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ROBERT FIELD: This is one of my favorite lectures for 5.61. And I hope you like it too.

OK, last time, we talked about the hydrogen atom. And it's the last exactly solved problem. And you've probably noticed that like the way I treated each of the exactly solved problems, I avoided looking at the exact solutions. I said we should be able to build our own picture based on simplifications.

And this is something that I really want to stress that, yes, the exact solutions are in textbooks. You can program them into your computers and ask your computer to calculate anything. But sometimes you want to know what it is you want to calculate and what is the right answer or approximately the right answer to build insights.

Now, in 5.112 and possibly 5.111 and certainly not 3.091 , you learn something about the periodic table. You learn how to make predictions about all properties of atoms based on some simple ideas. What are those simple ideas? I'm looking for three simple ideas. Yes.

STUDENT: Things with similar valence configurations behave similarly.

ROBERT FIELD: Yes, that's sort of a second order simple idea, that because-- I mean, it's using the idea that if you know that quantum numbers of the electrons and what orbitals are occupied, you can make connections between atomic and some molecular properties. Yes.

STUDENT: If you understand the interplay between nuclear charge and electric charge, you can derive large physical magnitudes.

ROBERT FIELD: Yes. I mean, there are things like electronegativity, shielding. And these are things where if we have some intuitive sense for how big orbitals are and what is the relative attractiveness to different nuclei of various orbitals, you build up everything. And most of it comes from this lecture.

And so I'm going to talk about the hydrogen atom as a model for electronic structure. And in particular, I'm to talk about quantum number scaling effects. And I'm going to be using this

So we know that for the hydrogen atom, you can factor the wave function into an angular part, which is universal. So if you understand it once for any problem, you understand it all the time. And so we can just put that aside, because that's a done deal.

And then there's the radial part. And the radial part is different for every central force problem. And so we want to be able to know what goes into the radial part and how to use those ideas to be able to understand almost any problem, even problems where there is more than one electron.

So I'm going to be making use of the classical, the semiclassical approach, where the classical momentum that's conjugate to the radius, in other words, the radial momentum, that we know what that is. It's related to the difference between the energy and the potential energy. And we get the momentum from that, the classical momentum function. And that gives us everything, because we use the DeBroglie relationship between the wavelength and the momentum. And I hope you believe what I'm going to try to do in the time we have for this.

So there are several important things that I didn't get to have time to do in lecture. And I want to mention them, because I probably will write a question on the final connected to spin orbit and Stern-Gerlach. So you want to understand those.

So the schedule for today is suppose you record a spectrum of the hydrogen atom. Now, that spectrum is going to reveal something that I regard as electronic structure, structure in this sense, not of bricks and mortar as you would talk about the structure of building, but what the architect had in mind and what the function of the building was. And so the structure is kind of a mystical thing, in which if you look at a little bit of it, you sort of get the idea of all of the rest.

And so here, I'm going to show you how you can approach a spectrum and to know where you are, because the spectrum can be really complicated. And there are certain patterns that knowing about electronic structure enables you to say, yeah, I've got a Google map. I know exactly where I am. And it's based on some simple ideas.

So this is first illustration of structure. Then I'm going to go and deal with the semiclassical methods for calculating all electronic properties of the hydrogen atom. And we get this business of scaling of properties with the principal quantum number. And that extends to Rydberg states of everything-- atoms and molecules-- not just the one electron spectrum.

And the Rydberg states are special because one electron is special. It's outside of all of the others. And what we're going to learn about next time when we have many electrons or more than one, we don't have to think about antisymmetrization. We don't have-- we can still take our simple minded picture of an electron interacting with something. And so we can then take what we knew from hydrogen and describe everything about Rydberg states of molecules. And that's kind of exciting.

And this will be followed by the bad news that when you have more than one electron, you have to do something else. You have to write antisymmetric wave functions, antisymmetric with respect to the exchange of all electrons. And that looks like it's going to lead to a tremendous headache. But it doesn't. But you do have to learn a new algebra.

OK, so let's go on to this. OK, so for the hydrogen atom, it's easy to solve the time independent Schrodinger equation. And we get a complete set of these Rnl radial functions, complete set, an infinite number. We don't care.

You can take this-- it's a simple one-dimensional differential equation. And you can solve it. You can tell your computer to solve it. You don't have to have any tricks at all. You can just use whatever numerical method to find the wave functions and calculate whatever you want. There's no insight there.

It's the same thing as recording a spectrum, where you have tables of observed lines and maybe observed intensities. You don't know anything. It's a description. And you can have a mathematical description, or you can have an experimental description. You don't know anything. You want to have your insight telling you what's important and how to use what you know about part of the spectrum to determine other things.

For example, we have two energy levels. Let's say $n$ equals 1 and $n$ equals 2. And there are several things that you would need to do in order to know what the selection rule for I is from this, because the $I$, the orbital angular momentum states of $n$ equals 2 are degenerate. And so you could use the Zeeman effect. You can use radiative lifetimes.

And what you would find is we have a p state and an s state. And the p state fluoresces to the $s$ state and the s state doesn't, unless you apply an electric field and it mixes with a p state and it then fluoresces. So there are all sorts of things that will alert you to the fact that there's more going on here than just this simple level diagram.

OK, so let's do some elementary stuff and then get to the Google map for the spectrum. We have this thing that makes the hydrogen atom interesting. The potential, the radial potential is a function of the orbital angular momentum. And the effective potential is given by $h$ bar squared I, I plus 1, over 2 mu r squared-- and that's with a plus sign. And we have ze squared over 4 pi epsilon 0-- that's just stuff from the MKS units for the Coulomb equation-- and 1 over r.

So we have an attractive thing that pulls the electron towards the nucleus. And we have a repulsion part, which keeps the electron away as long as I is not equal to 0 . So this is the actual effective potential. This is the thing we would use for solving the Schrodinger equation for the Rnl of R functions exactly if you wanted to.

And first surprise is that the energy levels come out to be-- for $n$ equals $1,2,3$, etc. So why are the energy levels not dependent on I? Because it takes more ink to write this than that. And this can be really important. But there is no I dependence. That's a surprise. It's not true for anything other than one-electron spectra.

But if it's true and it has to be, you have to have something that says, OK, for something that's not hydrogen. Maybe there will be some I splitting. Why? Why is that? How does this effective potential have an effect for something other than hydrogen? And we'll understand that in a second.

OK, now there's the question of degeneracy. So if we pick a value of $n$, we can have I equals 0,1 , up to $n$ minus 1 . That comes out of the mathematics. And I'm just assuming that you can accept that as a fact. We know from our study of the rigid rotor for the Ylm functions that the degeneracy of the I part of the wave function goes as 21 plus 1 . If we have an orbital angular momentum of 0 , there's a degeneracy of 1 . Angular momentum of 1 , it has a degeneracy of 3 . We know that.

So if we do a little game. And we look at the degeneracies for I equals $0,1,2,3$, the degeneracies-- so g subl I , is $1,3,5,7$. OK, now, the degeneracy for n is going to be all of the possible l's. And so if we have $n$ equals 1, we only have one l. And so the degeneracy is 1 . If we have $n$ equals 2 , we have $p$ and $s$. And so we have 4. And for $n$ equals 2 , we have--

I'm sorry, for $n$ equals 1 , we have only 1 . And then we have for $n$ equals 2,4 . And for $n$ equals 3 , 9 . So you see 1 plus 3 is 4 . 1 plus 3 plus 5 is 9 . And so the degeneracy for $n$ is $n$ squared.

So as you go really high end, you get lots of states. And for hydrogen, they're all degenerate. But if they're not split, maybe you don't care. Of course, you do.

I better leave this down.

Now, here we are for-- suppose you take a spectrum. And suppose it's an emission spectrum. You run a discharge through gas of something that contains hydrogen. And you'll see a bunch of lines.

And so one of the things you know is that the energy levels are separated-- they go as 1 over n squared. And so the energy levels-- well, actually, they're converging. And so let's just indicate that like this.

So suppose you ask, well, suppose I'm at this level, there are going to be a series of transitions converging to a common limit from it. And that's a marker, a pattern in the spectrum. If you have essentially an infinite number of levels converging to a fixed point, that's easy to see.

And so for each level, there will be convergence to the same fixed point. And so that tells you there's a kind of pattern recognition you would do. And you would begin to build up the energy level diagram and to know which levels you're looking at from these existence of convergent series.

So if we're interested in the spectrum, we have the energy level differences, z squared Rydberg 1 over n squared minus 1 over n prime squared. That's the Rydberg equation. And so this also tells you something.

So suppose you're in the nth level, well, you know this. And now this then converges to the ionization limit. But there's something else.

And that is suppose we observe two consecutive members, n an plus 1. You don't know what n is, but because you see the pattern of this convergent series, you can see two levels that are obviously consecutive members of a series. And the question is what is $n$ ?

And, again, you can solve that by knowing that the energy levels go as 1 over $n$ squared. So the difference between energy levels goes as 2 z squared r over n cubed. This is just taking the derivative of 1 over $n$ squared. We get 2 times 1 over $n$ cubed. And so that kind of a pattern enables you to say, oh, yeah, I know what n is.

So this is a kind of a hand waving, but this is what we do as spectroscopists. We're looking for a clue as to how to begin to put assignments on levels. And because there is this simple structure, which is represented by this Rydberg equation, we can say where we are. We know where we are.

We have two choices. One is this 1 over $n$ cubed scaling of the energy differences. And the other is the existence of a convergence of every initial level to a common final level. And that's very important. You can't assign a spectrum unless you know what the patterns are. And these are two things that come out of the fact that there is a structure associated with the hydrogen atom.

OK, now, I'm going to have to put some numbers on the board. And it's another illustration of structure.

Now, I'm just taking things from a table in McQuarrie. And this table is a table of expectation values of integer powers of $r$. And what is this? Every electronic property, anything you would measure is going to be a function of the-- is going to involve an integral involving a function of r. That's what we mean by electronic properties. And these electronic properties have a wonderful behavior.

So let's make a little table. Here is the integer power. Here is the expectation value. And that's I.

So we start with $n$ equals 2 . The result you get by actually accurately evaluating an integral-and these are doable integrals. They are not numerically evaluated. And they have a simple formula-- a0 squared $n$ to the fourth $z$ squared times 1 plus $3 / 2$ times 1 minus I, I plus 1 minus $1 / 3$. These are done integrals. I can't do them. I wouldn't care to do them.

So that's how any electronic property that goes as the square of $r$ behaves, we get this. This is the Bohr radius. This is approximately half an angstrom. And it's the radius of the n equals 1 Bohr orbit, which doesn't even exist. Right? There are no Bohr orbits. But we have this Bohr model, which explains these energy levels. And so we use that.

And there's nothing else here. That's the charge on the nucleus. Well, it's 1 for hydrogen. But there's nothing empirical here. And this is a sort of a fundamental constant now, but it's sort of empirical.

And then the next one, it has a very interesting initial term, a 0 not squared n squared over z . We've lost a power here. And it again is one of these complicated looking functions.

OK, this $r$ to the 1, that's how big an atom is, the radius of the atom. And again, we have a closed form. Notice that the I is present here, even though it's not present in the energies. 0, that just goes n to the 0 power. It's just a constant minus 1 , minus 2 , minus 3 .

Well, minus 1, that's what you have for the Coulomb attraction. And that goes as zover a0 n squared. And for minus 2, that goes as z squared a0 n cubed. And all that plus 1/2. And for minus 3 , we get $z$ cubed $a 0$ cubed $n$ cubed $I$, I plus $1 / 2$, I plus 1 . So there are all these formulas.

Well, the important thing is the leading term. And what you discover is that right here something happens. The leading term goes as 1 over $n$ cubed. It doesn't matter what the negative power of $r$ is. The leading term goes as 1 over $n$ cubed.

Why's that? Well, that's really important, because this 1 over n cubed behavior is telling you something very important.

So here's the nucleus. And here's the electron. We can think of it as a Bohr orbit.

If we have a negative power of $r$, then as you get farther and farther away from $r$, the property gets small. And so what happens is for large enough negative powers of $r$, the only thing that matters is the first lobe, the innermost lobe of the wave function. And it turns out that's the only thing that matters for almost everything. And so one of the things I'm going to show you is why does the innermost lobe matter and how do we use that to understand everything, not just about hydrogen, but about Rydberg states of everything.

So the scaling of electronic properties depending on the power of $r$ is another example of structure. And if you know one thing about the hydrogen atom, if you make one measurement, if you know how to use it, you know everything. You don't have to do all this other stuff. That's a really beautiful example of structure.

And this is insight too, because sometimes the structure that you have for hydrogen is only approximately valid for other things. And you're going to want to know what you can use and know how to modify it. And I guarantee you that nobody teaching a course like this would ever talk about that kind of stuff, because, you know, it's approximate. It's intuitive. And all the good
stuff is tabulated in the textbooks and you have to memorize it. But you don't know how to use it. And this is how you use it. This is really important.

So now let me draw some pictures. So this is hydrogen. This is sodium. This is carbon monoxide.

So the electron sees a point charge in hydrogen. That's easy. Now in sodium-- we don't know yet why, but once l've talked about helium and many atoms, you will know why-- there are a whole bunch of electrons in the nucleus or in the core of sodium.

And outside the core, you have something that looks hydrogenic. But there is this core. It's not a point. And that leads to the appearance of I dependence in the energy levels, because what you're going to find is that I equals 0 penetrates into the core. I equals 1 can't.

And so as you have higher and higher I, you're seeing less and less of this. And so as a result, there is an I dependence. But it's an s emphatically decreasing one. As I increases, you get less and less sensitivity to this inner part.

Now, CO isn't even round. But there are nuclei. But if you have an electron at a high enough end, it's outside of this core. But again, if you pick I-- now, you can't have I for something that's not round. But if you're far enough away from it, you can pretend it's round and use the not roundness as a perturbation.

And so you can have Rydberg states of CO. And you can use the same ideas that we developed for the hydrogen atom to explain the Rydberg states of CO, anthracene-- I don't even know how to say the names of biological molecules. So just consider it. If you had it in the gas phase and you could make a high enough Rydberg, high enough end state, it would look following this kind of extrapolation with features common to hydrogen.

OK, so now, semiclassical-- OK, remember, you can calculate this. If you want to use rigorous mathematics, you can find an analytic solution for this, for hydrogen. And that's good, but you haven't extracted any insight from it. You just have it. But the semiclassical theory extracts insight.

So semiclassical theory starts out with writing the classical equation for the momentum. And the momentum as a function of $r$, that's a no-no from quantum mechanics. You can't ever say we know the momentum as a function of $r$. And it's also true in quantum mechanics, whenever you calculate an integral that you need to evaluate some property, you're evaluating it over all
space. But what I'm going to show you is that many of these integrals accumulated a specific point in space, which is a reminder of the classical mechanics.

So there are things where quantum mechanics says you have to do something, but there's insight waiting to be harvested because many of the things you have to calculate are trivially interpretable in terms of semiclassical ideas. And the semiclassical means classical. You can do classical mechanics. You can calculate the probability of finding a particle at a particular place. And you can use that information here.

And so always the relationship between the classical momentum function and the potential is this equation. p squared over 2 mu is the momentum. And energy minus potential is the momentum, is the kinetic energy. And this is how you get there.

OK, so this is the function. And so that's one of the important pieces. And the other important piece is really unexpected, but wonderful.

And so we have this VI of r . If I is 0 , the inner wall of the potential is vertical. If I is not 0 , the inner wall of the potential isn't quite vertical, but it might as well be because when $r$ gets small, even the I I plus 1 over r squared term gets small. And so we get this vertical potential.

And so what happens is we can use the idea from DeBroglie and say, OK, where is the first lobe? Where is the first node? Well, it's half a wavelength from the turning point. So if we know where the turning point is we can draw something that looks like that. Now, it's a wave function, so it's going to be oscillating.

So the important thing is that the first lobe, the innermost lobe, of all n and I lines up because this is nearly vertical and the energy distance from here to the bottom of the potential at $r$ not equal to 0 is really large. And so if you change n or I by 1 or 2 , nothing much happens.

And so if you just say, OK, for $n$ greater than or equal to $6,6,36$, the Rydberg constant divided by 36 is not a big number, 3,000, 3,000 wave numbers. The vertical distance is more than 100,000 wave numbers. So the correction from $n$ equals 6 -- so if we have $n$ equals $6, n$ equals 7, there isn't much change. And so the first lobe is going to always be at the same place.

And so one thing that happens is they line up. The first node for all n and I is at the same place, to a good approximation. And the amplitude in this first lobe scales as $n--$ so the amplitude scales $n$ to the minus $3 / 2$. I'm going to prove that. This is where all the insight
comes from.

If you have a property, which is essentially determined close to the nucleus, because you have a negative power of the $r$ in the electronic property, then the amplitude of the wave function will scale as n to the minus $3 / 2$. And we can use this in evaluating all integrals, because everybody has a lobe here, at the same point. And the only thing that's different from one state, at one $n$ I and another is the amplitude of this lobe. And that goes as 1 over $n$ to $3 / 2$ power.

OK, that's what I was afraid of. OK.

So we're interested in turning points. And what's the definition of a turning point? Or what is the mathematical equation that tells you how to get the inner nuclear dis-- the $r$ value for the turning point. Yes.

## STUDENT: Derivative equals 0 .

ROBERT FIELD: I'm sorry.

STUDENT: $\quad$ When the derivative of VId r equals 0 .

ROBERT FIELD: I'm not looking for that. I'm looking for-- so when the energy is equal to VI of r , plus or minus. That's the equation that tells you where the turning points are. And these are simple equations. So it's child's play, adult child's, to calculate what the inner and outer turning point is as a function of n and I .

And so we know the effective potential. We pick an energy. We know what it is because it's the Rydberg over n squared. So we have enough to calculate this function, which is a 0 n squared 1 plus or minus 1 minus I I plus 1 over $n$ squared square root.

Now I could derive this. You could derive this. It's a simple closed form equation. And that's the foundation of all of this.

Now, the thing that's common for everything is the inner turning point, $r$ minus, because what we're interested in is this. Where is the maximum or where is the first node and what is the amplitude? And so we're going to use this equation to get all that.

All right, so the semiclassical theory lambda n I-- that's the wavelength-- is equal to h over Pr of $r$. That's DeBroglie. But it's generalized to a potential, which is dependent on $r$, or a
momentum function, which is dependent on $r$.

So now, we have to calculate several important things in order to build our model. One is the classical oscillation period. So if I told you we have a harmonic oscillator, we know the energy level spacing things are h bar omega. And they're constant. If we make a superposition state of a harmonic oscillator, there's going to be beat nodes at integer multiples of omega.

So we can simply say, well, for Rydberg states or for anything, we can define the period of oscillation as $h$ over, in this case, $n$ plus $1 / 2$ minus $n$ Vn minus $1 / 2$. This is the energetic separation between levels-- or even not levels. We have a formula that's giving the independence of the energy. So this is related to the period that we get from the harmonic oscillator. So this is a perfectly legitimate way of knowing the period.

Well, when we do that, this is something I wrote down before, the energy separation of two levels differing in n by 1 centered at n is going to be the Rydberg divided by $2 \mathrm{n}-\mathrm{-}$ well, I'll just write it down.

So we have h. And now this hcR 2 over $n$ cubed. And $n$ cubed is really important. It came just from taking the derivative of the 1 over $n$ squared energy dependent. So this is a formula that's perfectly legitimate. What n tells us is the period is proportional to n cubed. The higher you go, the slower you go.

Second, node to node probability. So how long does it take-- you have this well. And I don't mean to draw it like a harmonic oscillator, but it's a well. And so you have a node here, and you have a node here. And you have a particle that's moving, classically.

How long did it take for the center of the particle to go from here to here? That's an easy thing to calculate too, because we know classically what the momentum is at any point in space. The momentum is related to the energy difference between here and here.

So what we're going for is the ratio of the time node to node, or to next node, to delta t turning to turning point. OK, well, this is $1 / 2$ the period, right? So we know what $1 / 2$ the period is. And the period goes as n cubed.

So this is the probability of finding the particle within one lobe of the wave function. So we can calculate the probability of finding the particle within one lobe. And it's clearly going as 1 over $n$ cubed.

Now, we want an amplitude. What is the amplitude? It's square root of the probability. All of a sudden, we start to see that the amplitude in whatever lobe we want goes as 1 over n to the $3 / 2$. Now, because we have this lining up of nodes, the first node and the first lobe being identical, what we have now is the scaling of the probability or the amplitude in the first lobe of the wave function.

And the next thing is again something that's almost never talked about in textbooks, but it's a really fantastic tool for understanding stuff is suppose we want to know the value of an integral. So we have an integral. And that will be, say, the electronic wave function in this chi representation, as opposed to the Rnl representation.

OK, so this is the integral we want. But what we really want is a way of saying, I can convert this integral to a number that I can figure out on the back of a postage stamp. No methods for integration. No numerical methods. Just insight.

So we have some electronic property, which comes from this integral. But now, this is a rapidly oscillating function. This is another rapidly isolating function. And so if we were to ask, well, how does the integral accumulate? In other words, let's say we're integrating from $r$ minus to $r$ prime chi $n$ I of $r$ r of $k$ chin prime I prime of $r$ Vr. So if we plotted the integral, the value of the integral, as it accumulates-- so we're not evaluating the whole integral. We're evaluating the integral up to the $r$ point, the $r$ prime point.

And what we see that there is a stationary phase point, where at some point in space, the two functions are oscillating spatially at the same frequency. And we already saw this for Fermi's golden rule, right. You have a time integral where you have rapidly oscillating functions. And then when the applied frequency is resonant with the difference in frequency, we get the integral accumulating. So same thing. It's easier.

And so we have this idea that there is a stationary phase point. And the integral accumulates from 0 to its final value there. And then there's just little dithering as you go out the rest of the way.

You get in complications when they're two stationary phase points, because then there's destructive or constructive interference between them. But it's very rare that you have two.

You only have one. And so if you know the amplitude of the wave functions at a stationary phase point, you can calculate the integral as a product of three things. No integration, just
one number. And the thing that we care about is that almost all electronic properties accumulate in the innermost lobe, because they're the same. The wave functions are the same. And they get more and more different as you go farther out.

And as a result, since the amplitude in this innermost lobe goes as 1 over $n$ to the 3/2 and you've got two functions-- you've got the nl function and the n prime I prime function-- you have that the integral is proportional to 1 over $n$ to the $3 / 21$ over $n$ prime to the $3 / 2$. So not only do you get expectation values, you get off diagonal matrix elements.

Now this is not exact. But it tells you this is the structure of the problem. And if I look at enough stuff, this is really important to say, how does everything scale? And if you know how things scale, you know that if you're combining things that aren't part of that scaling rule, that they're just not going to be relevant.

This is a fantastic simplification, because, yes, you can do it exactly by programming your computer to calculate the integral numerically. And that's not a big deal. But you don't know anything. And here, you know what to expect. And this is a professional spectroscopist who survives by recognizing patterns and using patterns. This is beyond numerical integrals. This is actually understanding the structure of the problem.

And the fact that the molecule gives you this beautiful-- or the atom gives you this beautiful lobe always at the same place, you know stationary phase. Now, there are other problems where you use the stationary phase approximation. You always want to be trying to use stationary phase.

For example-- and I'm going to stop soon-- suppose you have two potential energy curves. Now, you don't know what a potential energy curve for a molecule is yet. But you can imagine what there is. And so they cross.

And this is the place where at this energy, this curve is exactly the same as the momentum on that curve. And so the integral accumulates at this curve crossing point. Isn't that neat?

If you know what the curve crossing point is, you know the amplitude of the wave function. And you can estimate any integral. So this is something you would use if you're actually creating new knowledge again and again, because it's deeper than the actual experimental observation. It's the explanation for it. And it's what you're looking for and how you use your knowledge of what you're looking for.

That's why I like this lecture, because it really gives the approach that I take to all scientific problems. I look for an approximate way where I don't have to do any complicated mathematics or numerical integration. I can do that just sitting at my desk.

OK, so on Friday, we'll hear about helium and why helium looks horrible, but isn't.

