

**PROFESSOR:** If you tell someone solve this equation for  $l$  equals zero-- so you have this effective potential for the real equation-- solve it for  $l$  equals zero and you find some energies. You solve it for  $l$  equals 1, and you've found some energies. You solve it now for  $l$  equals two and you found some energies.

Well, we found them all together, but something extraordinary happened there was no a priori reason the system should have been so simple. It might have happened that these states would have not been aligned with the previous states. Nothing we've explained in this course predicts that this would have happened, this perfect alignment with extreme amount of degeneracy.

Because you have an  $l$  equals 2 multiplet here. That means five states. So there is degeneracy, but that's implicit in angular momentum. It has an explanation. But why would there be a degeneracy between  $l$  equals 1 solutions and  $l$  equals 2 solutions? Total mystery, actually.

And this led to all kinds of interesting discoveries that have to do with the Runge-Lenz vector, which is some conserved vector in planetary orbits. In planetary orbits, in Newton's theory, an elliptical orbit is the general solution. Nevertheless, elliptical orbits do not precess.

So you have an ellipse, it goes like that. It's not going around and rotating the ellipse at the same time. The precession of an ellipse is not allowed by Newton's theory. It's allowed by Einstein's gravity theory, and in fact, the precession of mercury was measured.

But there is no precession in Newton's theory, and there's no precession in a hydrogen atom, in a sense, as you will see. And that explains, actually in a rather interesting way-- but I'm not saying how yet-- why there is this extra degeneracy. In fact, if you had solved the problem of an infinite spherical, well, you will solve that in 805.

Infinite spherical well. Suppose there's infinite square well-- infinite spherical well. Inside a sphere of radius  $A$ , the potential is 0. Outside the sphere of radius  $A$ , the potential is infinite. That potential that looks so symmetric-- the  $l$  equals 0 states are like this.

The  $l$  equal 1 states are like that. The  $l$  equal 2 states are like that, and there's never any coincidence. So this coincidence between the  $l$  equals 0,  $l$  equals 2,  $l$  equals 2 is very special.

It just doesn't happen often. It's a sign of an extra symmetry.

This could only be explained because the hydrogen atom has an extra symmetry you're not aware of. So that's why this Runge-Lenz vector has to do with that extra symmetry and explains this effect. And we'll get some intuition about it today. A few more remarks to get your intuition working on the hydrogen atoms.

$Z$  equals 1, we write the wave function. This is the most famous wave function.  $\pi a_0^3 e^{-r/a_0}$ . And this is for  $l$  equals 0,  $m$  equals zero-- the complete ground state.

It's interesting to note and try to think, OK, suppose they gave you the  $l$  equals 0 answer. How do you get  $l$  different from 0? Can I just do something with this solution? Well, somehow it's written here, but I don't give here the normalization because it's impossibly complicated to write the general form for the normalization.

So how should I think of changing if somebody would have told me this is the answer for  $Z$  equals 1? How do I get to  $Z$  different from 1? And then I think of the potential, and the potential was  $e^2/r$ .

That was the potential before,  $V$  of  $r$ . And it will pass to a  $V$  of  $r$  that has minus  $Ze^2/r$ . Because now you have a nucleus with  $Z$  protons interacting with one electron, so that's how it changed. So naturally, what seems to be the change here, and you could imagine just solving it without the  $Z$  and then adding the  $Z$ , is that everywhere that you have  $e^2/r$  you should put  $Z$  times  $e^2/r$ .

And then you think of  $a_0$ .  $a_0$  was  $\hbar^2/m_e e^2$ . We calculated that some time ago. And then if  $e^2$  goes to  $Ze^2$ , this will go to  $1/Z$  times  $\hbar^2/m_e e^2$ . So it will go to  $a_0/Z$ .

So you change  $a_0$  to  $a_0/Z$ . And these are the two changes. One is implicit on the other, but many times you write the formula in a mixed way. Look at that energy.

If you would have looked at this without the  $Z$  and you would have said, oh,  $e^2/r$  is replaced by  $Ze^2/r$ , you would have put a single  $Z$ . But there is a  $Z^2$  here, and it comes because  $1/r$  is here and the other  $r$  is in the  $a_0$  because  $a_0$  also has the  $e^2$ . So you have to be aware that we write these things. And this is intuitively a very nice way to write the energy, because it has the right units-- electric charge squared divided by distance. But

you could have written everything with  $\hbar$ , something like that, in which case the  $z^2$  might have been less surprising.

We see here, however, the  $z$  is appearing in the right place because of the  $a_0$ . So here, I was right.  $e^{-zr/a_0}$ . And can I get the normalization even right? At this moment, yes.

Let's do the same change here.  $\pi a_0^3 z^3$ . And this must be right, because, in fact, if this wave function was normalizable-- not normalizable; was normalized-- when you do the integral, somehow the  $a_0$  did not matter, must not matter.

You checked  $\psi^2$  integrated over volume is equal to 1. The  $a_0$  must be canceling here. And therefore, if it works for  $a_0$ , it must work for  $a_0/z$ , and that must be a wave function. So that's fine. That's one thing you could ask.

Another thing that you could ask is, at least intuitively, why did we get this factor here? Why did we get this exponential? And that's also not mysterious at all. This comes from the differential equation. It comes up rather immediately from the differential equation.

You have  $-\hbar^2/2m \frac{d^2 u}{dr^2}$ , plus some sort of number-- you don't care how much--  $u/r^2$  in the effective potential, minus some number over  $r$  times  $u$  is equal to  $E u$ . This was your radial differential equation. And this  $r$  goes to infinity. As  $r$  goes to infinity, you get  $-\hbar^2/2m \frac{d^2 u}{dr^2}$  is equal to  $E u$ , roughly. That's the key terms.

And from here,  $\frac{d^2 u}{dr^2}$  is equal to  $-2mE/\hbar^2 u$ . And that gives you an exponential, and the exponential must be of the right value, which we can calculate easily from the expression for the energy. So the expression for the energy gives you  $E = -\frac{z^2}{2a_0} \frac{e^2}{m a_0}$ , times  $1/n^2$ . And I can change this thing into  $-\frac{z^2}{2a_0} \frac{e^2}{m a_0}$ .

Recall what's the value of the fine structure constant. I can replace  $e^2$  from  $a_0$  to get the following thing over  $2a_0$  times  $\hbar^2/m a_0$ . That is  $1/m^2$ . A little bit of manipulation. So at the end,  $-2mE_n/\hbar^2$ , which is what I need from the differential equation.

I must multiply by  $-2m/\hbar^2$ . You see that minus the  $2m/\hbar^2$ , they

will disappear. So you get here  $z^2$  over  $n^2 a_0^2$ . A little bit of manipulation.

So what are we trying to get? We want to understand immediately where this came from. And we see it. It comes from the asymptotic form of the differential equation for a solution. So I calculate the value of the right-hand side is this, and therefore this differential equation now looks like the  $du/dr^2$  equals  $z^2$  over  $n^2 a_0^2 u$ .

Are indeed, from here, the solutions are exponentials of the square root of this, which is  $z$  over  $na_0 r$ . And that's a quicker derivation of a feature of the wave function. It's almost like you want to look at this wave function, and you want to say, I understand where everything comes from.

And I don't have to solve pages and pages of differential equations to see why I need this, why I need that much. I know I need this from  $r$  equals zero. I know this degree. I need it from the node theorem. Everything sort of has a reason for being there, and we should understand.