

PROFESSOR: For a couple of lectures, we're going to be discussing now the hydrogen atom. So you've seen the hydrogen atom before. You've seen it in 804. You've seen it in 805. Why do we see it again in 806? Well, the hydrogen atom is a fairly sophisticated example. It's the harmonic oscillator of atomic physics.

If some of you are going to be doing atomic physics, eventually, you have to understand the atom perfectly well, the energy levels, the degeneracies, why are they, how do you separate the levels, how do you split the degeneracies. It's a fantastically good example of perturbation theory, our degenerate perturbation theory, non-degenerate perturbation theory in some cases. But overall, it's a very important physical system that affects many areas of physics, astrophysics with hyper fine splitting, all kind of processes in atomic physics and lasers, and things like that.

So it's something we really want to understand well. And this time in 806, it's the right time for you to understand the fine structure of this atom. Bits and pieces of this have been done before. But now, we're going to do it in detail. So let's start with hydrogen atom fine structure.

Hydrogen atom fine structure. That is the main topic for a couple of lectures. So in terms of Hamiltonians, we've been talking of an unperturbed Hamiltonian, an H_0 . This Hamiltonian is known. It's the momentum squared over $2m$ minus e squared over r .

Here, this is the momentum in three dimensions. It's a three-dimensional system, of course. This m is the mass of the electron times the mass of the proton, divided by the mass of the electron plus the mass of the proton. And that's the reduced mass of the system, but it's approximately equal to the mass of the electron. So we will-- whenever we write m , it will be the mass of the electron.

Now, if you happen to have a nucleus with z protons, what you have to do is replace this e squared by $z e$ squared. And this is because the factor of e squared comes from the product of the charge of the electron times the charge of the nucleus. So if the charge of the nucleus becomes z times bigger, this e squared is replaced by this quantity.

What important length scales exist here is the Bohr radius is the most important length scale, and it's constructed with the quantities that appear in this Hamiltonian and \hbar . So in particular, doesn't involve the speed of light. There's nothing in this system that is relativistic.

So this quantity is h^2 over m_e squared. And that this has units of length is something that you should be able to derive from here in a few instances. Please make sure you know how to derive it without having to count mass, length, time units here. This is something you should be able to do very quickly.

One piece of intuition, of course, is that the e appears in the denominator, which is intuition that as the strength of electromagnetism is made smaller and smaller by letting e go to 0, the orbit of the electron would be bigger and bigger. So this is about 53 picometers, where a picometer is 10^{-12} meters. A nice unit. It's half an angstrom, roughly, but picometers is the right unit for people that think of atoms.

Then the energy levels are given by $-\frac{e^2}{2a_0} \frac{1}{n^2}$. This is a beautiful formula in terms of quantities that you understand. First, the energy just depends on n , and this $1/n^2$. And n is called the principle quantum number, principle quantum number, and it goes from 1 up to infinity.

This has units of energy, and that's why this is nice, because e^2/r is the units of potential energy in electromagnetism. So when you see this, you know that this has the right units of energy. And for the ground state of hydrogen, $n=1$, that energy is about minus 13.6 eV.

Now, in terms of thinking ahead for perturbation theory, some of the perturbation theory here will reflect the fact that electromagnetism is weak, and the other fact will reflect that the electron is actually moving with slow velocities. So let's see these two things.

First, we can write the energy, or in terms of defined structure constant. So α , which is defined structure constant. This e^2 over $[4\pi\epsilon_0 \hbar c]$ the units we're working with. And it's about 1/137. So whenever you see e^2/a_0 , which is a unit of energy, you should realize that-- if you wanted to change that, for example, for the case that you have a nucleus with Z protons, you cannot just do e^2 going to Ze^2 , because in fact, a_0 itself, has an e . So don't think that the energy depends like e^2 . It actually depends more like e^4 to the fourth times other constants.

So let's do that. So we have here m_e to the fourth over h^2 , using the value of a_0 . And then we can use e^4 from this equation. So it would be $\alpha^2 m_e \alpha^2 \hbar^2 c^2$ over \hbar^2 . And it's equal to $\alpha^2 m_e c^2$.

A nice way of thinking of the ground state energy of the hydrogen as a small quantity α squared times the rest energy of the electron. After all, the system begins just with an electron, and it has some rest energy, and there should be a natural way of expressing this. Of course, you start seeing this c squared here. But the c squared really is nowhere there. We've put it for convenience.

But it allows us to think of scales, and in particular, the rest mass of the electron is α is much bigger, because α squared is about 1 over 19,000. $1/137$ squared is about that. So the energy, E_n , can be written in a way that we will use often as minus $1/2$ α squared mc squared 1 over n squared.

All right. And another observation, the momentum of the electron, we could estimate it to be \hbar over a_0 . So this is me squared over \hbar . And we use the e squared for what it is. So this is α . Well, I'll put m , αhc over \hbar . So this is αmc .

It's a nice thing, αmc . It says that the momentum that you could construct relativistically, the mass of the electron times the velocity, you still have to divide by 137. But it's clearer if you write it like $m \alpha c$, and then momentum, which is mass times velocity, at least for slow velocities. Now is mass times α times c . So the approximate velocity that we estimate on the electron is c over 137. So that's very nice. It's kind of non-relativistic.

OK. So this is the basic things. But the most important stuff is really getting the table of how the atom looks. So this is still review. Half of this lecture, in a sense, is review. We put here, not in scale, n equals 1, n equals 2, n equals 3, and n equals 4.

In reality, the hydrogen atom, if this is 0 energy, and this is the ground state, the ground state that's here, the second excited state is here, the third is here, the fourth is here, fifth, they all accumulate here. But that I've written it this way. Now, we'll have l equals 0 here, l equals 1, l equals 2, l equals 3. And there is another notation for this state. I don't know why, but there is. A capital l that is a function of l .

So capital l of l equals 0 is called s . So these states are called s states. Capital l of l equals 1 is called p . So states with l equal 1 will be called p . Then d and f . These are names. We'll use those names. They're OK. And here are the states. For n equal 1, there's just one state here. And here there's one state as well. But for n equal 2, there is a state with l equal 0, and there is a state with l equal 1.

For n equal 3, there's 0, 1, and 2. For n equal 4, there's 0, 1, 2, and 3. So these are the states in the spectrum of hydrogen, something that we should know very well. And what are the patterns here. They're degeneracies. Why? Because when we talk l equal 2, for example, that means a multiplet of angular momentum with total angular momentum 2. And that comes with as azimuthal angular momentum that goes from minus 2 m to plus 2, that is five states.

So in principle, each bar here is five states, five states. l equal 1 has m equal 1, 0, and minus 1. So three states, three states, three states. And here, really zero states. So there's lots of degeneracy. That's why we spend lots of time studying degenerate perturbation theory, because this gigantic degeneracies here.

So to determine the origin or the way we parametrize the degeneracy, there's just one formula that says it all. And that formula is degeneracies. It's the formula that explains it all, and it says that the principle quantum number is equal to capital n plus l plus 1, where n is the degree of a polynomial in the wave function. Wave function. l is the orbital angular momentum.

So this says, for example, that this degree of the polynomial n can be 0, 1, 2. It cannot be negative. l can also be 0, 1, and go on. But here, for example, you see the main rule that for a fixed n , you can have l equals 0, 1, 2, up to n minus 1, because by the time you take l equals to n minus 1, this whole thing is equal to little n , and capital n is 0. And that's as far as you can go.

So the angular momentum cannot exceed the principle quantum number minus 1. That is what we see here for n equal 3. You can have up to l equal 2. For n equal 4, you can have up to l equal 3. So this is kind of well known. Now, for each l , each l , you have m from minus l all the way to plus l . And that's $2l$ plus 1 values.

So the degeneracy at n , at the principle quantum number equal n is the sum from l equals 0 up to n minus 1. Those are all the possible values of l of the number of states in each l multiplet. And you've done this one before, and that actually turns out to be equal to n squared, which says there should be four states at n equal 2, indeed one state for S equals 0, three states here is 4, 1, 3, 5.

It's that property that the sum of consecutive odd numbers comes up equal to the square, a perfect square. It's a very nice thing geometrically. So the wave function-- we'll write it here-- the wave function ψ_{lm} . These are our quantum numbers and principal quantum number.

Once you know n , you know the sum of capital N plus l . But l is a little more physical than n .

So we'll use l , and once you know l , you still need to know where a given state, which value of m you have. So those are your three quantum numbers, and this wave function goes like a constant times r over a_0 to the l times that polynomial we spoke about, $1 + \beta r$ to the r over a_0 all the way up to a number times r over a_0 to the capital N times e to the minus r over $n a_0$ times Y_{lm} of θ and ϕ .

So that's your wave function. Those numbers l have not determined. I have not determined the normalization. But if you're looking at the wave function, the easiest place to see the principal quantum number is here. The easiest place to see the orbital angular momentum is here. You identify it from here. It must be multiplying a polynomial that begins with 1, because the leading power in the solution must be r to the l , and has degree n here.

And the m quantum number you see it from the spherical harmonic. So in particular, here you have a state with l equals 0, n equal 1. So this must have n equals 0. This must have n equals 1, because you must get to 2 with a capital N and l equals 0 and a 1 there. So this is n equal 1. This would be n equal 2, n equal 3. Similarly here, n equals 0, n equals 1, n equals 2, n equals 0, n equals 1, n equals 0 here.

The n 's decrease in this direction as l increases, keeping the sum of capital N and l constant and equal to little m minus 1. Interestingly, this makes sense as well. If you may remember, the quantum number N , capital N , tells you the number of nodes of the wave function, because a polynomial of degree n can have n zeros, and therefore, this wave function has no nodes, one node, two nodes, three nodes. The number of nodes increase. That's another thing that wave functions should have.

So a couple more comments and this. We'll write-- I'll write the ground state wave function. I'll put it here. I'm cluttering things a little bit. But the ground state wave function is one that we can have and normalize easily. Square root of π over a_0 cubed e to the minus r over a_0 . That's the ground state wave function.

OK. Comments on this thing. First, there is a very large degeneracy here. And it has a nice interpretation. This correspond to states with different values of the angular momentum. Semi-classically, if you were doing Keplerian motion, and think semi-classically of the electron orbit, all the orbits here corresponds of orbits of the electron with the same semi-major axis, but with different eccentricity.

So as it turns out, the orbit with least l is the most eccentric of all orbits. And as you go in this direction, the orbit becomes more and more circular. So if you want an immediate intuition, as to why are all these states distinguishable, it's because they are orbits with different eccentricity. There are ellipses with different eccentricity, all with the same semi-major axis. So it could be a circle like that, or it could be just an ellipse like that.

So those are it. Then, most important complication we've ignored here, it's the spin of the electron. Electron has spin. So we know the spin of the electron represents a degree of freedom described by a two-dimensional vector space. So there's two states in every one of this. So we will have to consider that. And if I want to put the number of states on each one, here there was one state we said, but now we know there are really two states.

And here, there's two states is l equals 0, two states, two states. Here is l equal 1. That's three configurations of orbital angular momentum. But the electron has, again, up or down possibilities. So these are six states, six states, six states. l equals 2 is five states, but with the electron, there is 10 states and 10 states here.

In this one, l equals 3 is 7 states, $2l + 1$, but with the electron degrees of freedom is 14 states. So these are the right number of states. When we'll do the fine structure, we'll have corrections due to the spin and corrections due to relativity. Both things will make our corrections. And by the time we do that, we may also want to explore the atom by putting it in an electric field. That's the Stark effect. It will change energy levels, and you learn more about the energy levels of a system. You can put it in a magnetic field, and that's a Zeeman effect. And the magnetic field can be weak, or it can be strong, and it's a different approximation, and there's several things we have to do with it.