

## Chapter 6

# Quantum Theory of the Hydrogen Atom

### 6.1 Schrödinger's Equation for the Hydrogen Atom

Today's lecture will be all math. Advice: grit your teeth and bear it.

Now that we have discovered a "new" theory (quantum mechanics as exemplified by Schrödinger's equation) we ought to test it out on something.

What should we use as a test?

How about the simplest system that we can think of.

What's the simplest physical system *containing interaction potentials* (i.e., not just an isolated particle) that you can think of?

That's right -- the hydrogen atom. One proton, one electron, and the electrostatic (Coulomb) potential that holds them together.

The potential energy in this case is simply

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

which is the attractive potential between charges of +e and -e separated by a distance r.

Now, this potential looks quite simple. But notice that it is a function of r, not x or (xyz). What can we do about that?

One approach would be to express V in terms of (xyz), where

$$x^2 + y^2 + z^2 = r^2.$$

In some cases you might be able go get away with that, but here you would make the problem quite difficult (the square root of the sum of squares is a pain to deal with).

The appropriate approach is to let the symmetry of the potential guide you in your solution. Here, the spherically symmetric potential tells us to use spherical polar coordinates.

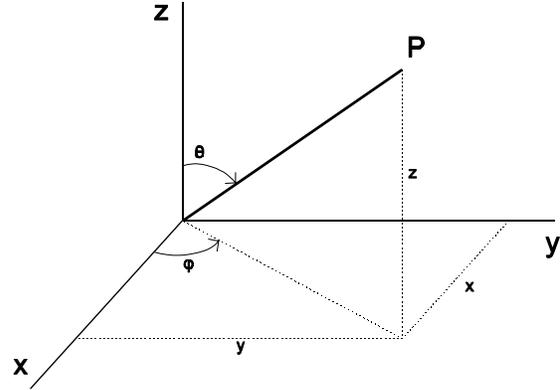
In spherical polar coordinates, r is the length of the radius vector from the origin to a point (xyz):

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

Another coordinate is  $\theta$ , the angle between the radius vector and the +z axis.

$$\theta = \cos^{-1} \left( \frac{z}{\sqrt{x^2 + y^2 + z^2}} \right).$$

The third coordinate (because we are in three dimensions, we need three coordinates) is  $\phi$ , the angle between the projection of the radius vector onto the xy plane and the +x axis.



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

Note that we have three coordinates,  $(r\theta\phi)$ , which we have related to  $(xyz)$  above. We can also express  $(xyz)$  in terms of  $(r\theta\phi)$ :

$$x = r \sin \theta \cos \phi \quad y = r \sin \theta \sin \phi \quad z = r \cos \theta.$$

Now we can re-write Schrödinger's equation

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{2m}{\hbar^2} (E - V) \psi = 0$$

in spherical polar coordinates as

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2m}{\hbar^2} (E - V) \psi = 0.$$

If we plug in our potential  $V$  and multiply both sides by  $r^2 \sin^2 \theta$ , we get

$$\sin^2 \theta \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \sin \theta \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2m r^2 \sin^2 \theta}{\hbar^2} \left( \frac{e^2}{4\pi \epsilon_0 r} + E \right) \psi = 0.$$

Let's talk about this equation.

It looks nasty, but we will see that it isn't quite as bad as it looks.

This equation gives us the wave function  $\psi$  for the electron in the hydrogen atom. If we can solve for  $\psi$ , in principle we know everything there is to know about the hydrogen atom.

When we solved Schrödinger's equation in one dimension, we found that one quantum number was necessary to describe our systems. For example, in the Bohr atom, the electron

moves in an orbit, but we need only one parameter to specify its position in the fixed orbit, so we only need one quantum number.

Here, in three dimensions and with three boundary conditions, we will find that we need three quantum numbers to describe our electron.

Beiser at the end of this section tells what the quantum numbers for the hydrogen atom are, and gives their possible values, but until we see where they come from and what they mean, they aren't of much use to us.

Another comment: we are really solving Schrödinger's equation for the electron in a hydrogen atom, aren't we. Nevertheless, we talk about doing the "hydrogen atom," because our solution will provide us with much of what we need to know about hydrogen.

## 6.2 Separation of Variables

We now discuss the technique for solving our equation for the electron in the hydrogen atom.

Here are some things we like, in decreasing order of liking (in my judgement):

- linear algebraic equations
- coupled algebraic equations (i.e.  $xy$  multiplied together)
- linear differential equations
- coupled differential equations (i.e., derivatives of different variables appearing together).

When we have an equation like the one above, we like to see if we can "separate" the variables; i.e., "split" the equation into different parts, with only one variable in each part.

Our problem will then be much simplified if we can write

$$\psi(r,\theta,\varphi) = R(r)\Theta(\theta)\Phi(\varphi) = R\Theta\Phi.$$

Let's *assume* we can write  $\psi$  like that, and see where it leads us.

If our assumption works, in the orderly world of mathematics we know it must have been right.

Here's how we take the partial derivatives in Schrödinger's equation:

$$\frac{\partial\psi}{\partial r} = \Theta\Phi\frac{\partial R}{\partial r} = \Theta\Phi\frac{dR}{dr}$$

$$\frac{\partial\psi}{\partial\theta} = R\Phi\frac{\partial\Theta}{\partial\theta} = R\Phi\frac{d\Theta}{d\theta}$$

$$\frac{\partial^2 \psi}{\partial \varphi^2} = R \Theta \frac{\partial^2 \Phi}{\partial \varphi^2} = R \Theta \frac{d^2 \Phi}{d\varphi^2}$$

where the partial derivatives become full derivatives because  $R$ ,  $\Theta$ , and  $\Phi$  depend on  $r$ ,  $\theta$ , and  $\varphi$  only.

To separate the variables, plug  $\psi=R\Theta\Phi$  into Schrödinger's equation and divide by  $R\Theta\Phi$ . The result is

$$\frac{\sin^2\theta}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{\sin\theta}{\Theta} \frac{d}{d\theta} \left( \sin\theta \frac{d\Theta}{d\theta} \right) + \frac{1}{\Phi} \frac{d^2\Phi}{d\varphi^2} + \frac{2mr^2\sin^2\theta}{\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0 r} + E \right) = 0.$$

Note we have separated out the  $\varphi$  variable; the term

$$\frac{1}{\Phi} \frac{d^2\Phi}{d\varphi^2}$$

is a function of  $\varphi$  only. Let's put it over on the right hand side of the equation. This gives us

(Below is Beiser eq. 6.7 --- need to leave this one on the board)

$$\frac{\sin^2\theta}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{\sin\theta}{\Theta} \frac{d}{d\theta} \left( \sin\theta \frac{d\Theta}{d\theta} \right) + \frac{2mr^2\sin^2\theta}{\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0 r} + E \right) = - \frac{1}{\Phi} \frac{d^2\Phi}{d\varphi^2}.$$

Notice the form of the equation. It is in the form

$$f(r,\theta) = g(\varphi),$$

where  $f$  is a function of  $r$  and  $\theta$  only, and  $g$  is a function of  $\varphi$  only.

Under what conditions can this equation be satisfied?

If an  $r$  or  $\theta$  shows up on the LHS, it can't be satisfied, because  $r$  and  $\theta$  never show up on the RHS. Similarly, if a  $\varphi$  shows up on the RHS, the equation can't be satisfied because  $\varphi$  never shows up on the LHS. The only way for the equation to be satisfied is for

$$f(r,\theta) = a \text{ constant, independent of } r, \theta, \text{ and } \varphi = g(\varphi).$$

Notice what we've done.

We've taken the one nasty equation for  $r$ ,  $\theta$ , and  $\varphi$ , and separated it into two equations, one

in  $r$  and  $\theta$ , and the other in  $\varphi$  only.

If we're lucky, we'll also be able to separate the  $r$  and  $\theta$  parts.

At this point, we will begin quoting some results from differential equations.

As we have seen several times before in this course, some differential equations can be solved only if certain conditions are satisfied. These conditions have led us to quantum numbers. They will do so in this case also.

Let me follow Beiser's development, and anticipate some of the requirements.

It turns out (although we won't do the math in this course) that the constant in the last equation on the previous page is the square of an integer. Thus, we can write the RHS of Beiser's eq. 6.7 as

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

We will hear more about this  $m_l$  later.

The LHS of Beiser's eq. 6.7 also must equal  $m_l^2$ . If we set the LHS equal to  $m_l^2$ , divide by  $\sin^2\theta$ , and rearrange, we get

$$r \frac{1}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{2mr^2}{\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0 r} + E \right) = \frac{m_l^2}{\sin^2\theta} - \frac{1}{\Theta \sin\theta} \frac{d}{d\theta} \left( \sin\theta \frac{d\Theta}{d\theta} \right).$$

Once again we have separated variables. The LHS is a function of  $r$  only, and the RHS is a function of  $\theta$  only.

Again, the only way to satisfy this equation is for LHS=a constant=RHS.

Conditions on the constant will arise from the solutions of the differential equations. In this case, we call the constant  $l(l+1)$ .

We conclude this section by taking our three differential equations for  $r$ ,  $\theta$ , and  $\varphi$ , rearranging them slightly, and writing them in the form

$$\frac{d^2\Phi}{d\varphi^2} + m_l^2 \Phi = 0$$

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

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \left[ \frac{2m}{\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0 r} + E \right) - \frac{l(l+1)}{r^2} \right] R = 0$$

All of the above seems like a lot of work, but we have separated our "big" partial differential equation into three simpler ones, each of which is a function of a single variable, and each of which is much "easier" to handle.

We have gone to a lot of trouble to separate Schrödinger's equation for the hydrogen atom into three separate equations, one for each variable  $r$ ,  $\theta$ , and  $\varphi$ .

Why did we bother to do this. It looks like we now have three differential equations instead of one.

But one of the equations is quite simple, and the other two are "easier" than our starting equation.

### 6.3 Quantum Numbers

In this section, we write down the quantum numbers which characterize the solutions to Schrödinger's equation. We also tabulate some of the simpler solutions.

In later sections, we will explore the significance of each of the quantum numbers.

Quantum numbers are constants which identify each solution to Schrödinger's equation. We will find three here.

We find the first quantum number by solving the differential equation for  $\varphi$ .

$$\frac{d^2\Phi}{d\varphi^2} + m_l^2 \Phi = 0$$

That equation should look familiar to you; you've seen it a number of times before. It has solutions which are sines and cosines. We write the general solution

$$\Phi(\varphi) = A e^{jm_l\varphi}.$$

We will get the constant  $A$  by normalization.

Now, since  $\varphi$  and  $\varphi+2\pi$  represent a single point in space, we must have

$$A e^{jm_l\varphi} = A e^{jm_l(\varphi + 2\pi)} .$$

This happens only for  $m_l=0, \pm 1, \pm 2, \pm 3, \dots$

For reasons which are not yet obvious,  $m_l$  is called the *magnetic quantum number*.

Our differential equation for  $\Theta$  is

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

It involves the term

$$l(l+1) - \frac{m_l^2}{\sin^2\theta} .$$

It turns out that from differential equations that the equation for  $\Theta$  can be solved only if  $l$  is an integer greater than or equal to the absolute value of  $m_l$ .

We have found another quantum number, the *orbital quantum number*, and the requirement on  $l$  can be restated as  $m_l=0, \pm 1, \pm 2, \pm 3, \dots, \pm l$ .

Finally, the radial differential equation is

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \left[ \frac{2m}{\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0 r} + E \right) - \frac{l(l+1)}{r^2} \right] R = 0 .$$

It can be solved only for energies  $E$  which satisfy the same condition as we found on the energies for the Bohr atom:

$$E_n = -\frac{me^4}{32\pi^2\epsilon_0\hbar^2} \frac{1}{n^2} = \frac{E_1}{n^2}, \quad n = 1, 2, 3, \dots$$

This  $n$  is known as the *principal quantum number*.

Note that the product  $l(l+1)$  shows up in the equation for  $R$ . It turns out, again from differential equations, that the equation for  $R$  can be solved only for  $n$  greater than or equal to  $l+1$ .

We express this requirement as a condition on  $l$ :  $l=0, 1, 2, \dots, (n-1)$ .

We summarize this section by noting that solutions to the Schrödinger equation for the hydrogen atom must be of the form

$$\psi = R_{nl} \Theta_{lm_l} \Phi_{m_l},$$

with conditions on the quantum numbers  $n$ ,  $l$ , and  $m_l$  as discussed above.

We aren't going to go any further with our solutions to the Schrödinger equation, other than to note that they are well-known, and Beiser tabulates some of them in Table 6.1.

Note how Table 6.1 is set up. For  $n=1$ , the only allowed possibilities are  $l=m_l=0$ . For this case, Beiser lists the three solutions  $\Phi$ ,  $\Theta$ , and  $R$ .

For  $n=2$ ,  $l$  can be either 0 or 1. If  $l=0$  then  $m_l=0$ . If  $l=1$  then  $m_l=0$  and  $m_l=\pm 1$  are allowed. The solutions for  $m_l=\pm 1$  are the same. Beiser tabulates the three solutions.

Here's an example. Suppose we have an electron with a principal quantum number  $n=3$  (corresponding to the second excited state of the Bohr hydrogen atom) and orbital and magnetic quantum numbers  $l=2$  and  $m_l=-1$ .

Then, according to table 6.1,

$$\Phi(\varphi) = \frac{1}{\sqrt{2\pi}} e^{+j\varphi},$$

$$\Theta(\theta) = \frac{\sqrt{15}}{2} \sin \theta \cos \theta,$$

and

$$R(r) = \frac{4}{81\sqrt{30}a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}.$$

The wave function  $\psi$  is the product of all three of the above functions.

I wouldn't care to calculate and plot the wave function by hand, but with computers (e.g. MathCad) the problem is rather easy.

With the wave functions in Table 6.1, you can calculate all sorts of things, like ground state

energies (see the example on page 210), excited state energies, expectation values, probabilities, etc.

## 6.4 Principal Quantum Number

Our result for the principal quantum number  $n$  and dependence of the electron energy on  $n$  turn out to be exactly the same as for the Bohr model.

We ought to ask whether this is just luck or something deeper.

In fact, it is not just luck. Both results depend on the wave nature of the electron. The Bohr model is, however, unable to provide additional details which the full quantum mechanical solution does.

Electron energies in the hydrogen atom are quantized, and they are negative numbers.

Just as we had before, there is nothing that prevents us from having positive energies.

In fact, *any* positive energy may lead to a solution to Schrödinger's equation.

But a positive energy means the electron is not bound, so we don't really have a hydrogen atom.

None of this information is new; we have seen it all before.

## 6.5 Orbital Quantum Number

I've already written down the differential equation for  $R(r)$  several times. I won't repeat it again.

I will write it in an alternate form, which uses  $E=K+V$  and  $K=K_{\text{radial}}+K_{\text{orbital}}$  and  $V=-e^2/(4\pi\epsilon_0 r)$ .

The alternate form is

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{2m}{\hbar^2} \left[ K_{\text{radial}} + K_{\text{orbital}} - \frac{\hbar^2 l(l+1)}{2mr^2} \right] R = 0.$$

Now, kinetic energies are always positive. Furthermore, if the radial equation is to really have only radial dependence in it, it clearly cannot have an orbital kinetic energy term.

The only way for this to work (that is, to make  $K_{\text{orbital}}$  "go away" from this equation) is to have

$$K_{\text{orbital}} = \frac{\hbar^2 l(l+1)}{2mr^2}.$$

But the orbital kinetic energy is  $K_{\text{orbital}} = \frac{1}{2}mv_{\text{orbital}}^2$ . The orbital angular momentum is  $L = mv_{\text{orbital}}r$ .

Just as we can write kinetic energy in terms of momentum, we can write orbital kinetic energy in terms of orbital angular momentum:  $K_{\text{orbital}} = L^2/(2mr^2)$ .

Combining our two equations for  $K_{\text{orbital}}$ , we find that

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

Note that  $l$  is quantized ( $l=0,1,2,\dots,n-1$ ) so that  $L$  is also quantized.

In fact,  $L$  is quantized in units of  $\hbar$  (but not necessarily integral multiples of  $\hbar$ ).

The lowest possible nonzero  $L$  is  $L = (2)^{1/2}\hbar$ .

We label angular momentum states like this:

$l =$	0	1	2	3	4	5	6
	s	p	d	f	g	h	i

An electron with  $n=3$ ,  $l=2$  would be a 3d electron. Note that a 3d electron can have any of several allowed  $m_l$ 's.

See table 6.2, page 208 of Beiser for designation of atomic states.

## 6.6 Magnetic Quantum Number

An electron in the hydrogen atom is in an orbit. It has an angular momentum vector  $\mathbf{L}$  (a vector).

We found the magnitude of  $\mathbf{L}$  above:

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

Now, vectors have both magnitude (given above) and direction. What does the direction of  $\mathbf{L}$  in an isolated hydrogen atom mean?

Answer: not very much.

But an orbiting electron is like a current in a loop, which gives rise to a magnetic field, and can interact with an external magnetic field.

An external field therefore gives us a meaningful reference for specifying the direction of the orbital angular momentum vector in the hydrogen atom.

By convention, we put our hydrogen atom's z-axis along the direction of the applied magnetic field  $\mathbf{B}$ .

Then  $m_l$  gives the component of  $\mathbf{L}$  in the direction of  $\mathbf{B}$ .

$$L_z = m_l \hbar .$$

Where did this come from? I can't see it coming from anything we've done here. I think the best we can do now is accept it as true.

Can  $\mathbf{L}$  ever be parallel to  $\mathbf{B}$ ?

Answer:

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

but  $m_l$  is at most equal to  $l$ , so  $L_z = m_l \hbar$  is always less than  $L$ .

This is another seemingly "wierd" quantum result, but we will see in a while that it makes sense.

Suppose we apply a field. Is  $L_z$  always the maximum possible (i.e., does the hydrogen atom always try to "line up" with the field)?

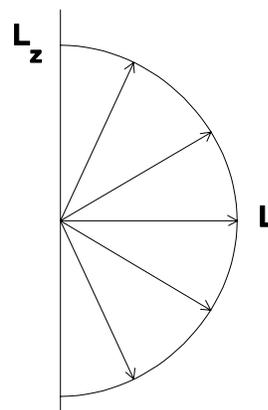
Answer: not necessarily. See figure 6.4. Understand this figure because I may ask you to explain/label it on a test or quiz.

Here's why  $L_z$  is always *less than*  $L$ .

If  $\mathbf{L}$  could point exactly along the z axis (magnetic field axis) then the electron orbit would lie exactly in the xy plane and the uncertainty in the z coordinate would be zero.

The momentum uncertainty in the z direction would then be infinite. This is intolerable for an electron in an atom.

The tilt of  $\mathbf{L}$  with respect to the z-axis lets us satisfy the uncertainty principle.



## 6.7 Electron Probability Density

Since Schrödinger's equation is separable in spherical polar coordinates, the three dimensional wave function is  $\psi=R\Theta\Phi$ . The probability density is then defined as

$$P(r,\theta,\varphi) = \psi^*\psi dV = P(r)P(\theta)P(\varphi) dV,$$

where  $dV$  is the volume element in spherical polar coordinates:

$$dV = r^2 \sin\theta dr d\theta d\varphi.$$

The coordinate-dependent probability densities are  $P(r)=R^*R$ , where  $r$  ranges from 0 to  $\infty$ ;  $P(\theta)=\Theta^*\Theta$ , where  $\theta$  ranges from 0 to  $\pi$ ; and  $P(\varphi)=\Phi^*\Phi$ , where  $\varphi$  ranges from 0 to  $2\pi$ .

Now, since the three dimensional wavefunction is separable, and since  $R$ ,  $\Theta$ ,  $\Phi$  are orthonormal functions, we can separate the three variables in  $dV$  and write the triple integral (which gives the probability density for finding  $\psi$  at  $r$ ,  $\theta$ ,  $\varphi$ ) as a product of three one dimensional integrals.

The product integral is normalized to one, and the individual wave functions are normalized to make each integral separately equal to one.

These equations may be written:

$$P(r) = \int R^*(r)R(r)r^2 dr,$$

$$P(\theta) = \int \Theta^*(\theta)\Theta(\theta)\sin(\theta)d\theta,$$

and

$$P(\varphi) = \int \Phi^*(\varphi)\Phi(\varphi)d\varphi.$$

The maximum probability comes at the peak of the probability kernel. The most probable value of  $r$  is at the peak of the probability kernel. The average value of  $r$  is equal to the expectation value of  $r$ .

You can use these equations to find the probabilities of finding an electron at various coordinates, and the most probable value for an electron's coordinates.

Some interesting results can be calculated. The most probable value for  $r$  for a 1s electron is  $a_0$ , as it ought to be, but the average value of  $r$  is  $1.5a_0$ . There's still no contradiction with the Bohr model, as the average electron energy works out OK.

Maybe I will copy pages 220 and 221 to transparencies and show them in class.

Figure 6.10 shows some electron probability density distributions, projected onto a plane. You have to imagine the z-axis in the plane of the paper, and rotate around the z-axis to get the 3-dimensional pictures.

Some other interesting ideas that come out of this section:

Quantum mechanics works very well for describing the hydrogen atom, but we need to modify our classical thinking in several ways.

(1) We can only give *probabilities* for finding an electron at some set of coordinates.

(2) The electron doesn't move around the nucleus in any conventional sense. You should think of figure 6.10 as representing fuzzy clouds. The clouds aren't electrons, but they show where electrons are likely to be found. The denser the "cloud", the more likely is the electron to be found.

## 6.8 Radiative Transitions

The idea here is fairly simple. First consider an electron in a state with principal quantum number  $n$ .

Its energy is  $E_n$ , its wave function has a frequency  $f_n = E_n/h$ , and its wave function is

$$\Psi_n = \psi_n \exp(-jE_n t/h).$$

This wave function now includes time dependence.

As Beiser shows, the expectation value of the electron's position is

$$\langle x \rangle = \int \psi_n^* x \psi_n dx,$$

which is independent of time.

There is nothing here which tells us the electron radiates energy, and in fact, it doesn't (the electron doesn't oscillate with time).

When the electron is excited to another quantum state  $m$ , it doesn't radiate energy after it reaches its final state; that is, as long as it is in the state  $m$ .

However, the electron does have to get from state  $n$  to  $m$ , and in the process it does radiate energy.

We calculate the energy radiated by considering the wave function

$$\Psi = a\Psi_n + b\Psi_m,$$

which represents an electron which may exist in state m or n.

The magnitudes of a and b tell us the relative probabilities of the two states.

It is straightforward, if slightly tedious, to calculate the expectation value  $\langle x \rangle$  for such an electron. I will expect you to be able to reproduce this calculation with some assistance on my part.

The only "trick" in the calculation is the fact that

$$\Psi_n^* \Psi_m = \Psi_m^* \Psi_n,$$

and

$$a^* b = b^* a.$$

The above two equations come from a more thorough investigation of the mathematics of quantum mechanics. Here, we just have to accept them.

The result of the calculation is:

$$\langle x \rangle = a^2 \int \Psi_n^* x \Psi_n dx + b^2 \int \Psi_m^* x \Psi_m dx + 2a^* b \cos(2\pi ft) \int \Psi_n^* x \Psi_m dx.$$

where

$$f = \frac{E_m - E_n}{h}.$$

Note that if the electron is in state n,  $b=0$  and only the first integral contributes, just as we would expect; and similarly if the electron is in state m.

However, when the electron is in transition between states n and m, both a and b are nonzero, and all three integrals contribute.

The third integral corresponds to an electron "jumping" back and forth between quantum states n and m.

The cosine term gives the frequency of radiation emitted by the electron oscillating ("jumping") between quantum states n and m.

The important result here is that an electron radiates electromagnetic energy when it jumps between quantum states.

We do have a problem here--we've mixed classical (accelerated electron emits radiation) and quantum theory.

Strictly speaking, according to this interpretation, the electron should emit electric dipole radiation instead of a single photon.

Beiser clears this up in the next section. Our ideas are OK; a complete treatment requires quantum electrodynamics, and there we find that photons are, indeed, emitted.

## 6.9 Selection Rules

Notice above that for an electron to get from one quantum state to another, it must radiate energy. For this to happen, the integral

$$\int \Psi_n^* x \Psi_m dx$$

must be nonzero.

If the integral is zero, the electron can never get between the two quantum states.

Thus, calculation of the integral tells us which transitions are allowed (the integral is finite) or forbidden (the integral is zero).

The wave functions for the hydrogen atom are known, and the integral can be evaluated for all possible transitions. The result is

$$\Delta l = \pm 1 \quad \text{and} \quad \Delta m_l = 0, \pm 1 .$$

These are **selection rules** for the allowed transitions. In other words, the integral is nonzero only for these particular changes in  $l$  and  $m_l$ .

Note that  $\Delta l = \pm 1$  implies a change in the angular momentum of the atom during an allowed transition. Angular momentum must be conserved, so the photon must carry off angular momentum.

When  $\Delta m_l = 0$ , there is no change in the angular momentum along the  $z$  axis. This means that the photon is emitted in the  $x$ - $y$  plane. When  $\Delta m_l = \pm 1$ , the photon is emitted along the  $\pm z$  axis.

Study figure 6.11. Be able to explain parts of it to me on an exam or quiz.