Freshman Organic Chemistry: Lecture 9 Transcript

September 22, 2008 More Dimensions: Chladni Figures and One-Electron Atoms

Overview: Double-minimum potentials generate one-dimensional bonding, A different technique is needed to address multi-dimensional problems. Solving Schroedinger’s three-dimensional differential equation might have been daunting, but it was not, because the necessary formulas had been worked out more than a century earlier in connection with acoustics. Acoustical “Chladni” figures show how nodal patterns relate to frequencies. The analogy is pursued by studying the form of wave functions for “hydrogen-like” one-electron atoms. Removing normalizing constants from the formulas for familiar orbitals reveals the underlying simplicity of their shapes

Professor Michael McBride: <<rings bell>> Okay, we're ready to go. You like my bell? I borrowed it from Kline Science Library. You'll see why. Okay, so we have the promise of the knowledge of everything, at least everything within a certain category, and we saw how we could see quantized energy last time, and structure, and structure-related dynamics, how nuclei vibrate and how it's different for heavier atoms. Today we're going to look again at a different kind of dynamics, and also at bonding. So in the one-dimensional world this is the payoff. We have to go to the three-dimensional world.

Okay, so you did problem sets for today and you're now familiar with things like this. What do you know about the blue curve and the red curve here? Anybody got a suggestion of what to do, or what they tell you about what the true solution is? Yes Angela?

Student: It looks like the true solution is somewhere between them.

Professor Michael McBride: I can't hear very well.

Student: It looks like the true solution will be somewhere between them, because it looks like --

Professor Michael McBride: Yes, the true solution should be between them. The red one is too hot and the blue one is too cold. Right? So there'll be, in between them, there'll be one that'll just come back down to the baseline for Hooke's law. Now the problem is that this isn't Hooke's law, because I didn't show you the whole picture. It's in fact a double minimum. Right? And those are both true solutions. So the correct ***single*** minimum energy would lie between those two, but for the double minimum there's one, there's a solution that's lower in energy and a solution that's higher in energy. Now what would happen if we moved the wells further apart? Here you see the separation of the two wells as 0.6 angstroms. Suppose we moved it apart to be 1.3 angstroms. Right? Now we have blue and red solutions. But now you notice the blue solution (or the red solution, they're the same in the left), they're both the same as the single minimum. So if you get the wells far enough apart they look like single minima with respect to their wavefunction. Okay?

Now, closer wells. If we move the wells closer together, we get a lower minimum energy than for the single well solution. Okay? And we get a higher energy for the next higher one. But they both look like the single minimum -- but they both started when the wells were far apart, looking like the single minimum solution, one with no nodes, one with one node. When the wells were far apart they had the same energy as the single minimum, but when the wells come together, the one with no nodes has less curvature, less kinetic energy and is lower energy than the single minimum, and the other one has one node, more curvature than the single minimum, and a higher energy; that is to say, there's a splitting between the energy of these two. If the wells are far apart, they're the same as the single minimum, both of them, the no-nodes and the one-node solution, are the same as the single minimum, but if you bring them together the no-nodes is lower in energy and the one-node is higher in energy.

So the energies split about the original single minimum structure. Now that's really important because that's what makes bonds. Right? So if we have two atoms or one-dimensional wells far apart, say A and B, and we get a solution in A and a solution in B, and if we want the solution for the whole thing, we just put them together that way, no nodes. Or we could flip B upside down, multiply it by minus one, add them together then and we get one node. But they have the same energy as the single ones would do. Right? But if we bring them together the energy gets lower, less curvature. Right? And that consists, or gives rise, to a stabilization of the particle. The particle is more stable when the wells are closer together. Right? What would you call that?

Student: A bond.

Professor Michael McBride: That's a bond. The energy is lower when they're close together. So that holds A and B together because the energy of the particle is lower when the wells are close together. So that's bonding. And part and parcel of this, the flipside of this, is that you have this wavefunction, which is higher. What will we call that?

Student: Antibonding.

Professor Michael McBride: Antibonding. So you get a combination of bonding and an antibonding combination because the kinetic energy changes when the wells come closer together. You get one that's less curved, one that's more curved. Okay, now that's bonding. How about dynamics? Well, suppose we have this double minimum and suppose we put a particle in and stop it there so it has zero -- that's our zero of energy -- and then we're going to let it go. What will it do if it's classical? It'll roll back and forth, right? Bingo, let it go. Roll across, to the same height, and roll back again, and then roll across again to the same height. With no friction it goes on forever, right? But here's what happens special, in real quantum mechanical systems -- oops, it went too far -- and now it's going to roll back and forth on the right; but every once in awhile it goes across, from one well to the other. Now, this is called tunneling, for obvious reasons. Right? But the word tunneling I hate. It's one of my pet peeves. It's misleading and mischievous, because it suggests there's something weird about the potential energy, that you can tunnel through and have a potential energy lower than you would've guessed from the potential energy curve. But that's not right. What happens is when it's in the middle you have negative kinetic energy. You have the potential energy that the curve shows, but the kinetic energy is negative. The potential energy can be higher than the total. And this happens in every bond and wavefunction, as you saw in your problem set, that the waves always go out into that forbidden region of negative kinetic energy where they curve away from the baseline. So there's the forbidden region, out to the left, to the right, and also in the middle for that energy. Right? And what really happens is that you go to negative kinetic energy and high positive energy to get over that hump, and then you get across to the other side.

Now how often does that happen? It turns out that the time to get from one well to the other, which I won't be able to prove to you because it requires time-dependent quantum mechanics, and we're talking about time-independent quantum mechanics, but let me just tell you that the answer is, if you know the energy difference between the blue and the red, that the rate of getting across is 5*10^-14 seconds, divided by whatever that energy is, expressed in kilocalories/mole. Right? This is just an assertion, and it's based on time-dependent quantum mechanics. It's true, but I'm not telling you why. So you won't be satisfied, I hope. Okay? So the energy difference here is 1.4 kilocalories/mole. So how rapidly does a particle then get from -- if it started out in the left, how long do you have to wait, on average, until it's in the right one? You have to wait 5*10^-14 divided by 1.4, which means about 4*10^-14 seconds it takes to, quote, “tunnel”; although it really doesn't bore through, it goes over with negative kinetic energy. Okay, so there's something else about dynamics. And we're hoping soon to get to reactivity, but that'll come after the exam, after we talk about atoms and molecules.

So now it looks like we're in a pretty powerful position, at least with respect to one dimension, because with this *Erwin* program we can find satisfactory wavefunctions for any complicated potential. We could make it anything we would like and just follow the recipe, find out allowed energies, shapes of wavefunctions, probability density, rates of tunneling, all this kind of stuff, and we can rank all the wavefunctions by their energy, or their curvature - the number of nodes they have. Here's an unsatisfactory wavefunction. What do you notice that's bad about it, just to show that you've learned something? Yes?

Student: It doesn't start at the baseline.

Professor Michael McBride: It doesn't start at the baseline, on the left. How about on the right, does it look okay on the right?

<<Students speak over one another>>

Professor Michael McBride: Lucas?

Student: It tends to be going down.

Professor Michael McBride: Ah, it crosses the baseline, in the forbidden region. If it crosses the baseline while curving away, it's bound to go to negative infinity, or positive infinity if it crosses in the other direction. Right? And on the left, because it didn't get to the baseline when it became flat, it's going to keep curving and go up to infinity. So you've internalized a lot of this stuff now. Congratulations on doing well on the problem set. Okay? So that was a bad one. Okay, so it looks like we're in pretty good shape. We even can handle multiple minima and understand tunneling and so on. The unfortunate thing is this curve tracing recipe doesn't work if you have more dimensions. Remember, the reason it would work is if you knew the potential and the total energy, then you knew the kinetic energy, and you could assign it to curvature. Right? But if you have two dimensions, then there are two different curvatures you could assign it to, and you don't know how much to put in each of them. So it's no longer such a clear-cut problem if you have more dimensions, especially *3n* dimensions. So when there are many curvatures, it's not clear how to partition the kinetic energy.

But Schrödinger had no trouble. The Schrödinger equation is what's called a differential equation, it involves derivatives. Right? And how many people have had differential equations? Okay, maybe a fifth of you I guess, or fewer. Right? So the rest of you are feeling, "Gee I wish I knew differential equations because then I could do this." But you don't have to, because people already have done it. You don't have to develop this from ground zero, right? And Schrödinger didn't solve the differential equations either. Right? He knew what the solutions were, because people had been studying them forever, and the reason they studied it was because of studying acoustic waves, and light also. And Chladni is the guy who originated this.

And here we have a book by Chladni called *Acoustics*. I got it out of the library. This is in fact the new, unchanged edition from 1830. The original edition was something like 1805 or something like that; actually we'll see it here I think. There's Chladni, Ernst Florens Friedrich Chladni, and this is the title page of that book, *Acoustics*; the original one was 1803, ours is 1830. Okay, now what he did was take plates of different -- he also did violin strings and timpani heads and things like that. He was interested in all kinds of acoustics. But the particular experiment we're interested in was he would take a plate and suspend it in the middle and touch it in different places, while he was bowing it with a violin bow to make it vibrate. Okay? So you bow it in different places, and he put sand on the surface of this thing to see what patterns would be formed when the thing vibrated -- this is why violins have the shape they have, so that they'll vibrate in certain ways when you bow to make them vibrate -- and the sand collects where the plate isn't vibrating, because when it's vibrating it shakes it away. So you get a picture of the pattern of vibration.

Now, I'm going to try to show this to you. But it might not work, and just in case I can go to the Web. So what we have here is a -- I can't play a violin, but as you know I can play a bell. In fact, I can play a bell in several ways; not only that, <<Bell sound>> I can do it this way too. <<Bell sound>> Now, that's not a very pleasing sound. Why? Why is it -- what's noise? I'm not very good at playing the bell. <<Sound>> Why does dry ice make a bell ring? This was discovered in London by an ice-cream vendor who had a bell on his cart, and he asked a physics teacher, a woman in London, why his bell rang when the dry-ice from his ice-cream hit it. <<Sound>> See, when you touch metal like that, it gives heat to the dry ice, which causes it to give off the pressure of gas, but when it gives off the pressure and the metal moves away, then heat's not being transferred, so it stops. So you get rapid pulses of CO_2, which make the thing ring. But depending on how you touch it, you get noise, because there are many different patterns of vibration at different frequencies that are being generated. If I could do it just right, I would generate just one pure tone and then you'd say, "What a great player of bells he is."

Okay, now I'm going to try this, and I may fail in the same way, to do an experiment like Chladni's. But instead of using a violin bow -- I'm going to put sand on here -- instead of using a violin bow I'm going to use this piece of dry ice. Okay? And I have to -- if I just touch it, it won't do anything because I'll be touching sand and I won't get heat transfer. So I have to brush a little bit to get a clean part of the brass, and then let's see what happens here. <<Sound>> Now I'm doing the same thing I did with the bell, right? It's just noise. But let me try someplace else here. This is an empirical science. <<Sound>> <<amazed sounds and laughter>> Try something else here. Spread some around here. If you're lucky, this is really great. Hear that pure one? Maybe it's not sharp enough. We don't want to spend too much time doing this. <<Sound>> I want to try one more and then we're going to -- you can go to the website and see a much better once. Once I played just the lost chord, a really beautiful tone; and it's on, you can see it on the Web. <<Sound>> I'm trying to find where and how hard to touch so that I get a really pure tone. <<Sound>> Well, you can get patterns that way.

Okay, you can get much prettier patterns and prettier tones than I'm able to coax out of the thing right now, and you can look at it on the Web to see it. <<projection adjustments>> Okay, so these are some crude Chladni figures that I've made in the past, three rings; two rings with a line through the middle, vertically. That's the one we just made now, I think, isn't it? Isn't it the same number? A ring and three diameters. And there's a circle and four diameters. I actually made that in class last year. Okay, these are ones that Chladni did back in the late eighteenth century, taken from that book, right? And here, the first ones are just diameters, and the next ones are rings, together with a certain number of diameters, or two or more rings. Now let's see what that picture means. Below you see a vertical diameter and two rings. On top you see color coded as to whether the plane, at an instant of vibration, whether it's toward you or away from you, as it's vibrating; that's the pattern. Because those lines don't move, but either side of the line, one side moves up, the other side moves down. Okay? Or you could look at it this way. The dotted patterns and the circles and the line don't move as the rest of the thing deforms. This would be like a drum head on a timpani. Got the idea? So that's the pattern of motion.

Now Chladni was interested in sound, right? So he found what pitch each of these different patterns corresponded to. So this table shows the number of diameters that are nodes, the number of circular nodes, and what pitch it corresponds to, and the little lines may mean it's a little sharp or a little flat, something like that. For example, the one with two diameters and no rings is the pitch C. Got the idea? So then he tried to figure out if there's a mathematical relationship among these things. These were fourty-seven patterns that he observed there. So here he says: "The pitch relationships agree approximately with the squares of the following numbers." So how many diameters, how many circles, and what he sees is the frequency is roughly the number of diameter nodes, plus twice the number of circular nodes, squared. This is his empirical observation. So, for example, you could have two diameters or one circle, both would give the number two, which you then square, to get something proportional to the frequency. Right? So there are two different ways to get the same pitch -- that's what's crucial -- either rings or lines. Or you can have a combination of rings and lines. So for higher frequencies you can get more and more combinations that give the same pitch. For example, the number eight, you can have four circles, three circles and two lines; two circles and four lines; a circle and six lines; or eight lines. All of them give the number eight and all give the same pitch, at least approximately. Okay? So this is what he -- but the lesson we want to take is that there are different ways of getting the same frequency, by combinations of these nodes.

Okay, now Chladni didn't solve his problem mathematically about how plates or strings or whatever vibrate. But there were great mathematicians working on this, like Bernoulli, Lagrange, Euler, who not only made a Communist Germany stamp, he also made a Swiss ten-franc note. Okay? Okay, so the Ψs for one-electron atoms -- now we're going from one dimension into three dimensions, for a real atom, electron and an atom -- so for one-electron atom there's going to be three variables, x, y, z for the electron, and the solutions, the waves we're going to get, involve what are called spherical harmonics, and they're 3D analogues of Chladni's 2D figures. These mathematicians could work in three dimensions as well as two. Okay, so a 3-dimensional H-atom wavefunction, Ψ, can be written as a product of three functions, an R function, a Θ function, and a Φ function. And these were available from other old-time mathematicians. The R function is called the Associated Laguerre Function, and it's named for Edmond Laguerre. And the Θ function is called the normalized Associated Legendre Polynomial, after Adrien-Marie Legendre. Okay? Now here are the solutions. Schrödinger didn't find these, he just looked them up. These guys had already done it, from acoustics, for 3-dimensional things vibrating. Right? So here's a table that *you* can use, the same way Schrödinger would've used it, to find out what wavefunctions for electrons in one-electron atoms actually look like. In all your books you've seen pictures of these things but you've never seen -- my guess is -- you've never seen the real thing, and you should wonder, “Are these pictures that people have shown me right?”

<<projection adjustments>>

Now how do you understand? This looks pretty complicated, this table, and in a sense it is. But if you look at it the right way it's really pretty simple. It relates to the position of an electron, shown on the right there, relative to the nucleus. And there's only one electron; it's a one-electron atom, otherwise we have more dimensions. But the nucleus can have any charge you want it to. So it's a one-electron atom of any nuclear charge, and we have the coordinates, x, y, z, and we have a potential. What's the potential law that's given to us, whose law?

Student: Coulomb's.

Professor Michael McBride: Coulomb's law. So it's $1/r^2$. And how do you write r^2?; r^2 is $x^2 + y^2 + z^2$. Right, everybody know that? Everybody know that? Good, nod, yes; good, okay we're on the same page here. Okay, but that's a pretty complicated function, right? So the equations that involve that are going to be really, really complicated. But there's a clever way to get around this. Do you know what that way is? What's the clever way of getting around this? The clever way of getting around it is to change the coordinates of the system that you're using to one that's more natural for the problem. And the one that's natural for the problem is spherical polar coordinates. So the three dimensions are r, the distance, and θ, the angle down from the z axis, and φ, the angle rotated around from the x axis.

Student: Isn't it the other way around?

Professor Michael McBride: Well you can define it any way you want to. This is the way it's defined for these purposes. Okay? Now, so that simplifies the expression for potential enormously. Instead of being $1/\surd x^2 + y^2/c^2$, it's $1/r$, or some constant over r. Okay? And what that means is -- and this is the mathematical payoff -- that the wavefunction can be written as a product of three functions, each of which is the function of only one variable. Instead of having x^2 and y^2 and $z^2{}^2$ all mixed together in this complicated function, you have a function only of r, a function only of θ, and a function only of φ, and you multiply them together and you get the solution to the Schrödinger equation for a one-electron atom. Now, that -- this table -- gives you those functions, the R function, the Θ function, and the Φ function. It's like a restaurant where you get to choose one from column A, one from column B, one from column C -- right? -- here's your appetizer, your main course and your dessert, right? So you choose one of these, one of these, one of these, multiply them together, and you have the true function. Right?

Now they look very, very complicated. You can't choose any combination you want to. Once you've chosen one -- once you've chosen your appetizer -- you can only have certain main courses, and once you've chosen that, you can only have certain desserts, to get solutions. Right? This is what these mathematicians had all figured out. Okay? And so how do we go about doing it? Well we can name the Ψ we're going to get by a nickname, like *1s* or $2p_x$ or something like that, but you can also name it by the numbers that name these individual functions, and those are n, l and m, which I think you've encountered before probably. So let's make a try at it. No, actually notice something about the complicated form of the functions. First, every one of them has Z/a_0 to the 3/2 power. Z is the nuclear charge; a_0 is a unit of length of about half an angstrom about. Okay, so to the 3/2 power; that's pretty weird. But remember what you're going to do with the wavefunction? What do you do with wavefunctions, other than find energy?

Students: Probability.

Professor Michael McBride: Get probability density, and what do you do to do that Sam?

Student: Square it.

Professor Michael McBride: You square it. So when you square it, it's going to be $(Z/a_0)^3$, when you square it. Everybody with me on that? Okay, so what that means is you're going to get units that are Z^3 per unit volume; because remember a_0 is a distance. So a_0^3 is a volume. So it's going to get a number -- the nuclear charge is a number Z, the atomic number is a number -- so it's going to get a number per unit volume, which is the right units to have for probability density. What is it per unit volume? Okay? So this is just the bit that scales it right so that you get the right density and the right units. So you can drop that out, that's not something very fundamentally interesting. Okay, let's try making up a *1s* orbital. Where do you start? Can somebody tell me where to choose? It's not hard. They're labeled with red, right? If you want *1s*, you choose the top one. Okay? And now if you've done that, n is one and l is zero. So when you come to the next one, l has to be zero. Now m can be either zero or one; or no, actually wait a second, if it's 1 -- no, if l is zero, then m has to be zero, it says in the second column. Does everybody see that? See up at the top? It says if l is zero, then m can be zero; lm. Okay? For m, pardon me, to be non-zero, like here, you have to have an l that's greater than zero. Okay? So to get a solution, if you chose n one and l had to be zero -- because remember that's the only choice here, you can't have a higher l -- then m is also going to be zero. So you've got to take this times this times this. Okay? Now how complicated are those functions? Okay, $\sqrt{2}/2$, that's just a constant, that's a nothing function. Or $1/\sqrt{(2\pi)}$, big deal. Why do you have these constants in there? Why do you care what constant you multiply the wavefunction by?

Student: No idea.

Professor Michael McBride: For what purpose?

Student: Normalization.

Professor Michael McBride: For normalization, right? If you want to get -- but if all you want is the shape, forget constants. So what's the real working part of the *1s* wavefunction? What's the part that varies? We have here the $(Z/a_0)^{3/2}$; forget that; two, forget that, $\sqrt{2}/2$ forget that, in fact the *2s* would cancel; $\sqrt{2}$ here would cancel that $\sqrt{2}$; so it's $1/\sqrt{\pi}$ times this, times what?; $e^{(-\rho/2)}$. That's the real working part of it. Right? When you square it, what are you going to get, for $e^{(-\rho/2)}$? What's $e^{(-\rho/2)}$ squared? Yes Alex?

Student: $e^{-\rho}$.

Professor Michael McBride: $e^{-\rho}$. Okay, so the probability density is going to be $e^{-\rho}$, times a constant. Okay, so here we got it. It's a constant times $e^{(-\rho/2)}$; when we square it, it's $e^{-\rho}$. Now, there's something -- there are ***two*** things that are interesting here. One, we wanted to get a function of r, θ and φ, but we don't have r in it. Right? We have ρ instead. Why do we substitute r by ρ? There's a good reason for that. ρ is defined -- which is, indeed, the Greek version of r is ρ -- it's defined as r times a constant. The constant is twice the atomic number, divided by n, the quantum level n, times that distance a_0. And why do you do it that way? It's because if you do it that way, then the same ρ works, no matter what the nuclear charge is, and no matter what n is. So you get the same -- so it makes the table very compact, because you use the same thing no matter what atom you're dealing with, if you work in units of ρ rather than r; that is scale r, to take into account the fact that you can have various nuclear charges. Okay, allows using the same $e^{(-\rho/2)}$ for any nuclear charge (Z) and any n. And notice, every one of these has $e^{(-\rho/2)}$ on it. Now, why does that make sense? Why is it no surprise that these things have e^{-r}? Have we ever seen that before, e^{-x} as a wavefunction? What kind of wavefunction -- what does that mean when you have e^{-r}?

<<Students speak over one another>>

Professor Michael McBride: That's a constant negative kinetic energy, constant negative kinetic energy, which is going to be the situation for any nucleus and an electron. Once the electron gets pretty far away, the energy stops changing. Right? So the potential energy is constant, the kinetic energy is constant. Right? If the electron is bound to the nucleus, that means it can't just fly off to infinity, right? So it's below the ultimate potential energy. Then you have constant negative kinetic energy, when you're far from the nucleus, right? So $e^{-\rho}$ So it doesn't surprise you that every one of these has $e^{-\rho}$ in it.

Okay, now let's just look at this scaling quickly. Okay, so here's $e^{-\rho}$ and ρ -- as a function of ρ. Okay? Now suppose -- so we can rearrange this. r is that. If we wanted to make a new plot, which has the horizontal axis being r, being distance instead of ρ. Okay now, so r for a hydrogen atom, the *1s* orbital of a hydrogen atom, is 0.53 -- so n is one, a_0 is half an angstrom, Z is one; so it's .53/2 times ρ. So we could just put a new scale on there. So here's half an angstrom for a hydrogen, here's one angstrom for a hydrogen. Everybody with me on this so far, how I did that? Right? I just went through and found out for any given ρ here, that I already had, one, two, three, four, five, $e^{-\rho}$. For any give ρ, what would the r be if I were talking about a hydrogen atom? Okay?

And I just put a new scale on there. Now if I were talking about a carbon atom, which has a nuclear charge of plus six, then this number Z is going to be much bigger, it's going to be six times as big. What effect will that have on the scale? So suppose we're at five, for ρ. Instead of dividing by one, for Z here, I'm going to be dividing by six. So I'm going to get much shorter distances, real distances, rather than ρ. Right? Does that surprise you -- that the function is going to squash in if I have a plus six nuclear charge? Does it surprise you or not? It's what you expect. A bigger charge is going to suck the electrons in more. Okay? So if I do it for carbon, I get .53/12 instead of .53/2, and the scale is going to look like that. Instead of this being 0.5 here for hydrogen, it's 0.1, right? So then if I squash it in so that they're on the same scale -- those are different angstrom scales for carbon and hydrogen -- if I make them the same scale, the bigger nuclear charge sucks the 1s function in by a factor of six, and it looks like that. But now, of course, if I want the real, the normalized function, it's got to be higher, so that the total area is the same. I have the squared function here, *e^-ρ*; remember that the wavefunction was *e^(-ρ/2)*; the density is *e^-ρ*.

To get the same thing I'm going to have to multiply that by six. So it's going to look like that. So that's how the radial distribution, probability density distribution, looks different, for a one-electron atom with a plus one or a plus six nuclear charge. Carbon holds its core electrons in much more tightly than hydrogen does; no big surprise there. Okay. So here's something to think about. How would it differ if instead of talking about the *1s* orbital of carbon, I was talking about the *2s* orbital of carbon? Right? Now, *ρ* is going to be different, and here, instead of one, it's going to be twp. So it's going to change the scale by a factor of two. So the *2s* are further out. Okay, so for Wednesday I want you to do these problems -- you can do them in groups if you want to -- some about Chladni Figures, and then some things about energy and some atomic orbital problems. Okay?

Now we already looked at the *1s*. Let's look at some other atomic orbitals. Incidentally, this function, the Coulombic function, is simpler in three dimensions than it is in one dimension. It was that complicated thing in one-dimension, remember that had the cusp on it. It was a really complicated function, but it's really simple in three dimensions, it's just exponential in *r*. How does it vary with *θ*? As you come down from the axis, how does the wavefunction vary, the *1s*? What does it say? How does it depend on *θ*?

Student: It doesn't.

Professor Michael McBride: It doesn't. How does it depend on *φ*?

Student: It doesn't.

Professor Michael McBride: It doesn't. So what shape does it have?

Student: A sphere.

Professor Michael McBride: It's spherically symmetric, it depends only on *r*. And the dependence on *r* is as easy as pie, it's just *e^-r* (or *ρ* -- it depends on what units you measure *r* in). Okay, now let's look at

2s. Now tell me what to do. How do I write a *2s* function from this table? First I have to choose the appetizer. Where do I go?

Student: Second one.

Professor Michael McBride: Second one down is *2s*. Okay? So I take this one, and now *2s*, that means *l* is zero. So where do I go; what direction do I go? Here. And then what direction do I go?

Student: Straight across.

Professor Michael McBride: Straight across, because *m* is zero. Okay. So here's -- there's *2s*; multiply those together. Now what's interesting, there are a bunch of constants that are going to give me -- make it normalized. So that's a constant, that's a constant, just like they were before; this is a constant, that's a constant. But this part is interesting: (2-*ρ)* times *e^(-ρ/2)*. That's the function that we're interested in, (2-*ρ)* times *e^(-ρ/2)*. That has an interesting thing. What happens when *ρ* has the value two? It has the *e^(-ρ/2)*; that's just decaying, all of them have that. But how about the 2-*ρ*? That gives an interesting thing. What's its value when ρ is two?

Student: Zero.

Professor Michael McBride: Zero. So there's a node. What shape is the node? Is it a point, is it a line, is it a wiggly thing?

Student: A sphere.

Professor Michael McBride: It's a sphere, it's spherically symmetric again. So there's a spherical node. So inside -- and at a node, the wavefunction changes sign. So inside it's one sign, outside it's the opposite sign. Okay? Now how about a *2p_z* orbital? So where are we going to go? *2p*, we'll start with this, and for *p_z*, we do this one, and for *z* we do this one. So it's this times this times this. I think I have that circled here; let's see, yeah. Is this one interesting?

Student: No.

Professor Michael McBride: No. Is this one interesting?

Student: Yes.

Professor Michael McBride: What part of it is interesting?

Student: Cosine.

Professor Michael McBride: $\cos(\theta)$ is interesting, right? That's real variation. And what part's interesting here? It's ρ times $e^{(-\rho/2)}$. Okay, so it's some constant times ρ times the cosine of θ times $e^{(-\rho/2)}$. You always have the $e^{(-\rho/2)}$; forget that. It just means it decays as you go out. Now ρ times $\cos(\theta)$. What does that mean?; ρ, which is this distance, times the $\cos(\theta)$, what is that? Russell? It's z. So I can simplify this a lot, if I mix my metaphors between polar and Cartesian coordinates, it's z times $e^{(-\rho/2)}$. That's the $2p_z$ orbital. Now, can you guess what the $2p_x$ and the $2p_y$ look like? Can somebody guess the $2p_y$? Josh?

Student: You replace x with --

Professor Michael McBride: Replace what?

Student: Replace z with x.

Professor Michael McBride: Replace z with x, you get the $2p_x$ orbital; replace z with y, you get the $2p_y$ orbital. Pretty straightforward functions. Now how about -- you've seen pictures of p orbitals. Now that you know what the functions look like, it's interesting to go back to the pictures you've seen and see what they mean. How do they relate to the actual formula? So you could plot -- remember, it's three parts, an R function, a Θ function, a Φ function. We could look at each of those functions separately, if we wanted to. Okay? We've been talking about the R function, how it would behave. But how would the Θ function behave in this, cosine θ? So we'll do a polar plot that shows the value of cosine θ as a function of θ. Everybody with me? Okay, so what is it when θ is zero; what's cosine of θ?

Student: One.

Professor Michael McBride: One. Okay, so there it is, and we'll put a point there, okay? Now let's go to + and -30°. Cosine is 0.86, and we'll put points there. And let's go to 45°, it's the $\sqrt{½}$, 0.71, put points there. At 60°, it's ½; put points there. What is it if it's 90°? If it's 90°, the cosine is zero. So we got a point at the origin. Right? So you can see what the shape is. What if you go the other direction, what if you go beyond 90°, what happens to the cosine?

Student: It's negative.

Professor Michael McBride: Changes sign. So you've got another circle that's negative on the other side. So there's a p orbital. But I'm not showing the whole p orbital, I'm just showing how the angular part varies. So you've seen pictures like that of p orbitals, which is the Θ function. Or I could square it, in order to look at probability density, as a function of θ, and it would look like that. So you've seen pictures more or less like that. Or I could make a picture like that, which is a contour plot showing how big it is, on a slice, through the nucleus. Right? So it's ρ times $e^{(-\rho/2)}$ times $\cos(\theta)$; that multiplied by a constant is the wavefunction. Okay, so you can see it's positive up at the top, negative at the bottom. And let's look at it a little bit. And, notice it doesn't depend on *φ*, the angle of rotation around here. So we can take that picture and rotate it to give a three-dimensional dumbbell. Okay? We're just looking at one slice here, in order to be explicit. Okay, now so there's a certain point there that has a certain *ρ* and a certain *θ*, and therefore it has a certain value. Now, let's find the maximum, of that function. Okay? So first it depends on *cos(θ)*. What will *θ* be in order for this to be a maximum?

Student: Zero.

Professor Michael McBride: Zero. So it has to be along the axis. Okay? Now, so *θ* has to be equal to zero. Okay, now how do we find where it's going to be maximum with respect to *ρ*? We take the derivative with respect to *ρ*, set it equal to zero. So that's this, or simplified that, or simplified that; *ρ=2*. So there's the maximum. And if we put the constants in, we could find the true probability density anywhere; just plug in *θ*, plug in *ρ*, and square it, multiply it by the constant. That's the electron density at any given, at the point you're talking about.

Now, or you could have a computer do it for you, and that's where we're indebted to Dean Dauger, who's a physicist. He went to Occidental College and actually wrote this program while he was there, but then he got a Ph.D. at UCLA in Physics, and he wrote this for physicists, but we'll use it. Okay, here's a picture of Dean Dauger. He also juggles. And here's a picture of him at an Apple Developer Conference, and he's juggling, the guy on the left there. He also drops one of the pins, he's not perfect. Okay. So this is his program. He's at the Apple Developer Conference. It works only on an Apple, so if you don't have an Apple, borrow somebody's Apple and look at the program, because it's really fun. This is the screen of the program, and I don't have time to take you through it now, but you should try it. So look at the PowerPoint of this on the next few slides to learn what all the different information is that's being given here, and the kinds of questions you can ask. There's a *1s* orbital, right? And it's as if the thing were really -- the electron were really colored, and it's a picture of how it would actually look if you could see electron density. But all, of course, he's done is used fancy computer graphics to plot the square of the wavefunction. Right? But it's a really nice program. We'll talk about this a little more next time. If anybody wants to try to beat me at Chladni you're welcome.

[end of transcript]