Section 13 - The Hydrogen Atom

"...the periodic table is a colossal waste of time. Nine out of every ten atoms in the universe are hydrogen..... The other ten percent of all atoms are helium."¹

Sam Kean

Schrödinger's Equation for the Hydrogen Atom

Having gained some experience with Schrödinger's equation, we are ready to apply it to the hydrogen atom. As usual, we will make a number of approximations, such as considering the proton to be a featureless point charge of infinite mass. Our goal is to find the wavefunctions and energy eigenvalues of a single electron in the proton's electrostatic potential field.

There is an advantage in that potential energy of the electron due to Coulomb's law is dependent only on its distance from the proton, but the kinetic energy terms then get pretty difficult.²

$$E = K + U = \frac{p^2}{2m} + \frac{-k_e e^2}{r}.$$

As a vector, the momentum can be broken up into perpendicular components, p_r and p_T , or the radial and tangential components:

$$\vec{p} = \vec{p}_r + \vec{p}_T$$
, so that $p^2 = p_r^2 + p_T^2$.

Now, we might remember that for a point particle such as an electron, $p_T = mv_T = mr\omega$, the moment of inertia I = mr², and the angular momentum L = I ω . Putting these relationships together shows us that $p_T = L/r$; since the Coulomb force is radial (no torques about the center), L is conserved and p_T varies only with the distance, r.

$$p^2 = p_r^2 + \frac{L^2}{r^2}$$

and so then,

$$E = \frac{p^2}{2m} + \frac{-k_e e^2}{r} = \frac{p_r^2}{2m} + \frac{L^2}{2mr^2} + \frac{-k_e e^2}{r}.$$

Converting this algebraic expression into operators, we should expect to obtain

¹ This is approximately correct. All the other elements are roughly 0.1% of atoms.

² This section is based primarily on Tipler's Modern Physics.

$$\left(\frac{\hat{p}_r^2}{2m} + \frac{\hat{L}^2}{2mr^2} + \hat{U}\right)\psi = E\psi \,.$$

where \hat{L} is (now) the angular momentum operator, which we'll need to derive. Let's sit on this for a while.

First, a Lot of Mathy Stuff *

Let's see if we can write the Schrödinger equation for this situation in terms of spherical coördinates: r, θ , and φ . It'll take some doing (*i.e.*, the next five pages). Start with the following transformation equations:³

$$x = (r \sin\theta)\cos(\phi)$$

$$y = (r \sin\theta)\sin(\phi)$$

$$z = r \cos\theta$$

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

Let's look at the kinetic energy term:

$$\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi$$

and use some chain rule antics:

$$\frac{\partial r}{\partial x} = \frac{1}{2} \frac{2x}{\sqrt{x^2 + y^2 + z^2}} = \frac{x}{r},$$
$$\frac{\partial \psi}{\partial x} = \frac{\partial r}{\partial x} \frac{\partial \psi}{\partial r} = \frac{x}{r} \frac{\partial \psi}{\partial r}.$$

Continuing,

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{\partial}{\partial x} \left(\frac{\partial \psi}{\partial x} \right) = \frac{\partial}{\partial x} \left(\frac{x}{r} \frac{\partial \psi}{\partial r} \right) = \left(\frac{\partial x}{\partial x} \right) \left(\frac{1}{r} \right) \left(\frac{\partial \psi}{\partial r} \right) + x \frac{\partial}{\partial x} \left(\frac{1}{r} \frac{\partial \psi}{\partial r} \right) \\ = \left(\frac{1}{r} \right) \left(\frac{\partial \psi}{\partial r} \right) + x \frac{\partial r}{\partial x} \frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial \psi}{\partial r} \right) = \left(\frac{1}{r} \right) \left(\frac{\partial \psi}{\partial r} \right) + x \left(\frac{x}{r} \right) \left[\frac{-1}{r^2} \frac{\partial \psi}{\partial r} + \frac{1}{r} \frac{\partial^2 \psi}{\partial r^2} \right] \\ = \frac{1}{r} \frac{\partial \psi}{\partial r} - \frac{x^2}{r^3} \frac{\partial \psi}{\partial r} + \frac{x^2}{r^2} \frac{\partial^2 \psi}{\partial r^2} = \frac{(r^2 - x^2)}{r^3} \frac{\partial \psi}{\partial r} + \frac{x^2}{r^2} \frac{\partial^2 \psi}{\partial r^2}.$$

Ouch. Well, at least the next two are easy:

³ The angle phi is measured around the z-axis, analogous to longitude on the earth, while theta is somewhat analogous to latitude, albeit measured from zero at the north pole rather than from the equator.

$$\frac{\partial^2 \psi}{\partial y^2} = \frac{(r^2 - y^2)}{r^3} \frac{\partial \psi}{\partial r} + \frac{y^2}{r^2} \frac{\partial^2 \psi}{\partial r^2},$$
$$\frac{\partial^2 \psi}{\partial z^2} = \frac{(r^2 - z^2)}{r^3} \frac{\partial \psi}{\partial r} + \frac{z^2}{r^2} \frac{\partial^2 \psi}{\partial r^2}.$$

Let's add them up. Remembering that $(x^2 + y^2 + z^2) = r^2$, we see that we're left with

$$\frac{-\hbar^2}{2m}\left(\frac{2}{r}\frac{\partial\psi}{\partial r}+\frac{\partial^2\psi}{\partial r^2}\right).$$

You might think that this expression will give us the kinetic energy, but it won't. The reason is that, when we went through the chain rule conversions, we only considered how x, y, and z changed with r, and not with either θ or φ . So, this term only accounts for the kinetic energy due to the radial movement of the electron, and not the transverse motion.

Next, we'll work on the angular momentum operators \hat{L}_x , \hat{L}_y , \hat{L}_z , and \hat{L} . In classical physics, the angular momentum \vec{L} can be expressed as

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

with

$$L_z = xp_y - yp_x, \quad L_y = zp_x - xp_z, \text{ and } \quad L_x = yp_z - zp_y \ .$$

We might hope the same for the operators, since we would expect, for example,

$$\hat{L}_z \psi = L_z \psi$$

So, let's try

$$\hat{L}_z \psi = (x \hat{p}_y - y \hat{p}_x) \psi = x \hat{p}_y \psi - y \hat{p}_x \psi = x p_y \psi - y p_x \psi = (x p_y - y p_x) \psi = L_z \psi.$$

Similarly for L_x and L_y,

$$\hat{L}_x = (y\hat{p}_z - z\hat{p}_y), \text{ and}$$

 $\hat{L}_y = (z\hat{p}_x - x\hat{p}_z).$

Let's try to find these operators in spherical coördinates. We'll look at L_z first, since it's easiest. Here are some useful transform relationships:

$$x = r \sin\theta \cos \phi$$
 $\frac{\partial x}{\partial \phi} = r \sin\theta (-\sin\phi) = -y$,

$$y = r \sin \theta \sin \phi \qquad \frac{\partial y}{\partial \phi} = r \sin \theta (\cos \phi) = +x,$$
$$z = r \cos \theta \qquad \frac{\partial z}{\partial \phi} = 0,$$
$$\frac{\partial \psi}{\partial \phi} = \frac{\partial x}{\partial \phi} \frac{\partial \psi}{\partial x} + \frac{\partial y}{\partial \phi} \frac{\partial \psi}{\partial y} + \frac{\partial z}{\partial \phi} \frac{\partial \psi}{\partial z} = -y \frac{\partial \psi}{\partial x} + x \frac{\partial \psi}{\partial y} + 0$$

and so,

$$\frac{\partial \psi}{\partial \varphi} = x \frac{\partial \psi}{\partial y} - y \frac{\partial \psi}{\partial x} = \left(x \frac{\hat{p}_y}{-i\hbar} - y \frac{\hat{p}_x}{-i\hbar} \right) \psi = \frac{1}{-i\hbar} (xp_y - yp_x) \psi = \frac{1}{-i\hbar} L_z \psi,$$

so, clearly,⁴

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \varphi} .$$

 L_x and L_y are harder, but since we've done one in the correct direction, we'll do the other two backwards, *i.e.*, start with the answers and show that they are equivalent to what we already know. So for L_x , we're told that ⁵

$$\hat{L}_x = i\hbar \left(sin\varphi \frac{\partial}{\partial \theta} + cot\theta \cos\varphi \ \frac{\partial}{\partial \varphi} \right).$$

Similar to above:

$$\begin{aligned} x &= r \sin\theta \, \cos\varphi & \frac{\partial x}{\partial \theta} = \, r \, (\cos\theta) \cos\varphi = \, r \sin\theta \, \cos\varphi \frac{\cos\theta}{\sin\theta} = x \cot\theta \,, \\ y &= r \sin\theta \, \sin\varphi & \frac{\partial y}{\partial \theta} = \, r \, (\cos\theta) \sin\varphi = \, r \sin\theta \, \sin\varphi \frac{\cos\theta}{\sin\theta} = y \cot\theta \,\,, \\ z &= r \cos\theta & \frac{\partial z}{\partial \theta} = \, -r \sin\theta \,. \end{aligned}$$

So,

⁴ We are going to need this later.

⁵ For example, in Serway, Raymond, Clement Moses, and Curt Moyer, <u>Modern Physics 5th ed.</u>, Thomson Brooks/Cole, Belmont (2005) p 275.

$$\begin{split} \frac{\partial \psi}{\partial \theta} &= \frac{\partial x}{\partial \theta} \frac{\partial \psi}{\partial x} + \frac{\partial y}{\partial \theta} \frac{\partial \psi}{\partial y} + \frac{\partial z}{\partial \theta} \frac{\partial \psi}{\partial z} = x \cot\theta \frac{\partial \psi}{\partial x} + y \cot\theta \frac{\partial \psi}{\partial y} - r \sin\theta \frac{\partial \psi}{\partial z} \\ &= \frac{-1}{i\hbar} \left(x \cot\theta \, \hat{p}_x + y \cot\theta \hat{p}_y - r \sin\theta \hat{p}_z \right) \psi \,\,, \end{split}$$

and, remember that

$$\frac{\partial \psi}{\partial \varphi} = -y \frac{\partial \psi}{\partial x} + x \frac{\partial \psi}{\partial y} = \frac{-1}{i\hbar} \left(-y \hat{p}_x + x \hat{p}_y \right) \psi.$$

Now, we get a minor mess:

$$\begin{split} \hat{L}_{x}\psi &= i\hbar\left(\sin\varphi\frac{\partial\psi}{\partial\theta} + \cot\theta\cos\varphi\frac{\partial\psi}{\partial\varphi}\right) \\ &= -\left(\sin\varphi(x\cot\theta\,\hat{p}_{x} + y\cot\theta\,\hat{p}_{y} - r\sin\theta\,\hat{p}_{z}) \right. \\ &+ \cot\theta\cos\varphi\left(-y\hat{p}_{x} + x\hat{p}_{y}\right)\right)\psi\,. \end{split}$$

Let's collect like terms and see what we get.

$$-(-r \sin \phi \sin \theta \hat{p}_z) = y \hat{p}_z$$
.

$$-\left(\sin\phi y \cot\theta \,\hat{p}_{y} + \cot\theta \cos\phi x \,\hat{p}_{y}\right)$$

$$= -\left(\sin\phi \left(r\sin\theta \sin\phi\right) \frac{\cos\theta}{\sin\theta} \,\hat{p}_{y} + \frac{\cos\theta}{\sin\theta} \cos\phi \left(r\sin\theta \cos\phi\right) \hat{p}_{y}\right) =$$

$$= -\left(\left(r\cos\theta \sin^{2}\phi\right) \hat{p}_{y} + \left(r\cos\theta \cos^{2}\phi\right) \hat{p}_{y}\right) =$$

$$= -\left(\left(\sin^{2}\phi + \cos^{2}\phi\right) \left(r\cos\theta\right) \hat{p}_{y}\right) = -z\hat{p}_{y}$$

$$\begin{aligned} -\left(\sin\phi(x\cot\theta\,\hat{p}_x) + \cot\theta\cos\phi\,(-y\hat{p}_x)\right) \\ &= -(\sin\phi(r\sin\theta\,\cos\phi)\cot\theta\,\hat{p}_x - \cot\theta\cos\phi(r\sin\theta\,\sin\phi)\hat{p}_x) = 0\,. \end{aligned}$$

So, as expected,

$$\hat{\mathbf{L}}_{\mathbf{x}} = (\mathbf{y}\,\hat{\mathbf{p}}_{\mathbf{z}} - \mathbf{z}\,\hat{\mathbf{p}}_{\mathbf{y}}).$$

Next, we'll show that

$$\hat{L}_{y} = i\hbar \left(-\cos\phi \frac{\partial}{\partial \theta} + \cot\theta \sin\phi \frac{\partial}{\partial \phi} \right)$$

by confirming that

$$i\hbar\left(-\cos\phi\frac{\partial\psi}{\partial\theta}+\cot\theta\sin\phi\frac{\partial\psi}{\partial\phi}
ight)=(z\,\hat{p}_{x}-x\hat{p}_{z})\psi.$$

So,

$$\begin{split} i\hbar \left(-\cos\varphi \frac{\partial\psi}{\partial\theta} + \cot\theta \sin\varphi \frac{\partial\psi}{\partial\varphi} \right) \\ &= \left(\cos\varphi (x\cot\theta \ \hat{p}_x + y\cot\theta \hat{p}_y - r\sin\theta \hat{p}_z) - \cot\theta \sin\varphi \left(-y\hat{p}_x + x\hat{p}_y \right) \right) \psi \\ &= \left(\cos\varphi x\cot\theta \ \hat{p}_x + \cos\varphi \ y\cot\theta \ \hat{p}_y - \cos\varphi \ r\sin\theta \hat{p}_z + y\cot\theta \sin\varphi \ \hat{p}_x \\ &- x\cot\theta \sin\varphi \ \hat{p}_y \ \right) \psi \,. \end{split}$$

Collect the similar terms:

$$\begin{aligned} \cos\phi x \cot\theta \, \hat{p}_x + y \cot\theta \sin\phi \, \hat{p}_x \\ &= \cos\phi \, (r \sin\theta \, \cos\phi) \, \left(\frac{\cos\theta}{\sin\theta}\right) \, \hat{p}_x + (r \sin\theta \, \sin\phi) \, \left(\frac{\cos\theta}{\sin\theta}\right) \sin\phi \, \hat{p}_x \\ &= (\cos^2\phi + \, \sin^2\phi) \, (r \cos\theta) \hat{p}_x = z \, \hat{p}_x \end{aligned}$$

$$\begin{aligned} \cos\phi \ y \ \cot\theta \ \hat{p}_y &- x \ \cot\theta \ \sin\phi \ \hat{p}_y \\ &= \ \cos\phi \ (r \sin\theta \ \sin\phi) \ \cot\theta \ \hat{p}_y - (r \sin\theta \ \cos\phi) \ \cot\theta \ \sin\phi \ \hat{p}_y = 0 \end{aligned}$$

 $-cos\varphi \,r\,sin\theta\, \hat{p}_z = -x\, \widehat{p}_z$

Adding the terms gives the expected result:

$$\hat{L}_{y} = (z \,\hat{p}_{x} - x \hat{p}_{z}) \,.$$

And now, the last step we need before we can actually do anything with the hydrogen atom! Find the operator $\widehat{L^2}$. Unsurprisingly,

$$\widehat{L}^2 = \widehat{L}^2$$

since we expect that

$$\widehat{L^2}\psi = L^2\psi$$

and, in fact (remembering that the value of L itself is a constant),

$$\hat{L}^2 \psi = \hat{L} (\hat{L} \psi) = \hat{L} (L \psi) = L (\hat{L} \psi) = L (L \psi) = L^2 \psi = \hat{L^2} \psi$$
.

Then, since classically,

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

we might expect that

$$\hat{L}^2 = \ \hat{L}_x^{\ 2} + \ \hat{L}_y^{\ 2} + \ \hat{L}_z^{\ 2} \, . \label{eq:L2}$$

OK. We already determined that

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \varphi}$$

so,

$$\hat{L}_{z}^{2} = -i\hbar \frac{\partial}{\partial \phi} \left(-i\hbar \frac{\partial}{\partial \phi} \right) = -\hbar^{2} \frac{\partial^{2}}{\partial \phi^{2}}$$

Similarly,

$$\begin{split} \hat{L}_{x}^{2} &= -\hbar^{2} \left(\sin \varphi \frac{\partial}{\partial \theta} + \cot \theta \, \cos \varphi \, \frac{\partial}{\partial \varphi} \right) \left(\sin \varphi \frac{\partial}{\partial \theta} + \cot \theta \, \cos \varphi \, \frac{\partial}{\partial \varphi} \right) \\ &= -\hbar^{2} \left(\sin^{2} \varphi \frac{\partial^{2}}{\partial \theta^{2}} + \sin \varphi \, \cos \varphi \, \frac{\partial}{\partial \varphi} \right. \\ &+ \cot \theta \, \cos^{2} \varphi \, \frac{\partial}{\partial \theta} + 2 \, \cot \theta \, \sin \varphi \, \cos \varphi \, \frac{\partial^{2}}{\partial \theta \, \partial \varphi} + \cot^{2} \theta \, \cos^{2} \varphi \, \frac{\partial^{2}}{\partial \varphi^{2}} \right) . \end{split}$$

Then,

$$\begin{split} \hat{L}_{y}^{2} &= -\hbar^{2} \left(-\cos\varphi \frac{\partial}{\partial \theta} + \cot\theta \sin\varphi \frac{\partial}{\partial \varphi} \right) \left(-\cos\varphi \frac{\partial}{\partial \theta} + \cot\theta \sin\varphi \frac{\partial}{\partial \varphi} \right) \\ &= -\hbar^{2} \left(\cos^{2}\varphi \frac{\partial^{2}}{\partial \theta^{2}} - \sin\varphi \cos\varphi \frac{\partial}{\partial \varphi} \\ &+ \cot\theta \sin^{2}\varphi \frac{\partial}{\partial \theta} - 2 \cot\theta \sin\varphi \cos\varphi \frac{\partial^{2}}{\partial \theta \partial \varphi} + \cot^{2}\theta \sin^{2}\varphi \frac{\partial^{2}}{\partial \varphi^{2}} \right). \end{split}$$

Adding these three expressions finally results in

$$\hat{L}^{2} = -\hbar^{2} \left(\cot\theta \frac{\partial \psi}{\partial \theta} + \frac{\partial^{2} \psi}{\partial \theta^{2}} + \frac{1}{\sin^{2} \theta} \frac{\partial^{2} \psi}{\partial \phi^{2}} \right)$$

.

This term will help us take care of the kinetic energy due to lateral motion of the electron. Now, we can at last write the time-independent Schrödinger equation for the simplest of elements, the hydrogen atom.

$$\frac{-\hbar^2}{2m}\left(\frac{2}{r}\frac{\partial\psi}{\partial r} + \frac{\partial^2\psi}{\partial r^2} + \frac{1}{r^2}\left(\cot\theta\frac{\partial\psi}{\partial\theta} + \frac{\partial^2\psi}{\partial\theta^2} + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right)\right) - \frac{k_ee^2}{r}\psi = E\psi.$$

Now, we just have to solve it.

Solving the Schrödinger Equation for Hydrogen

Let's assume that the wavefunction ψ is a function of r, θ , and φ , and that the solution is separable, as for the quantum box:

$$\psi(\mathbf{r}, \theta, \phi) = \mathbf{R}(\mathbf{r})\Theta(\theta)\Phi(\phi).$$

Here we go!

$$\frac{-\hbar^2}{2m} \left(\frac{2}{r} \Theta \Phi \frac{\partial R}{\partial r} + \Theta \Phi \frac{\partial^2 R}{\partial r^2} + \frac{1}{r^2} \left(R \Phi \cot \theta \frac{\partial \Theta}{\partial \theta} + R \Phi \frac{\partial^2 \Theta}{\partial \theta^2} + R \Theta \frac{1}{\sin^2 \theta} \frac{\partial^2 \Phi}{\partial \phi^2} \right) \right) - \frac{k_e e^2}{r} R \Theta \Phi$$
$$= E R \Theta \Phi.$$

As we did before, let's divide through, this time by $-2mR\Theta\Phi/\hbar^2r^2\sin^2\theta$:

$$r^{2}\sin^{2}\theta\left(\frac{2}{r}\frac{1}{R}\frac{dR}{dr} + \frac{1}{R}\frac{d^{2}R}{dr^{2}} + \frac{1}{r^{2}}\left(\frac{1}{\Theta}\cot\theta\frac{d\Theta}{d\theta} + \frac{1}{\Theta}\frac{d^{2}\Theta}{d\theta^{2}}\right)\right) + \frac{1}{\Phi}\frac{d^{2}\Phi}{d\phi^{2}} - \frac{2m}{\hbar^{2}}\frac{k_{e}e^{2}}{r}r^{2}\sin^{2}\theta$$
$$= -\frac{2m}{\hbar^{2}}r^{2}\sin^{2}\theta E.$$

Why do this, you might ask. Look in the middle of the left side and see that there is a term that is a function of only ϕ . Since, as phi alone changes, the rest of the equation can not be affected, that term must be a constant. Let's say that

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\Phi^2} = -m_l^2 \,.$$

Why that constant? Because I know what's coming. We've solved this differential equation before:

$$\frac{d^2\Phi}{d\phi^2} = -m_l^2\Phi \quad \rightarrow \quad \Phi(\phi) = Ae^{im_l\phi} \,.$$

EXERCISE 13-1

Verify that the solution given above solves the equation to its left.

Since this is a function of phi, and the wave function must be single-valued, there are restrictions on m_l , which must be an integer $(0, \pm 1, \pm 2, et c.)$, or in other words, there must be an integer number of cycles of the function in one 2π cycle about the z axis.

Let's return to the rest of the equation with the substitution for the phi term:

$$r^{2}\sin^{2}\theta\left(\frac{2}{r}\frac{1}{R}\frac{dR}{dr} + \frac{1}{R}\frac{d^{2}R}{dr^{2}} + \frac{1}{r^{2}}\left(\frac{1}{\Theta}\cot\theta\frac{d\Theta}{d\theta} + \frac{1}{\Theta}\frac{d^{2}\Theta}{d\theta^{2}}\right)\right) - m_{l}^{2} - \frac{2m}{\hbar^{2}}\frac{k_{e}e^{2}}{r}r^{2}\sin^{2}\theta$$
$$= -\frac{2m}{\hbar^{2}}r^{2}\sin^{2}\theta E$$

Rearrange again to get all r dependent terms on one side and all theta dependent terms on the other; we'll start that by dividing both sides by $\sin^2\theta$:

$$\left(\frac{2r}{R}\frac{dR}{dr} + \frac{r^2}{R}\frac{d^2R}{dr^2} + \left(\frac{1}{\Theta}\cot\theta\frac{d\Theta}{d\theta} + \frac{1}{\Theta}\frac{d^2\Theta}{d\theta^2}\right)\right) - \frac{m_l^2}{\sin^2\theta} - \frac{2m}{\hbar^2}\frac{k_ee^2}{r}r^2 = -\frac{2m}{\hbar^2}r^2E$$
$$\frac{2r}{R}\frac{dR}{dr} + \frac{r^2}{R}\frac{d^2R}{dr^2} + \frac{2m}{\hbar^2}r^2\left(E - \frac{k_ee^2}{r}\right) = \frac{m_l^2}{\sin^2\theta} - \frac{1}{\Theta}\cot\theta\frac{d\Theta}{d\theta} - \frac{1}{\Theta}\frac{d^2\Theta}{d\theta^2}$$

Since the left side is a function only of r and the right side of theta, they each must be constant. Let's call that constant -l(l+1).

O.K., so one at a time.

$$\frac{1}{\Theta}\frac{d^2\Theta}{d\theta^2} + \frac{1}{\Theta}\cot\theta\frac{d\Theta}{d\theta} - \frac{m_l^2}{\sin^2\theta} = -l(l+1),$$
$$\frac{d^2\Theta}{d\theta^2} + \cot\theta\frac{d\Theta}{d\theta} + \left(l(l+1) - \frac{m_l^2}{\sin^2\theta}\right)\Theta = 0.$$

The solutions to this family of equations for positive integer values of l are well-known to mathematicians. They are the *associated Legendre polynomials*, the forms of which depend on the values of l and m_l :

$$P_l^{m_l} P_0^{o} 1$$

$$P_1^{o} 2 \cos\theta$$

$$P_1^{1} \sin\theta$$

$$P_2^{o} 4 (3\cos^2\theta - 1)$$

 $\begin{array}{lll} P_2^1 & 4\sin\theta\cos\theta\\ P_2^2 & \sin^2\theta\\ P_3^o & 24\left(5\cos^3\theta - 3\cos\theta\right)\\ P_3^1 & 6\sin\theta\left(5\cos^2\theta - 1\right)\\ P_3^2 & 6\sin^2\theta\cos\theta\\ P_3^3 & \sin^3\theta\\ et \ c. \end{array}$

Note that there are solutions only when $|m_l|$ is less than or equal to *l*.

EXERCISE 13-2

Verify that P_1^{l} is a solution to the theta-only equation above when *l* and m_l equal 1.

And, finally, let's look at the R expression:

$$\frac{2\mathrm{r}}{\mathrm{R}}\frac{d\mathrm{R}}{d\mathrm{r}} + \frac{\mathrm{r}^2}{\mathrm{R}}\frac{d^2\mathrm{R}}{d\mathrm{r}^2} + \frac{2\mathrm{m}}{\hbar^2}\mathrm{r}^2\left(\mathrm{E} - \frac{\mathrm{k_e}\mathrm{e}^2}{\mathrm{r}}\right) = -l(l+1).$$

Keep in mind that everything we've done <u>so far</u> would allow us to replace the Coulomb potential with any other radial force potential. However, let's plough ahead. Solutions to this equation with the Coulomb potential form a family $R_{n,l}(r)$ for n and *l* positive integers that is, again, well known to mathematicians. Here are a few:

$$\begin{split} R_{1,0} &= e^{-r/a_0} \\ R_{2,0} &= (2 - r/a)e^{-r/2a_0} \\ R_{2,1} &= r/a \ e^{-r/2a_0} \\ R_{3,0} &= (1 - 2r/3a + 2r^2/27a^2)e^{-r/3a_0} \\ R_{3,1} &= (r/a)(1 - r/6a)e^{-r/3a_0} \\ R_{3,2} &= (r^2/a^2)e^{-r/3a_0} \\ et \ c. \end{split}$$

Solutions exist for natural number values of n and integer values of l such that l varies from zero to n-1. We'll determine the parameter a_0 in a moment.

Let's put it together. The solution for the wavefunction of the electron about the (unmoving) proton is

$$\psi(\mathbf{r}, \theta, \phi) = \mathbf{A}_{\mathbf{n}, l, \mathbf{m}_l} \, \mathbf{R}_{\mathbf{n}, l} \mathbf{P}_l^{\mathbf{m}_l} \mathbf{e}^{\mathrm{i}\mathbf{m}_l \phi},$$

with n = 1, 2, 3, ... l = 0, 1, 2, ..., (n - 1) $m_l = 0, \pm 1, \pm 2, ..., \pm l$.

Now, we have to figure out what all this means.

Interpretation of the Solution to the Schrödinger Equation

If we were to calculate the energy eigenvalues for these functions, we would see the following:

$$\begin{split} E_{1,0} &= -13.6 \text{ eV} \\ E_{2,0} &= E_{2,1} = -13.6/2^2 \text{ eV} \\ E_{3,0} &= E_{3,1} = E_{3,2} = -13.6/3^2 \text{ eV} \\ \text{and, generally,} \\ E_{n,l} &= -13.6/n^2 \text{ eV}. \end{split}$$

These are the same energies as predicted by the Bohr model, so the n here correlates to the orbit number n of the Bohr model; we now call this the *principal quantum number*.

EXAMPLE 13-1

The wavefunction for the n = 2, l = 0, $m_l = 0$ state is

$$\psi_{2,0,0} = A_{2,0,0}R_{2,0}P_0^0e^0 = A_{2,0,0}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}.$$

Let's substitute into the Schrödinger equation. Any derivative with respect to θ or φ will result in zero. That leaves

$$\frac{-\hbar^2}{2m}\left(\frac{2}{r}\frac{\partial\psi}{\partial r} + \frac{\partial^2\psi}{\partial r^2}\right) - \frac{k_e Z e^2}{r}\psi = E\psi.$$

The first derivative is

$$\frac{\partial \Psi}{\partial r} = A_{2,0,0} \left(-\frac{2}{a_0} + \frac{r}{2a_0^2} \right) e^{-r/2a_0}$$

and the second is

$$\frac{\partial^2 \psi}{\partial r^2} = A_{2,0,0} \left(\frac{3}{2a_0^2} - \frac{r}{4a_0^3} \right) e^{-r/2a_0}$$

Then, we have

$$\frac{-\hbar^2}{2m} \left(\frac{2}{r} \left(A_{2,0,0} \left(-\frac{2}{a_0} + \frac{r}{2a_0^2} \right) e^{-r/2a_0} \right) + \left(A_{2,0,0} \left(\frac{3}{2a_0^2} - \frac{r}{4a_0^3} \right) e^{-r/2a_0} \right) \right) - \frac{k_e e^2}{r} \left(A_{2,0,0} \left(2 - \frac{r}{a_0} \right) e^{-\frac{r}{2a_0}} \right) = E \left(A_{2,0,0} \left(2 - \frac{r}{a_0} \right) e^{-\frac{r}{2a_0}} \right); \frac{-\hbar^2}{2m} \left(\frac{2}{r} \left(-\frac{2}{a_0} + \frac{r}{2a_0^2} \right) + \left(\frac{3}{2a_0^2} - \frac{r}{4a_0^3} \right) \right) - \frac{k_e e^2}{r} \left(2 - \frac{r}{a_0} \right) = E \left(2 - \frac{r}{a_0} \right).$$

Now, we have three kinds of terms here, ones that are proportional to r, ones inversely proportional to r, and constant ones. We should be able to construct three independent equations.

$$\frac{1}{r} \text{ terms:} \quad \frac{2\hbar^2}{ma_0} - 2k_e e^2 = 0 \quad \to \quad a_0 = \frac{\hbar^2}{mk_e e^2} = 0.53 \times 10^{-1} \text{ m}$$

We recognize this as the Bohr radius, as was asserted above.

r terms:
$$\frac{\hbar^2}{8ma_0^3} = -\frac{E}{a_0} \rightarrow E = -\frac{\hbar^2}{8ma_0^2} = -\frac{(1.055 \times 10^{-34})^2}{8(9.11 \times 10^{-31})(5.3 \times 10^{-11})^2}$$
$$= -5.44 \times 10^{-19} \text{ J} = -3.4 \text{ eV} \quad .$$

This is in agreement with the Bohr model for the n = 2 orbit, and more importantly, also with spectroscopic measurements.

constant terms:
$$\frac{-\hbar^2}{2m} \left(\frac{1}{a_0^2} + \frac{3}{2a_0^2} \right) + \frac{k_e e^2}{a_0} = 2E \rightarrow E = -\frac{1}{4} \frac{mk_e^2 e^4}{2\hbar^2} = -3.4 \text{ eV}$$

The constant terms equation tells us nothing new.

HOMEWORK 13-1

Substitute the wavefunction for n = 1, l = 0, $m_l = 0$ state into the Schrödinger equation and confirm that the energy is indeed -13.6 eV.

HOMEWORK 13-2

Use the \hat{L}_z operator $-i\hbar \frac{\partial}{\partial \phi}$ on the wavefunction for n = 3, l = 2, $m_l = 2$ state and confirm that it returns the correct value for L_z .

Are there other agreements with the Bohr model? In terms of the 'orbit' sizes, generally the larger *l*, the farther out from the proton the wavefunction has its maximum; indeed, it can be shown fairly easily that the following correspondence is correct:

Bohr	Bohr model	Schrödinger state with wavefunction			
state	radius	maximum at the same value			
n = 1	0.53 Å	n = 1; l = 0 1s			
n = 2	2.12 Å	n = 2; l = 1 2p			
n = 3	4.77 Å	n = 3; l = 2 3d			
n = 4	8.48 Å	n = 4; l = 3 4f			

EXAMPLE 13-2

Show that the maximum probability for the n = 1, l = 0, $m_l = 0$ state (1s) occurs at the same distance from the origin as the Bohr radius.

The wave function is $\psi_{1,0,0} = A_{1,0,0} R_{1,0} (P_0^0) e^0 = A_{1,0,0} e^{-r/a_0}$. The probability of finding the electron in some region is then

$$Prob = \int \psi^2 \, dV = A_{1,0,0}^2 \int \left(e^{-r/a_0} \right)^2 r^2 \sin \theta \, dr \, d\theta \, d\phi = 4\pi \, A_{1,0,0}^2 \int \left(e^{-r/a_0} \right)^2 r^2 dr \; .$$

Let's find the maximum of what's left. If we set

$$\frac{d}{dr}(r^2 e^{-2r/a_0}) = 2r e^{-2r/a_0} - r^2 \frac{2}{a_0} e^{-\frac{2r}{a_0}} = 0$$

we get three solutions: r = 0, $r = \infty$, and $r = a_0$.

HOMEWORK 13-3

Verify that the probability for n = 2, l = 1, $m_l = +1$ has a maximum at the same distance from the origin as the second Bohr orbit radius, $4a_0$.

The wave function is

$$\psi_{2,1,1} = A_{2,1,1} R_{2,1}(P_1^1) e^{i(1)\phi} = A_{2,1,1} \frac{r}{a_0} e^{-r/2a_0} \sin \theta e^{i\phi}$$

The probability of finding the electron in some region is then

$$\text{Prob} = \int \psi^2 \, d\mathbf{V} = \frac{\mathbf{A}_{2,1,1}^2}{\mathbf{a}_0^2} \int \left(e^{-\frac{\mathbf{r}}{2\mathbf{a}_0}} \right)^2 \mathbf{r}^4 \sin^3 \theta \, d\mathbf{r} \, d\theta \, d\phi = \frac{8\pi}{3} \frac{\mathbf{A}_{2,1,1}^2}{\mathbf{a}_0^2} \int \left(e^{-\frac{\mathbf{r}}{2\mathbf{a}_0}} \right)^2 \mathbf{r}^4 d\mathbf{r}$$

Find the maximum of what's left. Set

$$\frac{d}{dr} \left(r^4 e^{-r/a_0} \right) = 0 \quad .$$

Finish.....

Next, let's examine m_l . We are pretty certain that

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

and

$$\psi(\mathbf{r}, \boldsymbol{\theta}, \boldsymbol{\phi}) = \mathbf{R}(\mathbf{r})\Theta(\boldsymbol{\theta})e^{\mathrm{i}\mathbf{m}_{l}\boldsymbol{\phi}}$$

So,

$$\hat{L}_{z}\psi = -i\hbar\frac{\partial\psi}{\partial\phi} = -i\hbar\frac{\partial(R(r)\Theta(\theta)e^{im_{l}\phi})}{\partial\phi} = -i\hbar R(r)\Theta(\theta)\frac{\partial e^{im_{l}\phi}}{\partial\phi} = -i\hbar R(r)\Theta(\theta) im_{l}e^{im_{l}\phi}$$
$$= m_{l}\hbar\psi,$$

which tells us that

$$L_z = m_l \hbar$$
,

that is, the z-component of the electron's angular momentum is quantized, or can have one of only a limited number of values, depending on the particular state. This is also reminiscent of the Bohr model, except that the angular momentum is associated with quantum number m_l and not with 'orbit number' n. In fact, the match is very poor: for Bohr, n = 1 has $L_z = \hbar$, but in the Schrödinger model, $L_z = 0$, and for n = 2, Bohr has $L_z = 2\hbar$, but Schrödinger has L_z as either 0 or $\pm \hbar$, and so forth.

Similarly, the index number l is also related to a physical quantity. Remember that we determined that

$$\hat{L}^{2}\psi = -\hbar^{2}\left(\cot\theta\frac{d\psi}{d\theta} + \frac{d^{2}\psi}{d\theta^{2}} + \frac{1}{\sin^{2}\theta}\frac{d^{2}\psi}{d\phi^{2}}\right).$$

But, back when we were separating out the solutions functions for the Schrödinger equation, we set this quantity in brackets to -l(l+1). So,

$$\hat{\mathrm{L}}^2 \psi = -\hbar^2 (-l(l+1)) \psi = \mathrm{L}^2 \psi.$$

This then tells us the possible values of the magnitude of the angular momentum:

$$\mathbf{L}=\sqrt{l(l+1)}\,\hbar$$

So how do we interpret these results? To recap, L is the angular momentum and L_z is the component of L along the z-axis. That is, not only is the magnitude of L restricted to certain values, but its direction is limited as well, lying on a cone of angle $\theta_{l,ml}$ from the z-axis:

	1		Ŧ	Ŧ	â
n	l	m_l	L	Lz	$\theta_{l, ml}$
1	0	0	0	0	
2	0	0	0	0	
	1	0	$2^{1/2}\hbar$	0	90°
	1	±1	$2^{1/2}\hbar$	±ħ	45°, 135°
3	0	0	0	0	
	1	0	$2^{1/2}\hbar$	0	90°
	1	±1	$2^{1/2}\hbar$	±ħ	45°, 135°
	2	0	6 ^{1/2} ħ	0	90°
	2	±1	$6^{1/2}\hbar$	±ħ	66°, 114°
	2	±2	$6^{1/2}\hbar$	±2ħ	35°, 145°

HOMEWORK 13-4

Consider an electron for which n = 4. Calculate the angle between \vec{L} and the z-axis for all 16 such states. Remember that L_z is the projection of \vec{L} along the z-axis.

Evidence for Angular Momentum: The Zeeman Effect

Is there any evidence that the electron actually has orbital angular momentum? We've discussed the spectral lines given off by electrons in a Bohr atom and that the Schrödinger model, in predicting the same energy levels, predicts the same emission wavelengths. What happens to these wavelengths if the atom is in a moderately strong magnetic field? The result is called the *normal Zeeman effect*. It is due to the orbital magnetic moment of the electron. Remember that, since the electron is negatively charged, the magnetic moment and angular momentum will be in opposite directions. A dipole in an external magnetic field B possesses energy

$$U_{\rm M} = -\vec{\mu}_{\rm M}\cdot\vec{\rm B}\,.$$

Let's estimate the moment, μ_M , using a classical picture of the electron orbiting in a circle about the proton at the center of the atom. The current in this 'loop' is the charge *per* time to complete one revolution (the period):

$$I = \frac{q}{P} = \frac{q}{\left(\frac{2\pi r}{v}\right)} = \frac{qv}{2\pi r} .$$

The magnetic moment of such a loop is

$$\mu_{M} = IA = \frac{qv}{2\pi r} \pi r^{2} = \frac{qvr}{2}.$$

Let the +z direction correspond to the direction of the magnetic field. The z-component of the electron's orbital angular momentum is

$$L_z = (mr^2)\omega = mrv$$
, but also $L_z = m_l\hbar$.

Then, the component of the magnetic moment parallel to the magnetic field is

$$\mu_{Mz} = \frac{qvr}{2} = \frac{q(mrv)}{2m} = \frac{qL_z}{2m} = \frac{e(m_l\hbar)}{2m} = m_l \frac{e\hbar}{2m}$$

and the potential energy is then

$$U_{M} = -\vec{\mu}_{M} \cdot \vec{B} = -\mu_{M z} B_{z} = m_{l} \frac{e\hbar}{2m} B$$

The quantity $\frac{e\hbar}{2m}$ appears often and is called the *Bohr magneton*; its value is 9.274×10⁻²⁴ J/T. The energy of the nth electron level is then

$$E_{n,m_l} = -\frac{1}{n^2} \frac{mk_e^2 e^4}{2 \hbar^2} + m_l \frac{e\hbar}{2m} B \ .$$

So, the energy levels of the electron should separate⁶ as a function of the applied magnetic field, B. This will show up as a split in the emission lines of the atom.

$$\begin{split} \mathrm{E}_{\mathrm{photon}} &= \mathrm{E}_{\mathrm{n}_{1},\mathrm{m}_{l\,1}} - \mathrm{E}_{\mathrm{n}_{2},\mathrm{m}_{l\,2}} \\ &= \left(\mathrm{E}_{\mathrm{photon}}\right)_{\mathrm{B}=0} + \Delta \mathrm{m}_{l} \frac{\mathrm{e}\hbar}{2\mathrm{m}}B \ . \end{split}$$

The graph shows the shift in the energy of one of the emission lines in cadmium as a function of applied magnetic field.^{7, 8} The slopes of the lines are each within about two *per cent* of the value of the Bohr magneton.

EXAMPLE 13-3

The H α line (656.28 nm) from a distant star's surface appears as three separate lines separated by 2.67 nm. What is the magnetic field B on the star's surface?



⁶ Just FYI, the linear behavior is only at fairly 'small' magnetic fields.

⁷ "Measuring the Zeeman splitting of the red cadmium line as a function of the magnetic field – spectroscopy using a Fabry-Perot etalon," LD Didactic GmbH.

⁸ As usual, the situation is more complex than we let on here. Each of these wavelengths is emitted by <u>three</u> transitions, although each with the same shift in energy.

$$\begin{split} E &= \frac{hc}{\lambda} \quad \rightarrow \quad \Delta E = -\frac{hc}{\lambda^2} \Delta \lambda \quad \rightarrow \quad \Delta m_1 \frac{e\hbar}{2m} \; B = -\frac{hc}{\lambda^2} \; \Delta \lambda \\ B &= -\frac{4\pi mc}{\Delta m_1 e\lambda^2} \; \Delta \lambda \quad . \end{split}$$

If there is no change in m_l , then the B-field could be anything. A change of 1 results in a shift of 2.67 nm, in which case

$$B = \frac{4\pi (9.11 \times 10^{-31})(3 \times 10^8)}{(1)(1.6 \times 10^{-19})(6.5628 \times 10^{-7})^2} (2.67 \times 10^{-9}) = \frac{133 \text{ T}}{133 \text{ T}}$$

But Wait! There's More!

Now, we've mapped out the possible states for an electron in the hydrogen atom. We might assume (correctly) that the same general scheme is present in multi-electron atoms. But here is a question: why do not <u>all</u> of the electrons of an atom eventually fall into the n = 1, l = 0, $m_l = 0$ state, which is, after all, the lowest possible energy state? This behavior is summarized by the *Pauli exclusion principle*, which says that there can be only one electron in any given state; if the lower states are filled, additional electrons can only go into higher states. Particles that follow this rule are now referred to as *fermions*. Now, this gives rise to an additional problem. Chemistry tells us that there can be <u>two</u> electrons in the n = 1, l = 0, $m_l = 0$ state. Somehow, the two electrons there must actually be in different states; we need another quantum number!

Let's finish off the analogy of the electron motion with that of a planet around the sun. Planets not only have orbital angular momentum (which we labelled \vec{L}), but also rotational angular momentum, \vec{S} . Particles such as electrons have an intrinsic magnetic moment, which we semiclassically interpret as due to the rotation, or *spin*, s, of the particle.⁹ The spin angular momentum S is also quantized according to the relationship

$$S = \hbar \sqrt{s(s+1)}$$
 ,

with the value of s determined by the particle. For electrons, protons, and neutrons, $s = \frac{1}{2}$. Later, we'll discuss particles with other values of s. Additionally, we expect the z-component of S to be quantized:

$$S_z = m_S \hbar , \qquad m_S = \pm \frac{1}{2} .$$

HOMEWORK 13-5

Find the angles the electron's spin \vec{S} makes with the z-axis.

⁹ Uhlenbeck and Goudsmit, Nature 117 p264 (1926).

Evidence for Electron Spin: The Phipps-Taylor Experiment

These two states are referred to as 'spin up' and 'spin down.' Experimentally, this was demonstrated by Phipps and Taylor,¹⁰ who projected a beam of fairly cool hydrogen atoms through a non-uniform magnetic field. The atomic beam split into two clear deflections. Since the atoms were cool, the electrons were mostly in the n = 1 lowest energy state¹¹ where the orbital angular momentum is zero, and so no magnetic moment was expected from the 'orbit' of the electron. The effect seen was orders of magnitude too large to be due to any magnetic moment of the proton, and so it <u>must</u> have been due to the spin moment of the electron.

EXAMPLE 13-4

First, let's estimate the spin magnetic moments of the electron and proton. Consider a point charge q moving uniformly in a circular path. Just above, we showed that

$$\mu = \frac{qL_z}{2m} \ .$$

Note that this expression does <u>not</u> depend on r or v, so let's shrink the orbit so that it begins to resemble a rotating sphere rather than a revolving point. The orbital angular momentum becomes the spin angular momentum, and we obtain, roughly,

$$\mu = \frac{qL_z}{2m} \quad \rightarrow \quad \frac{qS_z}{2m} = \frac{q(\frac{1}{2}\hbar)}{2m} = \frac{q\hbar}{4m}$$

EXAMPLE 13-5

Calculate the approximate values of the magnetic moments for the electron and proton:¹²

$$\mu_{M\,e} \approx \frac{(1.6 \times 10^{-19})(1.055 \times 10^{-34})}{4(9.11 \times 10^{-31})} \approx 5 \times 10^{-24} \frac{\text{Cm}^2}{\text{s}}.$$
$$\mu_{M\,p} \approx \frac{(1.6 \times 10^{-19})(1.055 \times 10^{-34})}{4(1.67 \times 10^{-27})} \approx 3 \times 10^{-27} \frac{\text{Cm}^2}{\text{s}}.$$

¹⁰ Phipps, T. E., and J. B. Taylor, 'The Magnetic Moment of the Hydrogen Atom,' *Phys. Rev.* **21** p301 (1927). This experiment presents much cleaner results than the more well-known Stern-Gerlach experiment.

¹¹ You actually had a homework question back when we were discussing the Boltzmann factor. The probability of a system at 600K being in a level 10.2 eV above the lowest level was just about zero.

¹² These calculations are correct to the order of magnitude. For the electron, it's about half the correct value. For the proton, the result is about one sixth the correct value. Surprisingly, the neutron has a magnetic moment, as well.

Let's do a quick derivation to see how this experiment works. Consider the magnetic moment to be due to a small bar magnet, consisting of north and south magnetic charges q_M (monopoles!) separated by distance d. In analogy with the electric dipole, we would have that

$$\mu_{M} = q_{M} d.$$

Let's shoot these dipoles in the x-direction through a non-uniform magnetic field in the z-direction, such that there is a field gradient dB/dz. There will be a force on each of the magnetic charges, $F_M = q_M B$, but the force on each charge will be different, due to the difference in field strength at each location. The net force on the particle will be



$$F_{NET} = B_N q_M - B_S q_M = (B_N - B_S) q_M = \Delta B q_M \frac{d}{d} = \frac{\Delta B}{d} (q_M d) \rightarrow \frac{dB}{dz} \mu_M \ .$$

Particles with their magnetic moments aligned with the field will be attracted to the region of stronger field, while those with anti-parallel alignment will be repelled to the region of lower field strength.

EXAMPLE 13-6

In the Phipps and Taylor experiment, a stream of hydrogen atoms moves in the x-direction from an oven at 390°C. They move through a tube of length 0.03 m in which there is a non-uniform magnetic field with dB/dz = 1250 T/m. Two beams are detected on a screen at the end of the tube, separated by 0.2 mm. At this temperature, the atoms are cool enough so that the electron is in the n=1, l = 0 state¹³ with no orbital angular momentum. Is this separation of the beams due to the magnetic moment of the electron, or of the proton?

The force on the atom is given by

$$F_{z} = \frac{dB}{dz} \mu.$$

The z-acceleration imparted by this force is

$$a_z = \frac{F_z}{m}$$

The distance traveled in the z-direction is:

¹³ As was discussed in a previous section, the electrons will be almost certainly in the n=1 state at this temperature.

$$\Delta z = \frac{1}{2}a_z \,\Delta t^2 = \frac{1}{2}\frac{F_z}{m} \,\Delta t^2 = \frac{\frac{dB}{dz} \mu}{2m} \,\Delta t^2$$

The time over which the force was applied is given by¹⁴

$$\Delta t = \frac{\Delta x}{v_x} = \Delta x \sqrt{\frac{m}{3k_BT}}$$

So,

$$\Delta z = \left(\frac{\frac{dB}{dz} \mu}{2m}\right) \Delta t^2 = \frac{\frac{dB}{dz} \mu \left(\Delta x \sqrt{\frac{m}{3k_BT}}\right)^2}{2m} = \frac{\frac{dB}{dz} \mu (\Delta x)^2}{6k_BT} ,$$

and

$$\mu = \Delta z \ \frac{6k_BT}{\frac{dB}{dz} (\Delta x)^2} = \ 1.9 \times 10^{-4} \frac{6 \ (1.38 \times 10^{-2} \)(663)}{1250 \ \times (0.03)^2} = \ 9.3 \times 10^{-24} \ \frac{Cm^2}{s}.$$

This value is approximately what we calculated for the electron,¹⁵ and three orders of magnitude greater than the value for the proton. Hence, the electron clearly has a spin angular momentum.

HOMEWORK 13-6

Consider an electron in a magnetic field of 5 Tesla (pretty strong!). What is the difference in the energies of the 'spin up' state and the 'spin down' state? Use the currently accepted value for the electron's magnetic moment, 9.28×10^{-24} J/T.

Some Additional Stuff

Here is one (of many) corrections to the model above. The interaction between the magnetic dipole moment of the electron and that of the proton in hydrogen splits the n = 1 energy level into two levels (the *hyperfine structure*) separated by 5.874 micro-electron volts. The math for this calculation is just barely beyond the scope of this course.

HOMEWORK 13-7

Calculate the wavelength of the photon emitted by the electron as it flips from one state (n = 1, l = 0, $m_l = 0$, $m_s = +1/2$) to the other (n = 1, l = 0, $m_l = 0$, $m_s = -1/2$). FYI, this emission is useful in astronomy for detecting cold neutral hydrogen in space.

¹⁴ The speed is estimated by the r.m.s. speed for ideal gases.

¹⁵ The currently accepted value is 9.28476×10^{-24} J/T.

Summary

We've applied the Schrödinger equation to a point particle moving through a central Coulomb field to determine the approximate energies of an electron in a hydrogen atom. There are many aspects of a real atom that we have ignored. For example, the proton is not infinitely massive, and therefor wobbles a bit as it and the electron 'orbit' their common center of mass. We've ignored a number of effects that we know we should have included, but even if we were to consider these perturbations, they are nothing compared to the effect of adding just one more electron.