Freshman Organic Chemistry: Lecture 8 Transcript

September 19, 2008 One-Dimensional Wave Functions

Overview: The magnitude of the curvature of a wave function relates to the kinetic energy of the system, and the square of the wave function relates to probability density. The requirement that the wavefunction not diverge in areas of negative kinetic energy can constrain total energies to certain values, a property which is explored for the harmonic oscillator, the Morse potential, and the Columbic potential. Consideration of the influence of mass reveals an “isotope effect” on dynamics and on the energy, vibration frequency, and length of bonds.

Professor Michael McBride: Are there any questions about the Wiki? I finally looked over all the ones up to date. So I think you did a very good job, in almost every case, and the standard thing for doing a good job is two points. If you do something that's really very good, I give you three. There weren't very many of those. Okay? And did you get the email? Some people, I put a question. Were people able to see on the classes website what they had been given and so on? You tried and you couldn't?

Student: In Post'Em --

Professor Michael McBride: Post'Em.

Student: It said there were no items listed. I tried last night.

Professor Michael McBride: Did other people try Post'Em and it worked?

Students: Yes.

Professor Michael McBride: How many found it didn't work? So maybe you happened to look between the time that I sent the email and the time I posted it, although I thought I'd posted it first, but anyhow. Okay, let's get underway. So you know what's coming, and I'll give a review session from eight to ten on Wednesday. I haven't got the room assignment yet but I'll let you know about that.

Okay, so last time we saw the jeopardy approach to solving the Schrödinger equation, which is to take the answer and find out what the problem was, and we saw that for a constant potential you got a sine wave. You could choose any length of sine wave you wanted, any wave period you wanted. It just turned out to be different energies and it had a relationship between the wavelength and the energy, the kinetic energy, or the total energy in that case. And we saw an exponential is -- corresponds to --

negative kinetic energy, which not very many people in the class liked, and not very many people ever like it, but suck it up because that's the way kinetic energy is for small particles. If you don't like to call it kinetic energy because you're so wedded to the fact that for big things it's ½mv^2, then just consider it the difference between total energy and potential energy. Okay? But anyhow it's kinetic energy.

Okay, so we looked at the jeopardy approach, to start with the answer and get the question. But we'd a lot rather do it the other direction, to start with the problem and find out what the answer is. And you can do that by guessing the energy. If you have a sufficiently simple system, that is, one particle in one dimension; and this is a great way to get the idea of what's special about quantum mechanics, make it as simple as possible and then we'll go to realistic systems. Okay, so we can rearrange the Schrödinger equation. Remember, this is the Schrödinger equation: $H\Psi=E\Psi$; divide through by Ψ and split the $H\Psi/\Psi$ part into the potential energy part, V, which is a nothing, it's given to you, and the kinetic energy part, which is a negative constant that involves the inverse mass times the curvature of Ψ *over* Ψ. So it has to do with the **shape** of Ψ. And remember, if you multiply Ψ by a constant, you multiply the curvature by the same constant, so the kinetic energy stays the same. So it's only what we say, the shape, not really the amplitude, because that scales with the curvature.

Okay, but now we can rearrange this, this way. So we have a formula here for the curvature of Ψ. Now if you have a formula for the curvature, if you know how a curve is going to change, how a line is going to change its ~~curvature~~ [slope], then you have a recipe for drawing it, if you know how to start. If you start with a certain height, and a certain slope -- suppose you know that, and you know the curvature, at that point, then you know if you take a little step in that direction what the next slope is going to be. Okay? Because that's how curved it is. And if you recalculate and know the curvature at that point, then you know what the curvature at the next point is going to be, and the next and the next and the next, and you can use this to just draw a curve that's bound to satisfy the Schrödinger equation because you're using the Schrödinger equation to generate it. Does everybody see this? This is really important. Do you want me to say it again, or you got it now? If you have a formula for the curvature -- that's how fast the slope is changing -- and if you know the initial height and the initial slope, then if you know the direction of the slope you know where the next point is going to be. So you go to that -- just think a tiny -- now this gets a problem in a computer. If the thing is really going like this and you take a finite step, the slope will have changed during your step and you won't get it just right. So you'll have to take smaller and smaller steps so that it doesn't change during the step. Chenyu?

Student: <<inaudible>>

Professor Michael McBride: Can't hear very well.

Student: Are you saying that the curvature is a second derivative?

Professor Michael McBride: Yes, the curvature is a second derivative, yes.

Student: How do we start with the correct slope?

Professor Michael McBride: We'll get to that. But if you have the initial slope, and the initial height, then you use the formula for the curvature to trace out the curve. Everybody got that now? Okay, so that's great, and it would be tedious to do this by hand, but that's what this little program, *Erwin Meets Goldilocks*, does is start the curve and draw it out, according to what -- if you know everything else in the equation. Okay, so, and remember it curves away from zero when the potential energy is greater than the total energy, and it curves towards zero when the potential energy is less than the total energy. Right? So the potential energy being greater than the total energy is a bad situation intuitively, right, it means the kinetic energy is negative, and it curves away from the baseline. And what's bad about that, or dangerous about that? Yes, Kevin? Pardon me?

Student: It's not bounded.

Professor Michael McBride: Yes, it'll keep going until it gets to infinity, if it's curving away. Okay, and that's not allowed, it has to not go to infinity. Okay, so now do we know everything else? Well we know m, the mass. We know the constant, C, and the V is given to us, the potential energy changes with position. Right? But we know how it changes with position; it's Coulomb's law typically, or we can do some other law if we want to. So this recipe then, you know everything on the right, except the total energy. Ψ you don't care about because you can scale it, you can make it anything you want, call it one. Okay? Then we can double it if we want to or whatever. So Ψ we know; m we know; C we know; V we know. We're going to guess E. So that means if we know the initial slope -- and for the problems we work on the initial slope will be zero, and you'll see why -- then we can use this formula to trace out the curve. Okay? And that's what the computer does for you. So people were worried last night about math. Don't worry about math. Let the computer calculate how these slopes change and so on. Right? All you have to do is think about the curvature. Okay? So you just have to think about the graph.

Okay, so we're going to talk now about nodes and quantization, in one dimension, using this program *Erwin Meets Goldilocks*. And there's a problem set for Monday, as you know, where you do this, and the answers are on the Wiki, but don't look at them before you've given it a good try. Okay, so let's -- there are simpler things to start with, like a constant potential energy or running into a wall or into a pillow more like. But the harmonic oscillator, or Hooke's law, is a very popular one to do; so we're going to do that. Okay, so here we're looking at the potential energy as a function of distance. And also on the -- so you see the distance goes from zero to two and a half angstroms and the potential energy goes from zero to 100 kilocalories per mole. You can change that if you want to on the computer. Okay? And the horizontal black line is a completely different plot. It's a plot of Ψ. That's the plot on top of this one where we're going to trace out the wavefunction. Okay? And that's zero of the wavefunction; here's zero of energy. Okay? And the reason we put them on top of one another is so that it's easy to see the influence

of one on the other, of the wavefunction on the potential energy and vice-versa, and because they're functions of the same thing. What's Ψ a function of? What's it a function of?

Students: Position.

Professor Michael McBride: It's a function of the position. Position of what? The one particle we're talking about. Okay? And the potential energy is also a function of the position. Okay, so the way we're going to do this then is to guess an energy, let the computer trace out this curve, and see whether it's okay. What will tell us whether it's okay? How will we know if it's okay? It's got to be continuous. We're not going to have a problem with that because the computer is tracing it out this way; it's not going to be discontinuous. But the main thing is that it doesn't diverge, that it doesn't go to infinity. Okay, so let's just guess twenty-one kcal/mole. Why not? Okay, now you can already tell me something about what the curve is going to look like. Notice that at those two distances, between these two distances, the total energy is higher than the potential energy. What's the curve going to look like in that region? The kinetic energy is going to be positive, right? What will the curve look like? Pat?

Student: Spike up in between them.

Professor Michael McBride: Can't hear very well.

Student: It's going to spike up in between those two lines.

Professor Michael McBride: It may go up, it may go down. Yes? Pardon me? It's not -- would it be a sine curve? Does anybody think it wouldn't be a sine curve? Why not Russell?

Student: It does sinusoidal behavior when the potential is constant.

Professor Michael McBride: That's when the potential is constant. It's not constant through here. Right? So it won't be an exact sine curve. If this isn't very high, it might be close to a sine curve because it's sort of constant-ish, if this is a very small distance. But what characteristic must it have?

Student: It'll curve towards zero.

Professor Michael McBride: Say it again.

Student: It'll curve towards zero.

Professor Michael McBride: It'll curve towards zero. So it might -- it'll look something like this. Always -- it's curving and going up and down, maybe going high, but it's always curving to go back toward the baseline. It's never going to go to infinity. Okay? Now, there's a problem, because if you go the other way, the rest of the graph, the kinetic energy is negative because the potential's higher than the total. So in that region there's great danger that the line is going to go to infinity, because it's going to be curving away from the baseline. Okay? Now how could you possibly avoid that? How could you have it such that the curvature divided by the value of the wavefunction gets very big and the curvature away from the baseline, but still it doesn't go to infinity? How can the kinetic energy be big and negative, the curvature divided by the value is enormous, but it doesn't go to infinity? How can that be?

Student: Do we have to bound it?

Professor Michael McBride: Pardon me?

Student: Bound.

Professor Michael McBride: Bound?

Student: Yeah bound what we're looking at?

Professor Michael McBride: No, it's not a question of bound. This thing is, the particle, if it has this total energy, is bounded, it can't go all the way to the left or the right, that's true enough. Okay, but that's not the secret of how the wavefunction avoids going to infinity. Yeah?

Student: Make it a constant.

Professor Michael McBride: Pardon me?

Student: Make it a constant.

Professor Michael McBride: We can't -- make what a constant?

Student: Like -- another one a little bit.

Professor Michael McBride: Okay. Russell?

Student: You'd have very little curvature.

Professor Michael McBride: But -- you say very little curvature. But the kinetic energy is enormous. The curvature divided by the value of the wavefunction has to be enormous. Mike?

Student: You could make the value of the wave function go to zero.

Professor Michael McBride: Ah, if the value of the wavefunction is almost zero, then you can have an enormous -- pardon me, wait a minute -- then you can have a tiny numerator, hardly any curvature at all, and still the quotient can be big. Right? The kinetic energy can be enormous, and negative, if the denominator is near zero. So that means that if you're in those red regions, you know what the wavefunction has to look like. What does it have to look like? It has to get down near zero and stay there so that it doesn't have the curvature that'll -- enough curvature to pull it away. So it's got to look like that, on the left. Right? Because out here, that parabola is going way up; it's enormous, curvature divided by wavefunction, but if the wavefunction is essentially zero, still the curvature can be essentially zero. Okay? And the same on the right. So we know that the curve is going to look like this, something like that. Okay? And all we have to do is connect the pieces. Okay, so let's try it. We guessed twenty-one kcal/mole. This we did in our head, just by thinking about it. But let's let the program do it, and start at the left. And now do you see why it has to start with zero slope? Because if it's out in this region and has a finite slope, or an appreciable slope, and it's curving away, you're in trouble, because it's going to go to infinity. So we're going to use *Erwin Meets Goldilocks*, this program, and we're going to start at -- here goes the curve, and there's the part where the kinetic energy is negative, right? It hasn't gone to infinity because it started low enough and with low enough slope out at the left. Okay, now what's going to happen when it crosses that line?

<<Students speak over one another>>

Professor Michael McBride: What?

Student: The curvature changes.

Student: Now the curvature is going to be toward the baseline, as we guessed it would be; so like that. And now what's going to happen? Now it's going to start curving away from the baseline again. Uh oh, you don't win them all, right? Okay, now did we have too much energy or too little energy here? Notice that -- what did we want it to do on the right? On the left is where we started, that looks great, but on the right we're having trouble. What do you need to do in the middle in order for it to behave okay on the right? It has to not curve so much toward the baseline. Does everybody see what I'm saying? If it curved less, then it could join that other line we had originally. Okay, so we'll give it a little less energy. Let's try twenty. That's too hot, too much energy. Okay, so we'll guess twenty kcal/mole. Okay, here we

go. Start out; almost exactly the same, it's nearly the same energy, so it doesn't surprise you that it looks about the same. And then it's going to curve in here, the way we expected, but a little bit less than it did before. Right? So now we're on the way to success. So what was that one?

Student: Too cold.

Professor Michael McBride: Too cold. And what do you need?

<<Students speak over one another>>

Professor Michael McBride: Someplace in between these, there's going to be one that's right. Okay? So it's between twenty and twenty-one. Now should we guess halfway between twenty and twenty-one, is that the reasonable thing to do? Which original guess was better? Which guess was better originally, and why? The red one or the blue one, which guess was better?

Student: The red one.

Professor Michael McBride: Why was the red one better?

Student: Because it curved close to the baseline.

Professor Michael McBride: It lasted longer before it went to infinity. So it'll be closer to the red than to the blue. And if you fiddle around -- and that's what I want you to do, because this is the way I think it gets into your head is by guessing numbers and saying "where should I make the next guess?" and so on. After you've done this a certain number of times -- but enough times that it really gets into your bones and your brain -- after you've done it enough times, then you can use the function that says "Solve" and it will do that guessing game for you. But do it yourself at the beginning. Okay, and it turns out that after you've done that, you get 20.74 da-da-da-da-da, like a lot of decimal points, decimal positions, and you get that one, just right. Okay? So that's the only math you need to do. Is it too hot or too cold or just right? Okay? And you have to know why it has to be that way, because of this curvature thing. Okay, so there we have it, 20.74 kcal/mole is a satisfactory energy, and it comes with this wavefunction, whatever that's good for. Okay? But the energy is what we were looking at, what energies are allowed for this system? Now, could there be a lower energy allowed for this system? Could you imagine a less curved wavefunction that would also have this property of not going to infinity? Can somebody guess what it would look like? Nick?

Student: You'd have one that would just go up.

Professor Michael McBride: Ah, it could just go up and then come back to the baseline -- it has to come back to the baseline -- but it could just go up rather than curving so much in the middle. Okay, so we guess a lower one. Could there be a lower energy Ψ? Yes indeed, there could be one at 4.15 -- it's actually .149-something-or-another, to a lot of decimal points. And there it is, exactly what Nick expected. Okay, so you got this. Could there be a still lower one?

Student: Yes, well in between the two.

Professor Michael McBride: Not in between. Can there be one lower than the blue?

Student: <<inaudible>>

Professor Michael McBride: Can you imagine a way to get it even lower than the blue, an even lower curvature than the blue? Yes, Angela? Pardon me?

Student: What if it curved, like the one --

Professor Michael McBride: Can't hear very well.

Student: If the blue one is going up, then there could be one going down.

Professor Michael McBride: Ah, there could be an upside-down blue one; absolutely true, there could be an upside-down blue one, but it's the same thing, because it's the blue one multiplied by minus one. Remember, you can multiply it by any number and it's still the same thing. Right? So it's exactly the same energy. It's not a different wavefunction, it's just multiplied by a constant. But you're right, that also does the trick, but it turns out to be the same thing. Can you imagine anything lower in energy than this? It's impossible, because if it had less curvature in the middle, it's bound to go to infinity when it got back in the other region. Okay, so that's -- the blue is the lowest one. Now could there be one in between these two?

Student: Yes.

Professor Michael McBride: How? It looks like -- how could you do it? Yes, Kevin?

Student: One peak is above the value and one peak --

Professor Michael McBride: Ah, one peak above and one below. Right? Could there be an energy in between? Yes indeed, there could be that one. Now could there be others in between? What happens as you add curvature? You have these nodes. A node is where the wavefunction is zero. It's not a node out here, where it's almost zero. A node is when it's exactly zero, and it has to be zero because it's going from being positive to being negative; obviously it has to go through zero. Out here, and out there, it's very, very, very small but it's not zero; that's not a node. A node is where it's zero because it's changing sign. Okay, now nodes are related to energy. Why? Notice that the lowest energy one, blue, had no node, the next one, the purple, had one node. The next one, the violet or whatever color it is, had two nodes. Why is there that relationship?

Student: I was noticing inflection points.

Professor Michael McBride: They are inflection points, but why do they get higher in energy when you have more nodes? Sam?

Student: Higher frequency.

Professor Michael McBride: Say it in terms of energy. Some people would say frequency is energy, that's true, but I want you to say it terms we've been talking about. How do you get more nodes? Yeah?

Student: A higher absolute value of curvature.

Professor Michael McBride: Yes, if the curvature gets bigger, you get more nodes, and curvature is the energy, the kinetic energy. Right? So more curvature, more nodes, more energy; or more energy, more curvature, more nodes. So we have zero nodes, one node, two nodes. Those are the lowest three you can get. And then there would be three nodes, four nodes, five nodes, six nodes, as many nodes as you want. Okay, now this is great. You can do all sorts of neat tricks for Monday, and what I want you to do with this program is just to fiddle around with it and make discoveries for yourself. And I'll show you some of the kinds of discoveries that you can do in the next slides here. But I warn you that if you have more dimensions, or more particles, things quickly become impossible. The only thing you can do this particular approach with is one particle and one dimension, because if you have more, then you don't know which curvature to change. You know the curvature -- remember, it's a sum of a bunch of curvatures, and knowing the kinetic energy, the difference between total and potential, doesn't tell you which curvature to change. If there's only one then you know that that's the one you have to do. So it's going to be a heck of a lot of work to do this for more complicated systems. Right? And that's not our purpose now. Our purpose is to understand how quantum mechanics works with this simple system. But the question is, is it going to be worth our effort to learn how it works if we're unable to do anything with it? Or another way of putting it is, “What's the reward, what are we going to get out of this? Is it worth spending some time on?”

Well, here's the reward for finding Ψ. <<Laughter>> The knowledge of everything. Okay? For example, you know what energies are allowed to a system; you know what the structures can be; you know how it behaves dynamically, how it moves; you know how bonds work -- that's what we're really after, remember? And you know what makes for reactivity. So there's a pretty good pot of gold at the end of this. So fasten your seatbelts and put your nose to the grindstone and all sorts of metaphors, and we'll do this for the next couple of weeks. Okay? First we'll look at allowed energies and structure. Okay now, of course, we already did this, right? No nodes, one node, two nodes. But what were the energies that were allowed? Okay, so here's a whole bunch of them. No nodes, one node, two nodes, three nodes, up to seven nodes or -- is it seven?; yes seven nodes. Now here are the energies: 4.15, 12.44, 20.74, 29.04, 37.34. Do you see any pattern to the energies? You might read the title if you have trouble seeing it. They're evenly spaced; after the first one they're evenly spaced. How about the first one compared with zero? How high is the first one if you know this spacing?

Students: Half.

Professor Michael McBride: It's half. The first one above zero is half as big as the spacing of the others. Right? So the energy is some constant, and that constant is what? 8.3 roughly, times an integer minus a half. Why do you have integers? Because nodes come in integers; you can't have half a node, right? It's zero nodes, one, two, three, four and so on. Okay? So that's pretty great. We know for springs, or harmonic oscillators, or an atom stuck on a bond, as long as the potential -- it doesn't vibrate so much that the potential deviates from looking like a parabola; at the bottom of the curve it looks like a parabola. So this is the way atoms should behave when they're attached by bonds -- approximately. Okay, now remember that doggerel poem from 1926: "We only wish that we could glean an inkling of what Ψ could mean." What have we used Ψ for so far?

Student: <<inaudible>>

Professor Michael McBride: We used it -- its not going to infinity -- to find out when we guessed the energy right. It was just a tool for telling us whether we had the right energy. But does Ψ really mean something, besides just being a handy tool for this purpose? And it was later, six months later, in 1926, that it was suggested what the meaning of it was. And it was in this paper by Max Born that the -- Ψ doesn't mean anything, but Ψ^2 is probability density, or proportional to probability density. If you scale it right -- remember you can scale Ψ by -- multiply it by any number you want. If you scale it right, it is the probability density of the particle. Now here's what he wrote in German, and what it says is: "If one wishes to translate this result into physical terms, only one interpretation is possible, Ψ signifies the probability [of the structure]." But there's a footnote there, because he made a mistake, and he corrected it after the thing was already set in type. So he put a footnote here which says: "A correction added in proof: more careful consideration shows that the probably is proportional to the **square** of Ψ." Why couldn't it be -- why couldn't the probability be proportional to Ψ? Because Ψ can be negative! You can't have a negative… Well that's one reason. There were other reasons too. I don't know how embarrassed

he was by this, but anyhow -- but since nobody else knew what Ψ was at all, I think he could be proud nonetheless, right? But anyhow, it's the square of Ψ, not Ψ itself, that gives probability density.

Now, six months later Albert Einstein wrote a letter to Max Born where he said something you've probably heard: "But an inner voice tells me that this is not the real thing. Theory yields a great deal, but it brings us no nearer to the secret of the Old One. Anyway I am convinced that He does not play dice." Right? So it's not probabilities. There's this fundamental determinism, Einstein thinks. But it turned out that in this respect Einstein was wrong. Right? It **is** probability.

Now, it's not probability, it's probability density, and we have to think a little bit about this, and we can think of it in -- by analogy, with mass density. Suppose you had a flask and it had mercury and water and oil in it, right? And you're going to ask the question, if the total mask in the flask is one kilogram, what fraction of that, or how much weight, is exactly one centimeter from the bottom? How many grams, or what fraction of the total do you think, would be exactly one centimeter from the bottom? Anybody got a guess? 5%, 1%, ½%, 10%?

Student: 12%.

Professor Michael McBride: 12%?

Student: Three.

Professor Michael McBride: There'll be -- this'll be an auction, right? Do I hear higher than 12%? Do I hear lower than 12%? Who's bidding? Yes, what do you say?

Student: Zero.

Professor Michael McBride: Zero?

Student: It's an exact value.

Professor Michael McBride: Why zero? Well obviously it has to do -- different heights would have different densities, right? So it'd be a lot more in mercury than it would if I drew the line in oil or in water, right? But you say zero. Why?

Student: Because it's an exact value. It won't have --

Professor Michael McBride: Right. A plane, or a line, or a dot doesn't have any volume. Right? You need a volume -- it's zero, you're right, you need a volume. You have to multiply density, grams per cubic centimeter by volume, how many cubic centimeters, in order to get mass. And the same is true of -- so that in this case the real question would be how much is between one centimeter and 1.01 centimeters, or something like that? You could ask that question, but you can't say how much is exactly one centimeter? So you have to multiply by volume, multiply density by volume, to get the amount. Right? And so Ψ^2 is probability density. It's how probable it is to be in a small volume, a unit volume, around the point in question. So you go to some point in question, square Ψ, find the density, multiply it by the volume over which Ψ is constant -- because it doesn't vary real rapidly, so you could choose a really small one -- multiply, and that's the probability of being in that little block. Right?

Now, remember we said you could multiply, you could scale Ψ by any constant you wanted to, even minus one or -π or whatever. Okay? Is there a good value, a preferred value to scale it by? You could scale it by such a number that when it's squared and you've multiplied by volume over every place, sum up all these little boxes, you get one. Why do you want to get one? Because the total probability is one that it's someplace, right? So that process is called normalization. We don't usually worry about that, right? We usually just take whatever numbers we want, that's convenient to plot on the graph, and know that we have to scale it such that if we want to calculate actual probability density that's going to sum to one. Okay, so here's an example where above we show two of these curves and below we show squares of those, not properly scaled together. There's, I think, a little more area in the red than in the blue, although maybe I'm bad. They should have the same area, if the thing were normalized. Okay, so that shows what it is. Now there's an interesting thing about that. If you have a pendulum, or a thing on a spring, and it's going back and forth, where does it spend most of its time?

Student: Extremes.

Professor Michael McBride: At the extremes, because it's going so slow there. Right? In the blue one where does it spend most of its time? Where does it spend most of its time? Where is it most dense if it's the blue wavefunction, the lowest wavefunction, the zero-node wavefunction? Obviously it spends its time in the middle, not at the extremes. But notice if you get to the seventh wavefunction; one, two, three, four, five, six, seven; the seventh wavefunction is going to have seven humps -- that then it's most probable at the extremes, and as it gets -- as you get higher and higher it gets more and more focused at the extremes, and that's why when you get to something that's really heavy it behaves the way you expect a pendulum or a thing on a spring to behave. Okay? This is not normalized. But notice something else that's really valuable here, really crucial, which is that this line is where the potential and the total are the same for the red curve. Right? So here is zero kinetic energy. In here the kinetic energy is positive, out here it's negative, and the thing can be out here. Right? So the thing exists in a region of negative kinetic energy. There's nothing special about that. Okay? It's just that that's the way things work. Kinetic energy can be negative. And in the case of the blue one, here was the point where the kinetic energy was zero, and all this out here is probability in a region of negative kinetic energy.

Now, what if we do it with a Morse potential? Notice if we look at the first one with a Morse potential, it looks the same as it would in a Hooke's-law harmonic oscillator. Does that surprise you? No, because the potential looks that way, pretty much. Right? But as you go higher and higher and get here to whatever that is, the twelfth or something like that, you can see that it's very different and it's spending a lot of time far out. It's shifting its average to the right. But that doesn't surprise you because the well moves out to the right, as you move up, in the Morse potential, as you move to higher energy, because low kinetic energy, which is what you have as you move to the right, means low curvature. Why does that make it high probability? Because as long as you have high curvature-over-wavefunction, whenever the wavefunction peeks up, it gets pulled down again; it can't stay up. But if you have very low curvature toward the baseline, very low kinetic energy, then it can go up and you don't mind, because the kinetic -- you don't need much curvature when the wavefunction is big. Okay, so it's like that, and then out in here it's pretty much like an exponential decay. Does that surprise you? Kate you look like it didn't surprise you.

Student: No it didn't.

Professor Michael McBride: Why not? When do you expect the wavefunction to be an exponential decay, under what condition?

Student: When the potential energy --

Professor Michael McBride: Can't hear very well.

Student: When the potential energy is constant.

Professor Michael McBride: Ah, when the potential energy is constant, and what else to be exponential? The sine wave is also constant.

Student: Right, but it has to be --

Professor Michael McBride: Right? What makes it exponential, rather than a sine wave? Yes?

Student: Negative kinetic energy.

Professor Michael McBride: Ah, the kinetic energy is negative, the potential's higher than the total. But that's exactly the case on the right, because there's the potential, there's the total, and the kinetic energy is going down; it's negative, the difference between the two. Okay? Now, here are a whole bunch of

these for the harmonic -- for the Morse potential. How does it look different from Hooke's law? Does the spacing of energies look the same as it did in Hooke's law? Again, it's zero nodes, one, two, three, four and so on. But how is it different? Yes?

Student: <<inaudible>>

Professor Michael McBride: Ah, the spacing gets closer as you go up. So real bonds, which have a potential that looks more like this than like a spring, will have their energy levels get closer as you get more and more vibrational energy. Okay, they're not evenly spaced as they are for Hooke's law. As the energy increases, along with the number of nodes, the well widens more than it would for Hooke's-law parabola. So the wavelengths become longer, those nodes are spaced over a bigger distance, and the energies are lower than expected for Hooke's law, because you don't have as much curvature. You have the same number of nodes -- like the eighteenth level has the same number of nodes as it would in Hooke's law, but they're spaced over a wider distance, so there's less curvature, so the energy doesn't go up as much. Okay now, this is interesting. Look if you have the blue energy. Right? Now the wavefunction looks like this. It's no longer bounded. Does it surprise you that the wavefunction goes on out to infinity when the total energy is higher than that potential energy at the right? No. It means you have enough energy to break the bond. So the particle could just keep going. Okay, now what does this look like? In this region it looks like it does in a Hooke's law or something like that, more or less. What does it look like out at the right? It's a sine wave. Why? Sam, does that surprise you that it looks like a sine wave?

Student: Because the potential is just --

Professor Michael McBride: Ah, the potential is constant, effectively constant out there, and lower than the total. So it's a constant. It's about a sine wave because you have a constant positive kinetic energy when the total energy is above that dissociation limit. So there's the potential, there's the total, and now the kinetic energy is positive and about constant, so it's approximately a sine wave. Okay, now Coulombic potential is a more complicated one. The reason it's complicated is the energy goes to infinity when *r* becomes zero; when the positive and the negative are on top of one another it becomes infinitely favorable. So it's hard to do this numerically, and the program will screw up sometimes when you try to do Coulombic potential. And it's one-dimensional, and it turns out, curiously enough, that the system is simpler in three dimensions than in one dimension, for a Coulombic potential. Don't worry about the technical aspects of that. But at any rate, this is using the program for that, and you can see that the lowest -- that you have very, very high curvature when you get near zero because you have such high kinetic energy when the particles get very close to one another, and because the Erwin program is approximate, taking finite steps, you get in trouble often. Okay, but anyhow you get the idea that again as you get higher energy, you get waves that spread out. And they spread out a lot for the same reason they did in Morse potential, although here we're using a much lighter mass, we're using an electron. Right? But it spreads out much more because the well spreads out so much. Okay? So higher levels

spread way out, and now the sequence of energies -- here's the lowest, the next and the next. You have a big spacing first and then it gets much, much smaller. It turns out that the energy is some constant divided by n^2. So the number one level has an energy of -k, the next one is -¼k. The blue line is only a fourth as far down as the green, from zero, which is up at the top. Well zero is that grey line at the top, because it keeps going out to zero far out there. And the next one is 1/9th of the way from the top to the lowest level.

So the reward for finding Ψ was "the knowledge of everything." We've seen the allowed energy and structure. Now we're going to see another case where we get structure and we also see something about dynamics that's interesting, about the motion of the atoms. So here's -- suppose this is a proton attached by a bond to something that's heavy. So the heavy thing doesn't move, the hydrogen does the moving. Okay? And here's its wavefunction. This is the bond distance, the minimum energy. If you stretch the bond the energy goes up; if you compress the bond the energy goes up. And that's the wavefunction for the position of the hydrogen atom. Right? Now suppose we increase the mass and instead of talking about a hydrogen atom we talked about a carbon atom which had say fourteen, depending on which isotope we're using -- suppose we went to fourteen. How is that going to change things, if we have mass -- can we use the same function, if we use mass of fourteen? Notice that we're using the same potential. So the kinetic energy at any point is going to be the same for the two. How does mass enter into kinetic energy? Yes?

Student: Would it be more concentrated?

Professor Michael McBride: Can't hear.

Student: Would it be more concentrated?

Professor Michael McBride: Why do you say it would be more concentrated? What would make it more concentrated?

Student: Higher nuclear charge, so the electrons would want to—

Professor Michael McBride: Yes, but you're not thinking about quantum mechanics. You're thinking that the higher -- well no, wait a second, we're not talking nuclear charge here. All we're talking is mass. It's held by a spring, we're thinking, okay? So electrostatics doesn't come into it, it's a spring that's stretching. Elizabeth?

Student: In that equation that you showed us before, the curvature is proportional to mass?

Professor Michael McBride: Yes, the kinetic energy has one over mass in it. So if you increase the mass, and keep the same wave, what are you going to do to the energy?

Student: Decrease.

Professor Michael McBride: You're going to decrease the energy. But it's the same energy as it was for hydrogen. You can't just decrease the energy, at a given position, if you know the total. Okay, so you want it to be -- to get the same energy it has to be more curved. Okay, everybody with me? To have the same energy, if you have a bigger mass in the denominator, you're going to have more curvature, fourteen times as much curvature, to compensate for the bigger mass. So it's going to curve more toward the baseline. Okay? So if we used that same energy and had the higher mass, so we got more curvature for the same energy, then it's going to curve a lot more, it's going to go through and go up to infinity, and it's even higher energy than the second wave would be. It's curved way too much. So how would you find the lowest energy, what would you do in your guessing? If you wanted to find the lowest energy what would you do? You'd lower your guess to make it less curved toward the baseline. Okay? And if you do that, so lower the energy, from that, and there we've got the answer. Right? So hydrogen has a much higher vibrational energy than carbon does for the same bond, to get the lowest energy. I think this will be clear to you when you have time to think about it. If not, ask questions. Okay? Now what if you had U-235 or a marble at the end of the same spring? What do you think its wavefunction would look like, the lowest energy wavefunction?

Student: A spike.

Professor Michael McBride: It's just a spike. The heavier it is, the narrower it gets. Right? So if you have something like a baseball held by a bond, it's going to sit right there. You're not going to be able to see that it's spread out. But electrons are so much lighter than nuclei that electrons really spread out. Okay, now so there are the probability distributions for hydrogen and for carbon, held by a single bond. Why is their average not in the same position? See what I mean? Elizabeth? Pardon?

Student: Acceleration has to do with mass.

Professor Michael McBride: No, no. It has to do -- yes?

Student: Because the electrons are not attracted equally.

Professor Michael McBride: No, no, it's -- remember, electrons aren't entering into this. We're just supposing that we have a nucleus held by a spring and that spring is the strength of a single-bond.

Okay? What is the potential for a bond? Is it Hooke's law? What's a better potential for a bond than Hooke's law?

Students: Morse potential.

Professor Michael McBride: The Morse potential, which broadens out, remember, as it goes up. So since hydrogen goes up more, it samples further out to the right, so it's displaced to the right from the carbon. Okay? Now so let's -- here they are at their minimum energy position, and they vibrate. The higher energy is shifted to the right in the unsymmetrical Morse potential. And here's the half-maximum of the -- so it spends -- it's half as probable -- the probability density here is half what it is there. So when you say, how far does it spread out? This thing goes out to infinity. But we can talk about how wide it is by saying how wide it is at half-height. So the hydrogen at half-height is from here to here, but the carbon at half-height is only from there to there; that is, if you think of these things vibrating, the hydrogen has a bigger amplitude than carbon, because it's lighter. So the hydrogen vibrates by 0.1 angstrom, 9% of the distance. The carbon vibrates only half as much, 3% of the carbon-X distance, just because of the mass difference. And remember we said before, last time, that typically the atoms are vibrating by about 0.05 angstroms in the crystal. That's where this came from, it's this quantum mechanical thing. That's the least that they can -- and when they're in their lowest possible energy state they vibrate by that much, right? And that's how much it is, that little yellow dot after it shrank. So we've seen allowed energies and structure. We've seen dynamics, the vibration. Now, next time, we're going to look at dynamics, and also the payoff, bonding, how we understand bonding in one dimension.

[end of transcripts]