

PROFESSOR: What is a Rydberg atom? Well, it's a-- an atom can be a Rydberg atom if the outermost electron is in a very high principal quantum number. That's a definition of a Rydberg atom. The last electron is an n -- little n , very large.

Now that is very interesting because when that happens, Rydberg atoms-- when that happens, you have a nucleus with charge ze and you have lots of electrons. And the last electron-- suppose the last electron is in an orbit further out. You see the orbits do become further out in general.

And suppose the last electron is in some large value of little n , so it's somewhat out. So here is the last electron. This electron sees a nucleus with charge z , but it also sees $z - 1$ electrons, all the other electrons. The last electron is outside the nucleus and the cloud of the other electrons.

So the last electron sees a charge plus $1 - z$ from here and $z - 1$ of the electrons. So the last electron sees charge 1 . So in some sense, to a good approximation, the last electron says, oh, there's a hydrogen atom here. I'm part of a hydrogen atom. I don't see my friends. The other electrons are too close to the nucleus. And I'm out there going around as if I were hydrogen. So that's a very nice application of hydrogen atoms.

So the first question that we want to understand, that it's, again conceptually, is what is the size. If n is large what is the size of the atom? Now I must say, I myself, when I look at these things after a few years that I don't teach quantum mechanics, I look at here and say, OK, this is the solution. Well, maybe the size is na_0 . Unfortunately, that's completely wrong. And we're going to try to explain what was wrong in looking there.

You know, you see your hydrogen atom wave function. There's nothing like really the size, there's no such precise definition as the size. But you could say, what's the expected value of the radius. That's a reasonable definition of size. And you know from this wave function, is going to come out to a_0 , a_0 over 2 , $2a_0$, maybe π over $2a_0$. Something like that.

So from here you would say, well, it's going to come out to π and na_0 or something like that. That is not true. So how do we see that it's not true? We'll take a little time in a few minutes. But how can we get the size of that atom correctly in an intuitive way? Again, we want to just understand a few results about hydrogen atom that become part of your intuition.

So the important result here is the virial theorem. Now whenever I think of the virial theorem I say, oh, there was a factor of 2 or a 1/2 there. How did it go? It takes me a few seconds to try to reconstruct that it's this.

For the hydrogen system, for any $1/r$ potential, there is this relation within the expectation value of the kinetic energy, the potential energy. You've seen that result probably a couple of times already in this course. Because it's a real important result. It looks like OK, just a theorem about these things. But the intuition is really important.

So how does one remember or picture that? One way is the following. And that's the way I like it. I imagine the energy line here. And here is 0. And the one thing I remember is that, yes, there is a kinetic energy here.

And actually the bound state energy is exactly the same, but the opposite. That's a way to remember that. That's really what is going on. That's the key thing. The kinetic energy and the bound state energy are just of opposite signs.

Why do we see that? Because then we have that V , from this equation, is minus $2T$. And if V is minus $2T$, means that $T + V$ is $T - 2T$. And $T + V$ is the total energy. So $T + V$ is equal to the total energy E of the bound state. For any stationary state, this is true. And this thing, given this condition, is minus T . So that's the way we think of it.

So we then have a nice result because the expectation value of the potential would then be minus 2 times the expectation value of T , which is itself minus the energy. So you have a minus 2 times minus the energy. And it's equal to the energy. And this is correct. The expectation value of V is the energy and the expectation value of E_b is negative, and the energy's negative.

So what is this? This is the expectation value of minus e^2/r . In fact, of-- yeah, I'll leave it like that. So I'm back to $z = 1$, because we're talking about Rydberg atoms. Oh, $2E_b$, I'm sorry, here. Thank you.

OK, so expectation value of the potential we have here. And 2 times the energy-- yeah, I would have gotten this wrong. Thanks for correcting it before it did damage to the derivation. We have it there, $e^2/2a_0$, $1/n^2$.

So what can we cancel? Well, the 2's cancel. The e^2 's cancel. The signs cancel. And we

get expectation value of $1/r$ is equal to $1/n^2 a_0$, which is suggesting very clearly that the typical radius is not na_0 . It's $n^2 a_0$. So this is exact. The virial theorem is exact. The energy is exact. This is exact.

That's not quite the expectation value of r . The expectation value of r is not the inverse of the expectation value of $1/r$. It's somewhat related. But there's no theorem, because it would be false, that the expectation value of 1 over a random variable is the expectation value of 1 over the expectation value of the random variable. It's just not true.

This nice result for $1/r$ is exactly true. And it's l independent. On the other hand, the expectation value of r can be calculated with a bit more effort-- a lot more effort. And it's equal to this. It's just the same thing and 1 , with a little correction, which is $1/2 (1 - l(l+1)/n^2)$. So actually, the expectation value of r in the hydrogen atom is l dependent. Not terribly strongly l dependent, but somewhat l dependent.

To get an idea, this is equal to $n^2 a_0$ times $3/2$ for l equals 0 . When l is equal to 0 , you see this whole bracket becomes $3/2$. And for the maximum l , l equals $n - 1$, this is roughly 1 . This is roughly 0 , to a good approximation but not exactly. It becomes $n^2 a_0$ with corrections that are very, very small. It's pretty accurate.

All right. So, first thing we've learned is that we got a radius, expected radius, that goes back $n^2 a_0$. So it's kind of interesting to see what went wrong if you would have thought with a form of the solution. So $\psi_{nlm} = R_{nl}(r) Y_{lm}(\theta, \phi)$, a polynomial, e^{-r/na_0} times Y_{lm} of theta and phi or $r^{l+1} e^{-r/na_0}$ times Y_{lm} of the solid angle.

And what do we know about this polynomial? It's of degree $n - l - 1$. That's it. And it depends on r . So what we're looking at is what was the error in thinking that the typical r was na_0 . And you see, when you make a mistake like this-- the mistake I made of saying oh, na_0 must be right-- and you find that it's wrong, it's very important to go back and learn why did you get the wrong answer. That's what we're doing now.

So the one question I can ask to begin with is what is a probability density to find the electron between some radius r and a radius $r + dr$. So, you know, this is a probability. And it depends on theta and phi. And it's very complicated. How about giving me a probability along r that they can integrate along r and visualize how this is dependant on r ?

So the probability to find the electron in this shell must be equal to the value of the wave

function squared times the volume element. And the volume element here is $\psi^2 r^2 \sin\theta dr d\theta d\phi$. So you have to integrate over solid angle. That is the volume element. And since I have to integrate over solid angle, I must have ψ^2 here. So that's the right equation.

If you want to make things look perfect, put the r^2 before the ψ^2 here. And the problem is that the r^2 is big enough that it, in some sense, has partial integrals. The ψ^2 notation is not perfect, but somehow you must imagine this whole volume element that is still infinitesimal but involves some integral already.

So you have this. And you get then $r^2 \psi^2$ and you have the integral, the $\int \psi^2 r^2 \sin\theta dr d\theta d\phi$. And that integral is exactly 1. Spherical harmonics are normalized.

So now I can cancel the dr . And I get that the radial probability distribution, which is a nice concept, is really $r^2 \psi^2$. Radial probability.

So our mistake-- my mistake must have been that I didn't include all that was relevant. The exponential is one part. But there is the polynomial. And the polynomial must be causing the trouble. Indeed, that's what is happening.

Let's look at ψ^2 from the top blackboard. That includes r^l times that polynomial. And it's a polynomial of that degree. So it begins like $a_0 + a_1 r + \dots + a_n r^n$. And then I have the exponential. OK.

Now I cannot do this-- I don't want to do this calculation exactly. It's too complicated. So let's ignore the lower part of the polynomial. And we're thinking the radius is going to be reasonably big. So it's a reasonable idea to keep the power of the polynomial that is the largest.

So what is the largest? And here you see a nice thing, actually r^l times this polynomial is a polynomial that begins with r^l and finishes with r^{n-l} . So it has like equal number of terms as reaches a value of $n-l$. The last term in the polynomial, when you multiply it in, this begins like r^l and the last term is r^{n-l} .

So let's take this to be proportional to r^{n-l} . And here is the part that actually changes the answer. Because this is ψ^2 . So actually I can write ψ^2 is proportional up to a constant of normalization, and the approximation they have then $r^2 \psi^2$. But I'm taking the last term of the polynomial, so we

get r to the $2n$ e to the minus $2r$ over na_0 . That's a probability distribution.

And with this probability distribution, then you see what's happening is that there is a fight between an exponential that has a typical length where it decays to half its value, that is related to na_0 but the maximum is delayed because it's multiplied by a function that the higher the value of n , the slower it is to take off. x squared or r squared takes off slower than r , takes off slower than r to the 4th.

So here you have a thing that just grows like that, but it takes forever to take off. And the result of this is a function that just picks up at some point over here. And we want to find the maximum.

So the maximum comes from taking a derivative. So the maximum of p of r is determined by setting the derivative of this equal to 0. So you get $2n$ over r times the same r to the $2n$ e to the minus $2r$ over na_0 .

So the first term, the derivative is $2r$ and r to the $2n$ minus 1, which is divided by r and the same thing. The second derivative gives you minus 2 over na_0 . And that's it. So from these two you get that n over r is equal to 1 over na_0 . So r equals n squared a_0 , as we had predicted. So it's the interplay of the polynomial with the other thing that makes the radius go very high.

So what about this Rydberg atoms in nature? Well, they've been observed in interstellar gases. You see, there was this phenomenon of recombination when protons captured electrons as the universe cooled off, and formed hydrogen atoms. And that recombination sometimes works in such a way that the proton can capture an electron. And it captures it in a very high quantum number. And it keeps happening as we observe this electron.

So people have observed in astrophysics n equal 350. And [INAUDIBLE] here the electron being captured, just not in the usual size but almost a million times bigger. So what happens for this thing r is equal 0.53 times 10 to the minus 10 meters. That's a_0 . And then you have 350 squared. And that gives you 6.5 microns. That's actually pretty big.

A blood cell is 8 microns. A red blood cell is 8 microns. They are not stable because eventually they spiral in. But if you have an atom that, for example, has an n equal to 5 , it jumps to n equals to 1 in 10 to the minus 7 seconds. These atoms are rather stable. Instead of lasting $1/10$ of a millionth of a second, they can last a millisecond, $1/10$ of a second, sometimes even

1 second. It takes a long time to go down that spiral.

The energy levels-- if you have energies that go like $1/n^2$, the energy levels, the separation between them, goes like $1/n^3$. So lots and lots of states there. And it takes a long time for it to decay from one to another.

So they observe them in the lab in different ways. They create them with lasers now. You have the outermost electron, you kick it to another orbit with one-- they use three lasers. In the lab at MIT, three lasers. One and two to kick it to an n equal 10, and then the third one to kick it to n equals 60.

And they detect those atoms by ionization. A normal atom, you can't ionize. You would need millions of volts per centimeter to ionize it with an electric field. These atoms you can ionize very easily. So they can see that they've been created that way.

So also in terms of sizes, the diameter of hair is about 50 microns. Hair is very thin. But you see it. So you're about a factor of 5 or 10 to being able to see that atom with your naked eye. It's pretty impressive. Incredible, in fact.

So a nice laboratory, those are almost semi-classical atoms. All what Bohr was doing of calculating, you can derive this law by assuming that the transitions between orbits in the hydrogen atom emit photons of the right frequency. It's all kinds of fun things.