

FEMALE

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SPEAKER:

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PROFESSOR:

So we're now starting to get into a really familiar territory, which is the hydrogen atom. And it's a short step from a hydrogen atom to molecules. And we're chemists. We make molecules. But one question that would be a legitimate question to ask is, what does a hydrogen atom have to do with molecules, because it's an atom and it's the simplest atom.

And what I hope to show is that what we learn from looking at the hydrogen atom has all sorts of good non textbook stuff that prepares you for understanding stuff in molecules. And I am going to stress that because you're not going to see it in McQuarrie and you've probably never seen it elsewhere except in freshman chemistry when they expect that you understand the periodic table based on some simple concepts. And they come from the hydrogen atom. And so I'm going to attempt to make those connections.

My last lecture was I told you something you're not going to be tested on. But it's about spectroscopy. That's how we learned almost everything we know about small molecules and a lot of stuff about big molecules too. The crucial approximations in that were the dipole approximation where the radiation field is such that the molecule field's a uniform but oscillating electromagnetic field.

In developing the theory that I presented, we assume that only one of the initial eigenstates is populated at t equal zero. And only one final eigenstate gets tickled so that it gets populated. And so even though there is an infinity of states, the theory specifies we start with one definite one and only one final state gets selected because of resonance. And this is what we do all the time. We have an infinite dimension problem, and we discover that we only really need to worry about a very small number of states. And then we deal with that.

There are a couple other assumptions that were essential for this first step into a time-dependent Hamiltonian. And that is the field is weak and so you get linear response. That means that the increase in the mixing coefficient for the final state is proportional to the coupling matrix element times time.

Now mixing coefficients can't get larger than 1, and so clearly we can't use a simple theory without saying, OK, we don't care about the mixing coefficients. We care about the rate of increase. And so by going from amplitude to rates, we are able to have a theory that's generally applicable.

Now what I did was to talk about a CW radiation field, continuous. Many experiments use pulsed fields. Many experiments use an extremely strong pulsed field. That I hope to revisit later in the course. But the CW probably is the best way to begin.

So now let's talk about the hydrogen atom. We did the rigid rotor, and that led to some angular momenta. Well, let's just picture. So we have this rigid rotor, and it's rotating about the center of mass. And the Schrodinger equation tells us the probability amplitudes of the rotor axis relative to the laboratory frame. And we got angular momenta, which we can denote by a little l , big L , J , and many other things.

And this is important because, if it's an angular momentum, you know it. You know everything about it. And you don't know yet that, if you have two angular momenta, you could know everything about the interactions between them. That's called the Wigner-Eckart theorem. That's not in this course. But the important thing is, if you've got angular momenta, you're on solid ground and you can do stuff that doesn't ever need to be repeated.

And so one of the things that we learned about the angular momentum was that we have-- even though it's going to be L as the angular momentum mostly in the hydrogen atom, I'm going to switch to J , which is my favorite notation. So J^2 operating on a state-- now I can denote it like this or I can denote it like this. It's the same general idea. These are not quite equivalent things. And you get $\hbar^2 J(J+1)$. And we have J_z operating on JM . And you get $\hbar M$. And we can have J_{\pm} operating on JM . And that's \hbar times this more complicated looking thing, $J \pm 1$ minus M , $M \pm 1$. So that's the only bit you have to remember.

And you might say, well, is it plus or minus 1 or minus or plus 1? And so if you choose-- M is equal to J . Then you know that if you have M is equal to J , this is going to be 0 if we're doing a raising operator. And so there's nothing to remember if you are willing to go to an extreme situation and decide whether it's plus minus or minus or plus.

Now the rigid rotor is a universal problem, which is solved. It deals with all central force problems. Everything that's round, the rigid rotor is a fantastic starting point. So one-electron

atoms for sure-- many-electron atoms, maybe. We'll see. But anything that's round, the rigid rotor is a good zero point for dealing with the angular part of the problem.

So for the hydrogen atom, we have a potential. It looks like this. And so the radial potential is new. For that rigid rotor, the radial potential was-- it's just 0 for the R is equal to R zero. And not zero-- then the potential is infinite.

Now here we have potential, which doesn't go to infinity here and it does something strange here because you can't get to negative R in spherical polar coordinates. So is it a boundary condition or is it just an accident of the way we use coordinates?

So we're going to apply what we know about angular momenta to the hydrogen atom. So our potential for the hydrogen atom is going to be expressed in terms of the distance of the electron from the nucleus and then the θ ϕ coordinates, which you already know. And the θ ϕ part is universal, and the R part is special to each problem that has physical symmetry. And there are different kinds of approximations you use to be able to deal with them.

The nice thing about it is it's one dimensional, and we're very good at thinking about one dimensional problems. And even if the problem isn't exactly one dimensional or it has some hidden stuff to it, we can extend what we know from one dimensional problems and get a great deal of insight.

And if you have a one dimensional problem, it's very easy to describe the potential in one dimension and the eigen functions in one dimension. And so we can begin to really understand everything. So we're going to have a wave function, which is going to have quantum numbers. And we're going to be able to write it as a product of two parts.

Well, this is the same thing we had before for the rigid rotor. So we're going to be able to take this rotary equation and separate the wave function into two parts, a radial part and an angular part. And this is old and this is new.

Because we've got this, we can use all of that stuff without taking a breath, except maybe getting the right letter L , J , S , whatever. So really the hydrogen atom is just one thing with some curve balls thrown at you in the latter stages.

One of the things you also want to be able to do-- because nodes are so important in

determining both the names of the states and how they behave in various situations, including external fields and excitation by electromagnetic radiation-- you want to be able to understand the nodal surfaces. And you already know this one.

So how many nodal surfaces are there if you have a particular value of L ? Yes.

AUDIENCE: L .

PROFESSOR: Right, and if you have a particular value of M , how many nodes are there in the xy plane? You're hot--

AUDIENCE: I mean, I know if M is 0, the entire angular momentum is tipped into the xy plane. So that means that the axis of the rotor has to be orthogonal to the angular momentum. So that means that the probability density is oriented along Z , I think.

PROFESSOR: Now you're saying things that I have to stop and think about because you're not telling me what I expected to know. So if M is equal to 0, L is perpendicular to the quantization axis, and there are no nodes.

AUDIENCE: Well, it depends on if you're talking about the nodes of the probability density of the rotor, where the axis is.

PROFESSOR: That's true, but where the axis is determined by θ . And when θ is equal to $\pi/2$, you're in the xy plane. And the number of nodes in the xy plane is M , or absolute value of M . The ϕ part of the rigid rotor is simple. It's a differential equation that everybody can solve. We already know that one, and we know what the wave functions look like.

We can write the hydrogen atom Schrodinger equation, and it's very quick to show separation of variables. And I'll do that in a minute. And then we have the pictures of the separated parts-- R_{nl} of R and Y_{lm} of θ ϕ .

And essential in these pictures is the number of nodes. In the spacing between nodes, remember the semiclassical approximation. We know that Mr. DeBroglie really hit it out of the park by saying that the wavelength is h/p . For every one dimensional problem, we know what to do with that. And we're going to discover that, for the radial problem, we have a very simple way of determining what the classical momentum is. And so we know everything about the nodes and the node spacing and the amplitudes between nodes and how to evaluate every integral of some power of R or Z .

And so there's just an enormous amount gotten from the semiclassical picture once you are familiar with this. And so we can say that we have the classical wavelength, or the semiclassical wavelength. It has an index R . So we have a momentum, a linear momentum with a quantum number on it for L . See, that's a little strange.

But that tells us what the potential is going to be and that tells us what to use in order to determine the wavelength. And this is really the core of how we can go way beyond textbooks. We can do-- in our heads or on a simple piece of paper, we can do this. And we can draw pictures, and we can evaluate matrix elements. Without any complicated integral tables, you can make estimates that are incredibly important.

And from that you can get expectation values and also off-diagonal matrix elements of integer powers of the coordinate. That's an enormous amount of stuff that you can do. Now you can't do it yet. But after Wednesday's lecture, you will. And so this will be Wednesday. And then we'll have evidence of electron spin. And I will get to that today.

So this is the menu. Now let's start delivering some of this stuff. I have to write some big equations. So the Hamiltonian is kinetic energy plus potential energy, and kinetic energy was-- I'm sorry. For the rigid rotor, V was zero. And everything was in the kinetic energy. Well, it's not quite true.

And so, for hydrogen-- so we know this is P squared over 2μ , and μ for the hydrogen atom, reduced mass. And we know this is just Coulomb's Law, minus e squared over $4\pi\epsilon_0 R$, \hbar squared. I'm sorry-- it was supposed to be e squared. So this is the classical--

So these are the parts. But the since it's spherical, we're not going to work in Cartesian coordinates. And in fact, that's a very strong statement. If you have a spherical problem, don't start in Cartesian coordinates because it's a horrible mess transforming to spherical polar coordinates. Just remember the spherical polar coordinates.

So you know how spherical polar coordinates work. I'm not going to draw it. So the kinetic energy term is-- and this is the Laplacian, and that's a terrible thing. And Δ squared-- it looks like it's going to be a real nightmare partial with respect to R , R squared partial with respect to R . And we have 1 over R squared sine squared theta partial with respect to theta, sine theta partial with respect to theta. And then a third term-- 1 over R squared sine squared. I got a

square here. That's wrong.

And this is sine squared theta. I heard a mumble over there. Yeah, but I'm just doing Del squared.

AUDIENCE: With your first Del, it's H plus squared.

PROFESSOR: My what?

AUDIENCE: Your first time you used the Del operator, it's H plus squared.

PROFESSOR: Oh, yes, yes.

AUDIENCE: And then the second one, if you could clarify that that's a Del--

PROFESSOR: I'm sorry.

AUDIENCE: The second Del squared, if you could clarify that's a Del squared. It looks like a--

PROFESSOR: It looks like a terrible thing. And the last part is a second derivative with respect to phi. This looks like a terrible thing to build on. But with a little bit of trickery-- and that is, suppose we multiply this equation by R squared-- then we have killed the R squared terms here and here. And we're going to be able to separate it.

And so we are able to write an equation which has the separability built in-- and so partial with respect to R, R squared partial with respect to R plus L squared plus 2 mu H R squared V of R minus E psi. That's a Schrodinger equation.

So we have an R dependent term and another R dependent term and a theta phi dependent term all in this one, nice operator that we've understood. So now there's one more trick. In order for the shorter equation to be separated into a theta phi part and an R part is we need a commutator. And so that commutator is this.

What is a commutator between L squared and any function of R? Yes.

AUDIENCE: Their operators depend on different variables?

PROFESSOR: Absolutely, that's really important. We often encounter operators that depend on different variables. And when they do, they commute with each other, which is an incredibly convenient thing because that means we can set up the problem as a product of the eigenfunctions of the

different operators. So this means that we can write a theta phi term, which we completely know, and an R term, which we don't know and contains all of the interesting stuff.

So let's forget about theta and phi. Let's just look at the R part. Well, the way we separated variables, we had the Schrodinger equation and we divided by the wave function, which would be of R of R, Y L M of theta phi. And on one side of the equality, we have only the angle part. And so when we do that, when we divide by R, we kill the R part on this side. And on the other side, it's the opposite.

And so we get two pieces-- one is only dependent on theta and phi and one is only dependent on R. So they both have to be a constant. So we get two separate differential equations. And we've already dealt with one of them.

So what you end up getting is 1 over R of R times stuff times R of R is equal to 1 over YLM L squared YLM-- sorry. So this is the separation. This is all R stuff. This is all theta stuff and separation constant. Well, this one is inviting a separation concept because L squared operating on YLM is H bar squared, LL plus 1. That's the separation constant.

So now let's look for the only time at the R part of the differential equation. And so this writing out all the pieces honestly-- we have-- there's one more. So that's the Schrodinger equation for the radial part. It looks a little bit annoying.

The important trick is that we've taken the separation constant, and it has an R dependence but when we divide through by $2\mu HR^2$. And we say, oh, well, let's call these two things together-- V_L of R. This is the effect of potential, and it depends on the value of L.

So this is just like an ordinary one dimensional problem except now, for every value of L, we have a different potential. And this potential is-- OK, when L is not equal to zero, this potential goes to infinity at R equals 0, which is bad, except it's good because it keeps the particle ever from getting close to the nucleus.

And that's what Mr. Schrodinger-- I'm sorry what Mr. Bohr was thinking about, that we have only circular orbits or we have only orbits that are away from the place where the Coulomb interaction would be infinite. And I mean, there are several things that's wrong with Bohr's picture. One is that we have orbits. And the other is that we don't include L equals 0, but this is telling you a lot of really important stuff because the value of L determines the importance of this thing that goes to infinity at R equals 0. And that has very significant consequences as far

as which orbital angular momentum states we're dealing with.

So we're going to get the usual LML quantum numbers, and we're going to get another one from the radial part. And since this is a 1D equation, there's only one quantum number. And we're going to call it L. And now there's this word principal, and there's really two words-- principle with an LE and principal with an AL. Which one do you think is appropriate? I'm sorry. I can't hear.

AUDIENCE: AL.

PROFESSOR: AL is the appropriate one. Principle has to do with something fundamental. Principal has to do with something that's important. And I can't tell you how many times people who should know better use the wrong principal. You'll never do that now because it was like, what's ν ? C over λ . So this is the right principal.

If we do something clever and we have the radial part and we say, let us replace it by 1 over R times this new function χ_L of R , well, when we do that, this equation becomes really simple. So what we get when we make that substitution is \hbar^2 over 2μ H second derivative with respect to R plus V_L of R minus E χ_L of R is equal to 0 . That looks like a differential equation we've seen before.

It's a simple one dimensional differential equation-- kinetic energy, potential energy. But it's not. There's some kinetic energy hidden in the potential energy. But this is simple, and we can deal with this a lot. I'm not going to. But if you're going to actually do stuff, you're going to be wanting to look at this differential equation. But I'm going to forego that pleasure.

One of the problems with the radial equation is the fact that R is a special kind of coordinate. It can't go negative. And so treating the boundary condition for R is equal to 0 is a little subtle. And it turns out that when L is equal to 0 , then R of 0 is not 0 . But for all other values of L , R of 0 is 0 .

And all of NMR depends on L being 0 because the electron feels the nucleus. It doesn't experience an infinite singularity. It feels the nucleus. And when L is not equal to 0 , then it's sensing the nucleus at a distance. And that leads to some very small splittings called hyperfine. And so there's different kinds of hyperfine structure. But anyway, this is a really subtle and important point. How much time left? Yes? No.

So now pictures of orbitals-- So the problem with pictures of orbitals is now we have a function

of three variables and it's equal to some complex number. So we need two degrees of freedom to present a complex number and we have three variables. And so representing that on a two dimensional sheet of paper is horrible. But we have this wonderful factorization where we have R_n of R . And we could draw that easily. We don't need any special skill. And we have Y_{lm} of θ ϕ .

And we've got lots of practice with that, although what we've practiced with may not be completely understood yet. So we have ways of representing these. And so we go through the understanding of the hydrogen atom by looking at these two things separately.

Now for the radial part, the energy levels-- where this is the Rydberg constant. It's a combination of fundamental constants. And for hydrogen, the Rydberg constant is equal to $109,737.319$ -- there's actually more digits, wave numbers-- times μ_H over μ_∞ . Well, this is actually the Rydberg constant for an infinite mass.

And so μ_H is equal to the mass of the electron times the mass of the proton over the mass of the electron plus the mass of the proton. Now the mass of the proton is much bigger than the mass of the electron. And so you can use this as a trick. You can say, well, what is it? Well, we know what this is. It's easy to calculate.

But there are two limits. What is the smallest possible reduced mass? And that would be for-- if the mass of the proton is infinite, then we just get the mass of the electron. That's the biggest reduced mass. And the smallest is, if we have positronium, where we have an electron bound to a proton-- and then when we do that, we get half. I'm sorry. It's not a proton. It's a positively charged particle, which we call a positron.

And so each of the terms here is the mass of the electron. And so the range is from $1/2 m_e$ to m_e depending on what particles you're dealing with. And so that's a useful thing. And so the Rydberg constant for hydrogen is smaller than the reduced mass of the infinite. I'm sorry. It's smaller than that for the infinitely mass nucleus. And it is the value that made Mr. Bohr very happy-- 679.

So the important thing is this mass scaled, or reduced mass scaled, Rydberg constant explains to a part in 10 to the 10 th all the energy levels of one-electron systems-- hydrogen, helium plus, lithium 2 plus. That's it. And that's fantastic.

Now we have to talk to become really familiar with this R_n of our function. And one of the

questions is, how many radial nodes. And you know that for 1S there aren't any nodes. And you know for 2P there aren't any radial nodes. And so what we need is something that goes like $n - l - 1$. The number of radial nodes, which is all you need to know about the radial A function, is how many nodes are and how far are they apart and what's the amplitude of each loop between nodes. Semi classical theory gives you all of that.

And often when you're calculating an integral, all you care about is the amplitude in the first loop. And so instead of having to evaluate an integral, you just figure out what is the envelope function based on the classical momentum function.

Now the thing that everybody's been waiting for. Spin. So remember, we know an angular momentum is $\mathbf{R} \times \mathbf{P}$, and we know that there isn't any internal structure. Or at least we don't know about internal structure of the electron or a proton. And so we can't somehow say, well, it's $\mathbf{R} \times \mathbf{P}$. So we have the Zeeman effect.

So we can look at the Zeeman effect for an atom in a magnetic field. And we have several things that we know. So we have the magnetic moment of the electron is equal to minus the charge on the electron times $2m_e$ times L . Well, that's an angular momentum.

So if we had circulating charge, well, that circulating charge will produce a magnetic moment, which has a magnitude which is related to the velocity. And what is L divided by mass? It's a velocity. And we have the charge here. So this is a perfectly reasonable thing.

And that's good because we know that, if we have electrons with some kind of internal structure, we know what this is going to do. Now the magnetic potential is equal to minus the magnetic moment times the external magnetic field. And so what we have is E, B, L, Z over $2m_e$.

Well, this is another very good thing because, not only do we know what this is, we know that it has only diagonal elements. And so we can do first order perturbation theory. If this is so easy, if this is the Hamiltonian, we can just tack that on and it adds an extra splitting to our energy levels.

The only tricky thing is, we don't know that it's L, Z . We just know that it has a magnetic moment or it could have a magnetic moment. And so this wonderful experiment-- suppose we start with a 1S state, and you go to a 2P state. Now this implies that we know something about the selection rules for electromagnetic transitions.

And so for an electric dipole transition, we go from 1S to 2P. Now this is not how it was done initially because the frequency of this transition is well into the vacuum ultraviolet. And in the days when quantum mechanics was being developed, that was a hard experiment. So one used an S to P transition on some other atom, like mercury, but let's pretend it was hydrogen.

So this is an angular momentum of 0. So we would expect it would be $ML = 0$. And here we have it could split into three components. And this is an $L = 1$, 0 minus 1 , because that's minus-- there with a minus sign somewhere. That's what we expect.

And so being naive, you might expect transitions like this. Well, the transitions where you do not change the projection quantum number are done with Z polarized radiation. And so if it's Z polarized, you get only $\Delta ML = 0$. And if you have x and y, you have $\Delta ML = \pm 1$.

So depending on how the experiment was done, you would expect to see one, two, or three Zeeman components. And they did the experiment, and they saw more than three components. They saw five components. And that's possibly for a number of reasons. But they saw five components. So they knew that there was something else going on.

And so you have to try to collect enough information to have a simple minded picture that will explain it all. So one thing you might do is say, OK, suppose there is another quantum number, another thing. And we're going to call it spin. And we don't know whether spin is integer or half integer. We know from our exercise with computation rules that both half integer and integer angular momentum are possible.

And so we can say we have a spin. And it could be $1/2$. It could be 1 . It could be anything. And then we start looking at the details of what we observe. And what we find is, all we need is spin $1/2$ to account for almost everything. However, if it were spin $1/2$, then you get two here. And you'd get two here, two, here and two here. And that's six. That's bigger than five.

So you need to know something else. And one thing is quite reasonable-- you can say, well, the spin thing is mysterious, and electromagnetic radiation acts on the spatial coordinates. And there aren't any spatial coordinates of the internal structure of the electron. And so we have a selection rule $\Delta MS = 0$.

That still doesn't do it. You still need something else, and that is that the proportionality concept between the angular momentum and the energy, which is called the g factor. For

orbital angular momentum, the g factor is 1, or the proportionality constant is 1. So the g factor is L . And the g factor for the electron turns out to be 2-- not exactly 2, just a little more than 2-- Nobel Prize for that.

And so with those extra little things, then every detail of the Zeeman effect is understood. And we say, oh, well, the electron has a spin of $1/2$, and it like it acts like an angular momentum. It obeys the angular momentum computation rules. It also obeys the computation rules. Well, I won't say that.

So I should stop-- there are other things that provide us information that there is something else. And one, I'm called by some people the spin orbit kid because I've made a whole lot of mileage on using spin orbit splittings. And the spin orbit Hamiltonian has the form $L \cdot S$ And this gives rise to splittings of a doublet P state, for example, as what you would see in the excited state of hydrogen into two components at zero field.

And so there's all sorts of really wonderful stuff. And I'm going to cheat you out of almost all of it because we're going to go over to the semiclassical picture next time. And we'll understand everything about Rydberg states and about how do we estimate everything having to do with the radial part of the wave function. And there are some astonishing things.