n\ell}}\left(\frac{Zr}{a_0}\right)$$

Now some comments about the energy. We can write it as

$$E_n = -\frac{\mu Z_1^2 e^4}{(4\pi\epsilon_0)^2 2\hbar^2}\frac{1}{n^2} = -\frac{13.6\,eV}{n^2} \leftarrow$$

"the Rydberg" or "Rydberg energy"



- The energies get closer and closer together as n gets bigger and bigger. They're close to continuous [for any arbitrary separation ϵ you can find an n such that for larger quantum numbers the energy levels are closer together than ϵ] which is what you expect from the correspondence principle.

- The minimum energy, for n = 1, is − 13.6 eV. That's the ground state energy of hydrogen and is known as the Rydberg or the Rydberg energy. = ionization energy

- Degeneracy. The energy only depends on n. So states with the same n but different l and m have very different space dependence, but they have the same energy. Different states with the same energies are said to be "degenerate" and this property is called "degeneracy." (Note that it's not unique to quantum mechanics - it happens in classical mechanics too.) Sometimes it's a consequence of the symmetry - e.g. the m_ℓ degeneracy in the H atom occurs because of the spherical symmetry of the potential - and sometimes it's just a coincidence - in the H atom, the ℓ degeneracy is from the $1/r$ form of the Coulomb potential!

Eigenfunctions + Probability Densities

When we pull the solutions together, we get the complete space dependence

$$\psi_{n\ell m_\ell}(r,\theta,\varphi) = R_{n\ell}(r)\,\Theta_{\ell m_\ell}(\theta)\,\Phi_{m_\ell}(\varphi)$$

where, to summarize,

$$\Phi_{m_\ell}(\varphi) = e^{i m_\ell \varphi}$$

$$\Theta_{\ell m_\ell}(\theta) = (\sin\theta)^{|m_\ell|} * \overbrace{\text{polynomial in } \cos\theta}^{\text{order } \ell}$$

$$R_{n\ell}(r) = e^{-Zr/a_0 n}\ \underbrace{r^\ell * \overbrace{\text{polynomial in } r}^{\text{order } n-\ell-1}}_{\text{order } n-1\text{, but details depend on } \ell}$$

The normalized wave functions for the first few quantum numbers are given on p.243. They start out with the relatively simple ground state wave fn $n=1$, $l=m_l=0$

$$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z_1}{a_0}\right)^{3/2} e^{-Z_1 r/a_0}$$

which is completely isotropic (indep. of θ, φ) and is just a decreasing exponential in r, to much more complicated higher terms. As the quantum numbers go up, the wave functions tend to get more complicated. [But notice that for any n, $l=m_l=0$ has no angular dependence.]

Example 7-2, p. 242, works through a calculation showing that ψ_{211} does indeed satisfy the Schrödinger eq'n

Now that we know the wave functions we can extract all kinds of information. Let's start with the probability densities, which give us the probability for finding the particles in particular regions in space. The prob. density is

$$\rho(\vec{r}) = \Psi^*\Psi = \psi^*_{nlm}\psi_{nlm} = |R_{nl}|^2 |\Theta_{lm_l}|^2$$

and $\Phi^*\Phi = 1$ – the prob. density is uniform in Φ

Let's focus on the prob. density in r. Strictly speaking, we can have any value of $r > 0$, up to ∞. But we know in practice that the electrons stay within about an angstrom ($1 \mathring{A} = 10^{-10} m$) of the nucleus. This should be reflected in the wave functions, so that the probability density is big close to the atom and is very small at distance scales larger than an angstrom.

In fact we can see that something like that happens just from looking at the potential and the energy levels. So back to the energy diagram on p. 4.17 of the notes (p.239 in the textbook).

Look at E_1. We have $E_1 > V(r)$ only for small values of r. For larger values of r we're in the classically inaccessible region, and we know the probability density falls off rapidly.

Now look at E_2. It has a larger, but finite, classically accessible region, and the trend increases as n gets larger. Eventually when n gets big enough the electron is only barely bound to the nucleus, and it takes just a slight energy kick to set the electron free, i.e. to ionize the atom.

Now let's see how this behavior is reflected in the probability densities. We want the radial probability density

$P_{n\ell}(r)\,dr$ = prob of finding the electron anywhere between r and r+dr.

To get this we have to take

$\Psi^* \Psi \, d^3r$ = prob of finding electron in $d\vec{r}$ = region between $\vec{r}$ and $\vec{r} + (dx, dy, dz)$

$d^3r = dx\,dy\,dz$

and integrate over angles. In spherical coordinates

$$d^3r = r^2 dr\, d(\cos\theta)\, d\varphi \qquad \text{with } 0 \le r \le \infty$$

$$-1 \le \cos\theta \le +1$$

$$0 \le \varphi \le 2\pi$$

Now $\Psi^* \Psi = |R|^2 |\Theta|^2$, so we have

$$|R|^2 dr \underbrace{\int_{-1}^{1} |\Theta|^2 d\cos\theta}\ \underbrace{\int_0^{2\pi} d\varphi}_{=2\pi} = P_{n\ell}(r)\, dr$$

⟶ The Θ fns have been normalized s.t. this integral = 2

e.g. $\Theta_{00} = 1$

$$\Rightarrow \quad P_{n\ell}(r)\, dr = |R_{n\ell}|^2 4\pi r^2 dr$$

⟶

and notice that $4\pi r^2 dr$ is just the volume of the spherical shell between r + $r+dr$.

Now let's look at this density $4\pi r^2 |R_{n\ell}|^2$ for the first few n + ℓ. It's shown on p. 245 in the book + 4.23 of the notes.

Comments

- Indeed, the region in which the prob density is appreciable is finite, as expected.
- Also as expected, those regions in r increase as n increases.
- For a given n, the densities for different ℓ have different behavior, and the average r (shown by the black triangles) actually decreases with increasing ℓ.
- Notice that the number of nodes in the prob. density is $n-\ell$

That follows from $R \propto r^\ell \times$ polynomial of order $n-\ell-1$

The polynomial has $n-\ell-1$ roots,* and the overall r^2 in $P_{n\ell}(r)$ guarantees another node at $r=0$.

*Are they all positive?

(4.23)

and $r + dr$. By integrating the probability density $\Psi^*\Psi$, which is a probability per unit volume, over the volume enclosed between spheres of radii r and $r + dr$, it is easy to show that

$$P_{nl}(r)\,dr = R^*_{nl}(r)R_{nl}(r)4\pi r^2\,dr \tag{7-28}$$

The factor of $4\pi r^2$ is present on the right side because the volume enclosed between the spheres is given by that factor. The use of the quantum numbers n and l as labels to specify the form of a particular radial probability density function is obviously appropriate, but the form of these functions does not depend on the quantum number m_l. Figure 7-5 plots several $P_{nl}(r)$, using dimensionless quantities for each axis.

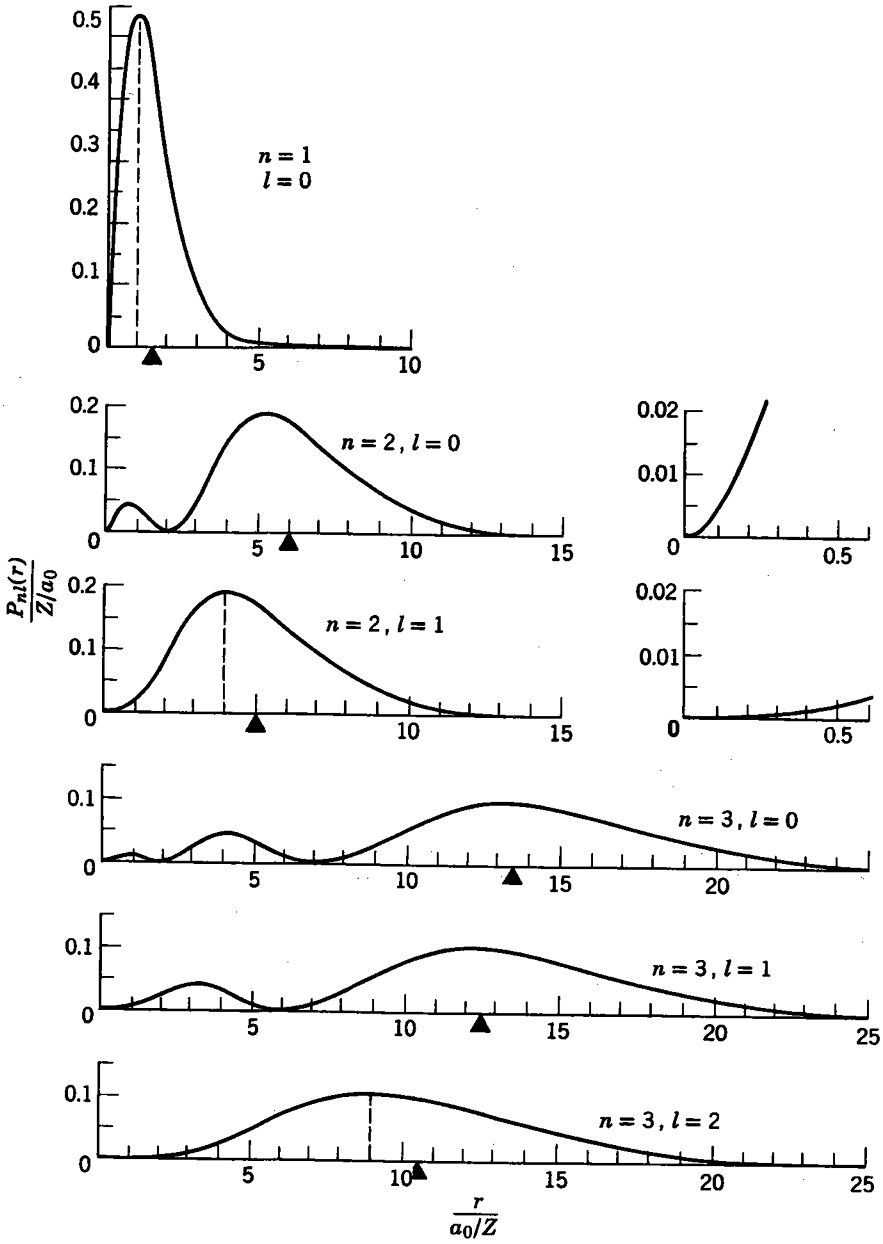


Figure 7-5 The radial probability density for the electron in a one-electron atom for $n = 1, 2, 3$ and the values of l shown. The triangle on each abscissa indicates the value of $\overline{r}_{nl}$ as given by (7-29). For $n = 2$ the plots are redrawn with abscissa and ordinate scales expanded by a factor of 10 to show the behavior of $P_{nl}(r)$ near the origin. Note that in the three cases for which $l = l_{\max} = n - 1$ the maximum of $P_{nl}(r)$ occurs at $r_{\text{Bohr}} = n^2a_0/Z$, which is indicated by the location of the dashed line.

We noticed that the average r seems to increase with increasing n, and that it also depends on ℓ. If we calculate the average r as a function of $n + \ell$, i.e. [illegible]

$$\overline{r_{n\ell}} = \int_0^\infty r\, P_{n\ell}(r)\, dr$$

$$= \int_0^\infty 4\pi r^3 |R_{n\ell}(r)|^2 dr$$

we get

$$\overline{r_{n\ell}} = \frac{n^2 a_0}{Z_1}\left\{1 + \frac{1}{2}\left[1 - \frac{\ell(\ell+1)}{n^2}\right]\right\}$$

which

- increases as n^2
- decreases w/ increasing ℓ, though the ℓ dependence is less strong than the n dependence, and is suppressed by $\frac{1}{n^2}$, so it gets weaker as n increases
- decreases w/ increasing Z_1. Higher Z_1 means higher charge on the nucleus, which means the atom is more tightly bound (i.e. the force between the nucleus and electron is stronger) so that the electron stays in closer to the nucleus.
- is similar to but not exactly the radius of the Bohr orbit $\frac{n^2 a_0}{Z_1}$

These $\overline{r_{n\ell}}$ are marked in the fig. on the previous page by ▲.

Example For the ground state of hydrogen, find

a) where the radial prob density is max, i.e. where electron is most likely to be found

b) the expectation value for r

a). $R_{10} = \frac{1}{\sqrt{\pi}} \frac{1}{a_0^{3/2}} e^{-r/a_0}$ with $Z=1$

Prob. density is

$$P_{10}(r) = 4\pi r^2 |R|^2$$
$$= \frac{4}{a_0^3} r^2 e^{-2r/a_0}$$

To find max, take $\frac{dP_{10}}{dr} = 0$ (+ note that overall norm. doesn't matter)

$$\frac{dP_{10}}{dr} = \frac{4}{a_0^3}\left[2r e^{-2r/a_0} - \frac{2}{a_0} r^2 e^{-2r/a_0}\right]$$

$$= \frac{4 \cdot 2}{a_0^3} e^{-2r/a_0} r \left[1 - \frac{r}{a_0}\right]$$

$$= 0$$

$\Rightarrow$ $r = 0$: not a maximum

or $1 - \frac{r}{a_0} = 0$ $\Rightarrow$ $\boxed{r = a_0}$ max probability.

b) To find the mean, or expectation value of r, we can do the integral

$$\bar{r}_{10} = \int_0^\infty r P_{10}(r)\, dr$$

explicitly or use the expression for $\overline{r}_{n\ell}$ on p. 4.24. Doing the latter, and taking $n=1, \ell=0$, we find

$$\overline{r}_{10} = a_0\left\{1+\frac{1}{2}\left[1-0\right]\right\}$$

$$=1.5\,a_0$$

The expectation value is bigger than the point of max probability – not surprising, because the density fn P_{10} isn't symmetric about the peak. It stretches out to larger values of r, which shifts up the expectation value. The most likely value is simply not equal to what we'd get if we took a lot of measurements and averaged them.

---

end of example

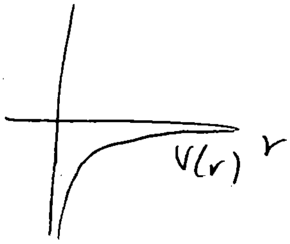
We found $r_{10,\underset{\text{prob}}{\text{max}}} = a_0$ and $\overline{r}_{10} = 1.5\,a_0$ for hydrogen in its ground state. That means it's reasonable to take a_0 as the order of magnitude of the size of the ground state: half an angstrom, as opposed to half a meter for example.

We can obtain this order of magnitude from an estimate based on the uncertainty principle (similar to a HW problem you did for the simple harmonic oscillator).

Example Use the uncertainty principle to estimate the size of the ground state of the hydrogen atom.

Physically, what happens? The potential energy

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



wants r to go to 0 – to minimize the potential energy. But we can't have $r \to 0$; there must be some momentum according to the uncertainty Principle (if $\Delta x = 0$, $\Delta p \to \infty$), and if there's momentum, the particle can't stay at one position. In terms of the energy, the negative potential energy is opposed by the positive kinetic energy. Let's find the balance that minimizes the sum.

Suppose the electron is in a region of size R. Then we must have

$$\Delta p \simeq \frac{\hbar}{R}$$

for any component of momentum. Since any component ranges from p to $-p$, it's reasonable to estimate that

$$\Delta p \simeq p$$

So the kinetic energy is approx

$$K = \frac{p^2}{2\mu} = \frac{(\Delta p)^2}{2\mu} = \frac{\hbar^2}{2\mu R}$$

We then take the potential energy to be

$$V = \frac{-e^2}{4\pi\epsilon_0 R}$$

so for the total energy we have

$$E = K + V = \frac{\hbar^2}{2\mu R^2} - \frac{e^2}{4\pi\epsilon_0 R}$$

Now in the ground state, this will be minimized, so we want $\frac{dE}{dR} = 0$

$$\Rightarrow \frac{dE}{dR} = -\frac{\hbar^2}{\mu R^3} + \frac{e^2}{4\pi\epsilon_0 R^2}$$

$$= 0 \Rightarrow \frac{\hbar^2}{\mu} = \frac{e^2 R}{4\pi\epsilon_0}$$

$$\text{or} \quad R = \frac{4\pi\epsilon_0 \hbar^2}{\mu e^2} = a_0$$

The resulting energy is

$$E = \frac{\hbar^2 \mu^2 e^4}{2\mu (4\pi\epsilon_0^2)^2 \hbar^4} - \frac{e^2 \mu e^2}{4\pi\epsilon_0 \, 4\pi\epsilon_0 \hbar^2}$$

$$= \frac{\mu e^4}{(4\pi\epsilon_0^2)\hbar^2}\left(\frac{1}{2} - 1\right) = -\frac{\mu e^4}{(4\pi\epsilon_0)^2 \hbar^2} \, \frac{1}{2}$$

which is just the ground state energy

end of example

One more comment about the radial dependence: only the $l=0$ wave fns have any reasonable prob. of finding the electron near the nucleus. That's because the wave fns have overall dependence

$$\psi \sim r^l$$

for small r; for $l \neq 0$, that means the wave fn is suppressed near $r=0$.

The angular dependence is discussed beginning on p. 249 + continuing through sec 7.7. You should read through this – we won't discuss it in any detail in class.

Orbital angular momentum

The quantum numbers l and m_l turn out to be directly related to the angular momentum of the electron. $L_{tot} \Leftrightarrow l$ and $L_z \Leftrightarrow m_l$

This turns out to be important for a number of reasons, one of which is that in a spherically symmetric potential, angular momentum is conserved. In QM, it also turns out to be quantized (Bohr already saw that with his model of the atom, but he didn't have the Schrödinger eq'n to tell him whence it came from). And last but not least, angular momentum is a measurable quantity, so QM better get it right.

(4.30)

(Notice that this is our first 3-D problem so it's the first time ang. mom. can come up - can't have it in 1D.)

So how do we get from angular momentum to l?

Recall

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

so that

$$L_x = y p_z - z p_y$$

$$L_y = z p_x - x p_z$$

$$L_z = x p_y - y p_x$$

Now to take this as a dynamical quantity in QM, we have to turn these into operators, which amounts to replacing the components of $\vec{p}$ with their corresponding differential operators

$$p_x \to -i\hbar \frac{\partial}{\partial x} \quad \text{etc.}$$

Now the angular momentum becomes an operator whose components are

$$L_{x,op} = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$L_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

$$L_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

Now this problem has spherical symmetry, and for any such problem angular momentum turns out to be interesting. We need $\vec{L}$ in terms of spherical coordinates. The relevant transformation is discussed in Appendix M. You get

$$L_x = i\hbar\left(\sin\varphi\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right)$$

$$L_y = i\hbar\left(-\cos\varphi\frac{\partial}{\partial\theta} + \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\right)$$

$$L_z = -i\hbar\frac{\partial}{\partial\varphi}$$

Now we also want

$$L^2 = L_x^2 + L_y^2 + L_z^2$$

This takes some algebra to get, because in e.g. L_x^2, the derivatives in one factor act on the other factor. You have to take

$$L_x^2 = (i\hbar)^2\Big[\sin\varphi\frac{\partial}{\partial\theta}\left(\sin\varphi\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right)$$
$$+ \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\left(\sin\varphi\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right)\Big]$$

nd not just square each term.

When you actually work through it all carefully (see Appendix M) you get

$$L^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]$$

We've seen something like this before! Recall that in spherical coords,

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]$$

Let's go back to the time-indep Schr. eq'n + rewrite it in terms of L, keeping in mind that the form of the eq'n is

$$\left[-\frac{\hbar^2\nabla^2}{2\mu}+V(r)\right]\psi = E\psi$$

and the operator in square brackets is

$$\frac{p^2}{2\mu}+V$$

which we can think of as the energy operator. It's called the Hamiltonian H.

Let's rewrite the energy operator in this eq'n in terms of L^2. We have

$$-\frac{\hbar^2}{2\mu}\nabla^2 = -\frac{\hbar^2}{2\mu r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{L^2}{2\mu r^2}$$

So the Schrödinger eq'n can be written

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)\right] + \left(\frac{L^2}{2\mu r^2}+V\right)\psi = E\psi$$

The $\frac{\vec{L}^2}{2\mu r^2}$ term looks like an addition to the potential that pushes the particle away fr/ the origin. In fact it has just the form of the "centrifugal potential" that shows up in classical mechanics when you have a particle moving around a force center.

So what does this have to do with l and m_l?

Let's calculate $L^2\psi$ and $L_z\psi$

$$L^2\psi = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]R\Theta\Phi$$

Now look at the 2nd term.

$$\frac{\partial^2}{\partial\varphi^2}R\Theta\Phi = R\Theta\underbrace{\frac{d^2\Phi}{d\varphi^2}}_{=-m_l^2\Phi} \quad \text{since } \Phi = e^{im_l\varphi}$$

That means we can write

$$L^2\psi = -\hbar^2\left\{\left[\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\right) - \frac{m_l^2}{\sin^2\theta}\right]\Theta\right\} R\,\Phi$$

Now go back to p. 4.4 where we did the separation of varables. We had

$$-\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{m_l^2}{\sin^2\theta}\Theta = l(l+1)\Theta$$

$$\uparrow$$

But the left-hand side is just what we have in the curly brackets in $L^2\psi$! So

$$L^2\psi = -\hbar^2\left\{-l(l+1)\Theta\right\} R\,\Phi$$

$$\boxed{L^2\psi = \hbar^2 l(l+1)\,\psi}$$

This pretty, simple result means

- l determines the total angular momentum, whose magnitude is

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

- ψ is an eigenfunction of total angular momentum (recall eigenfunctions means operator acting on function = constant * function) (we already knew that the wave function is an eigenfunction of energy).

Similarly, calculate $L_z \psi$:

$$L_z \psi = -i\hbar \frac{\partial \psi}{\partial \varphi}$$

$$= \Big(-i\hbar \underbrace{\frac{d}{d\varphi}\Phi}_{i m_\ell \Phi}\Big) R\Theta$$

$$= \hbar m_\ell R\Theta\Phi$$

$$\boxed{L_z \psi = \hbar m_\ell \psi}$$

which means

- m_ℓ determines the z component of the angular momentum, $\hbar m_\ell$
- ψ is an eigenstate of L_z

Now, as we mentioned back when we first discussed expectation values and variances (which we used to give uncertainties), when a function is in an eigenstate of some operator (we used energy before), then the state has a definite value of the corresponding physical quantity, and that value is the eigenvalue. So for example, the hydrogen atom wave functions we have found are energy eigenstates, with

$$E_{op}\,\psi_{n\ell m_\ell} = E_n\,\psi_{n\ell m_\ell}$$

where $E_n = -\frac{13.6\,eV}{n^2}$. So we have $\bar{E} = E_n$ and if we calculate $\overline{E^2}$ we get E_n^2. That means

$$\overline{E^2} - \bar{E}^2 = \text{variance in } E = 0$$

As mentioned above, that means that E can only be equal to E_n, its expectation value — it's never anything else. How do we know? Recall that the variance is also known as the mean squared deviation, i.e.,

$$\text{var}(E) = \int \psi^* (E-\bar{E})^2\,\psi\, d^3x$$

If E is ever different from $\bar{E}$, then the square guarantees a positive contribution to the variance, which is then not zero. So if the variance is zero the only possible value of the energy is the expectation value itself, $\bar{E}$.

Now, this argument applies to any eigenfunction of any operator and its corresponding eigenvalues. We can summarize this by saying

> If a system is in an eigenstate of an operator corresponding to some physical quantity, all measurements of that quantity will give the corresponding eigenvalue.

So if a hydrogen atom is in a state $\psi_{n\ell m_\ell}$, it has definite energy $= -\frac{13.6\,\text{eV}}{n^2}$

angular momentum $= \hbar\sqrt{\ell(\ell+1)}$

z component of angular momentum $= \hbar m_\ell$

What about the x + y components of angular momentum - do they have definite values? Nope. As you will show in the homework for a specific case, the wave functions we have found are not eigenfunctions of L_x and L_y.

Why is z special? Isn't the potential isotropic? Yep, and what direction you pick for z is arbitrary. Unless you indroduce something that picks out a direction physically, like a magnetic field.... See next chapter