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ROBERT FIELD: OK. So this is going to be a fun lecture because it's mostly pictures and language. And it's also an area of physical chemistry, which is pretty much-- I mean, there's three areas of physical chemistry where people have trouble talking to each other. There's statistical mechanics. There's quantum mechanics. And there's the time dependent, time independent forms of quantum mechanics. And these three communities have to learn how to talk to each other. And I'm hoping that I will help to bridge that gap.

OK. So last time, we talked about the time dependent Schrodinger equation. It's a simple looking little thing. Remember though, it's an extra level of complexity on what you already understand. Now, in the special case where the Hamiltonian is time independent, then, if you know all of the energy levels and wave functions for the time independent Hamiltonian, you can immediately write down the solution to the time dependent Hamiltonian.

And so you have a complete set of wave functions. And you have a complete set of energy levels. And with that, you can basically describe something that satisfies this thing. Another set of coefficients is often something that you arrange for simplicity or for insight. And I want to understand-- I want to talk about that.

OK. And so in the previous lecture, we talked about the probability density, which is $\psi^* \psi$. And that can move. And that can move in two ways. In the wave function, if there are two or more states belonging to two or more different energies, then you can have motion. And you can have motion like breathing, where probability moves towards the extremes, or motion where there is actually a wave packet going from one side to another.

So for anything interesting to happen, this probability density has to include at least two different eigenstates belonging to two different energy levels. Now, the total probability is just the integral over all coordinates of the probability density. And probability is conserved. So one of the things that happens-- when you do an integral, the wave functions go away. And in this particular case, $\int \psi^* \psi$, all you get is one. Or you get a constant, depending on how you normalize things. But it's not time dependent.

Now, in understanding motion from classical mechanics, we know Newton's equations. We know how the coordinate and the momentum depend on time. And so if we calculate the expectation value of the coordinate or the expectation value of the momentum, we get some results.

And it turns out that these things describe the motion of the center of a wave packet. A wave packet is anything that's not just a single eigenstate, so it moves. And so the motion of a single eigenstate-- the motion of a wave packet is described by Newton's laws. And this is Ehrenfest theorem. And it can easily be proven. But we're not going to prove it. We're just going to use it.

So we are very interested in expectation values of the coordinate and the momentum. And for a harmonic oscillator, this is duck soup. Then we have nothing but trivial integrals involving the a 's and a -daggers. And so even though in some ways the harmonic oscillator is a more complicated problem than the particle in a box, the harmonic oscillator is the problem of choice for dealing with motion and developing insight.

There's another useful-- OK. We have this wave function here. There is a huge amount of information embedded in it, too much to just look at. We need to have ways of reducing that information. And one of the nice ways is the survival probability. The survival probability tells you how fast does the initial state move away from itself. And this is very revealing.

Another very revealing thing is if this survival probability, which is a function of time and nothing else, because we've integrated over the wave functions-- if this survival probability goes up and down and up and down, there are recurrences. So at a maximum, which is usually a maximum at t equals 0 because the wave function is it at its birthplace, the survival probability will start high and go down, and come up, and go down.

And there's all sorts of information about recurrences. As the wave function returns to its birthplace, it might not return completely. And so we get partial recurrences. And these tell us something. And the times at which the maxima in the survival probability occur tell us a lot about the potential.

And there are some grand recurrences where, because all of the energy level differences are an integer multiple of a common factor, then you get a perfect recurrence. And these are wonderful for drawing pictures.

Now, you really want to understand the concepts of time dependent quantum mechanics pictorially and to develop a language that describes it. And there are a lot of little pieces here that you need to convince yourself you understand so you can use the language.

OK. One of the things I said at the beginning of the course is the central object in quantum mechanics is the wave function. Or we could generalize to this. This is actually the truth. This is a partial truth. This is everything that we can possibly know. But we can't know this. We can never observe the wave function.

However, we do observations. And we construct a picture, which is what we call the effective Hamiltonian. This effective Hamiltonian describes everything we know, mostly energy levels. We have formulas for the energy levels. And we determine the constants. There's all sorts of stuff that we collect by experiment. And so we create an object which we think is like the true Hamiltonian.

And by having the effective Hamiltonian, we can get these things. So we observe we make some observations. And then this is a reduced version of the truth. And we can get a pretty good representation of the thing that is supposedly hidden from us.

OK. So let's start now at t equals 0. At t equals 0, which I like to call the pluck-- and it really makes it contact with those of you who are musicians, that you know how to create a particular kind of sound, which will evolve in time. And it depends on the details of how you handle the instrument.

So at t equals 0, we have this thing which, if we have a complete set of eigenfunctions of the Hamiltonian, of the time independent Hamiltonian, we know we can write this as $c_j \psi_j$ of x . Now, often we don't need an infinite number of terms. But we know that there are lots of different kinds of plucks. And you can find out what these coefficients are by just calculating overlap integral of these functions with this initial state.

OK. So this is telling you what happens at t equals 0. And if you can write the initial state as a superposition of eigenstates, then you can immediately write the time evolving object this way. Now, we have a minus i . Well, why do we need a minus i ? Well, because we're going to take the time derivative of the Hamiltonian and multiply it by $i\hbar$. We're going to want to get the energy, not minus the energy. And so we need a minus i here. And we need a divided by \hbar here in order to satisfy the time independence or time dependence.

So this always bothers people. Why should there be an i here? And why should it be minus i ? And I recommend not trying to memorize it, but to just convince yourself. I need the minus i because I'm going to bring down a minus i over \hbar times e . And we have this $i\hbar$. The minus i times i gives plus 1.

OK. So now, in understanding how the time dependent Hamiltonian can be sampled, we build the superposition states with a minimum number of terms, like two or three. Even though, in order to create a very, very sharply localized state, it needs a huge number of terms here.

But you always build your insight with something you can do in your head. And so for some problems, you need only two states. And for others, you need three. And those are the ones you want to kill. You want to understand everything you can build with two and three state superpositions.

OK. So there's two classes of problems. OK so for a half harmonic oscillator-- so for a half harmonic oscillator, we start with harmonic oscillator and divide it in half and say this goes to infinity. And so this side is not accessible. And so if the potential is half of a harmonic oscillator potential, then we know immediately what the eigenvalues and eigenfunctions are. They are the harmonic oscillator functions that have a node in the middle.

So we know that we have v equals 1, v equals 3. No v equals 0 or 2. I mean, this corresponds to the lowest level, v equals 0 for the half oscillator. But this is basically-- now, what we're going to do is we create some state of a half oscillator. And then we take away the barrier. So that's a cheap way of creating localization. Of course, we can't do this experimentally. But you could, in principle, do it.

And so basically, you want an initial state, which is a superposition of vibrational levels. OK. And this initial state needs to have the wave function be 0 at the barrier. So since we're going to be looking at the full potential, we're taking away the barrier. We're allowed to use the even and odd states. And so let's take the three lowest states.

And so we have $c_0 \psi_0$ plus $c_1 \psi_1$ plus $c_2 \psi_2$. OK. This guy is OK. Yes?

AUDIENCE: When you create the states of the half harmonic oscillator, do you have to re-scale them so that they normalize?

ROBERT FIELD: Yes. We play fast and loose with normalization constants. We already always know that, whenever you want to calculate anything, you're going to divide by the normalization integral.

However, it's OK. Because we're going to be using the full harmonic oscillator functions, which do exist over here. And it's fine once we remove the barrier.

But we want to choose a problem which is as simple as possible. OK, now, this guy is not 0 at x equals 0. And this guy is not 0 at x equals 0. But you can say 0 is equal to $c_0 \psi_0$ of 0 plus $c_2 \psi_2$ of 0. We choose the coefficients so that these two guys together make 0 at the boundary.

And why do we do this? We're going to be calculating expectation values of x and p . And if we only have half of the energy levels, all of the intricacies are going to be 0. So we have to have three consecutive levels to have anything interesting.

OK, so the artifice of making these two-- arranging the coefficients so that you get a temporary node at x equals 0-- it won't stay a node. Because when we let things oscillate with time, these two will oscillate differently. And the node will go away. But that's how you do it. That's how you build a superposition. OK.

OK. Now, what we want to do is to be able to draw pictures of what's happening and also to calculate what's going on. And one of the things we use for our pictures is the expectation value of x and the expectation value of p . So you know how to calculate the expectation value of x . We have this $\langle x \rangle = \int \psi^* x \psi dx$. And so we get to $c_0 c_1 x_0 \cos(\omega t) + 2 c_1 c_2 x_{12} \cos(\omega t)$. Now, how did I do that?

Oh, come on. You can do it, too. So what is this x_0 ? Well, x_0 is the integral $\psi_0^* x \psi_0 dx$. And we know we can replace x by $a + \text{constant}$. We always like to forget that concept. We only bring it in at the end anyway. And so, well, this has a value-- it's a constant, the constant that we're forgetting-- times 1 square root, right? And x_{12} is the same sort of thing. It's going to be the same constant times 2 square root.

This is easy. So getting from this symbol to this, that just requires a little practice, and then simplifying further to know what these x 's are, and then the constraints on c_2 and c_0 . We have all that stuff.

OK. And now, we can draw a picture of what's going to happen. So here we have the full oscillator. And let's just draw some energy which is-- now that's complicated. We have a time dependent wave function, which is composed of several different energy eigenstates. So what is its energy? Well, you can evaluate what the energy is by taking the expectation value of the

Hamiltonian. And so you can do that.

So what we've made at t equals 0 is something that looks like this. It's localized on the left side. Or it's more localized on the left side. Now, sometimes, you're going to worry about phase. And so many times when you're working symbolically rather than actually evaluating integrals, there are symbolic phase choices that what you're using has made.

And for example, for the harmonic oscillator, if you look in the book, you'll see that, for all of the harmonic oscillator functions, the outer lobe is always positive. And the inner lobe is alternating with the quantum number. So that's a phase convention that's implicit in everything that people have derived.

And as long as the different things you combine in doing a calculation involve the same phase convention, which is implicit-- we don't want to look at what functions. We want to look at these ψ 's. OK. And so those things that we're manipulating have a phase implicit in how you define them. But that's gone in your manipulation. So you want to be a little careful.

OK. So we start out and the expectation value is on this side. And the $\psi^* \psi$ is localized on this side mostly. And at a later time-- so this is a later time. I shouldn't make it bigger. At a later time, this thing has moved to the other turning point. Back and forth, back and forth.

Now, since we have three energy levels-- and well, actually, we have a coherence term which involves the product of ψ_0 and ψ_1 and ψ_1 and ψ_2 -- they differ in energy both by ω . So these two things have the same oscillation frequency. And so what's going to happen is the wave function, the wave packet, is going to move from this side to that side, back and forth always forever at the same frequency, no dephasing.

In the middle, I can't tell you what it's going to look like. I don't want to tell you. Because you don't care. You care mostly about what's it going to look like at a turning point. Or what is it going to look like when it returns to home base? And all sorts of insights come from that.

OK. Now, I said, well, if we want to know the energy of this wave packet, well, we take the expectation value of the Hamiltonian. And the expectation of the Hamiltonian is $c_0^2 e_0$ plus $c_1^2 e_1$ plus $c_2^2 e_2$.

These things are easy once you've gone through it a couple of times. Because what's happening is you have these factors, $e^{-i E_j t / \hbar}$. And they cancel when

you do a $\psi^* \psi$. Or they generate a difference, ω \hbar ω , when you have different values of the energy.

So this is something that you can derive really quickly. And the fact that your eigenfunction-- the ψ 's in your linear combination up there are eigenfunctions of the Hamiltonian. So every time the Hamiltonian operates in a wave function, it gives the energy times that wave function. And then you're taking the expectation value. And so we have the wave function time itself integrated. And that goes away.

So after doing this a few times, you don't need to write the intermediate steps. And you shouldn't. Because you'll get lost in the forest of notation. Because one of the things you probably noticed in the last lecture is the equations got really big. And then we calculate something else. And it gets twice as big. And then all of a sudden, it all goes away. And that's what you want to be able to anticipate.

OK. So you can really kill this half oscillator problem. There's nothing much happening except you create a localization. And when you take away the other-- when you restore the full oscillator, everything oscillates at ω . And so you have a whole bunch of terms contributing to the motion of the wave packet. And they're all very simple. Because they're all oscillating at the same frequency.

Now, as an aside, I want to say there's a huge number of stuff that's up in this lecture that's going to be on the exam, a huge amount. So if for example you wanted to calculate something like x^2 , well, fine. You know what the selection rule for x^2 is. It's Δv of 0 plus or minus 2. And so this thing is going to generate some constant terms and some terms at 2ω .

OK. So there are a lot of things about the harmonic oscillator that make it really wonderful to consider a problem, even a complicated problem, which is not explicitly a harmonic oscillator problem. Because you can get everything so quickly without any thought after a little bit of investment.

OK. Now, we haven't talked about electronic transitions and potential energy curves. But we will. And I think you know about them. And so we have some electronic ground state. And we have some electronically excited state. And so each of these states has a vibrational coordinate. And we can pretend that it's harmonic even if it's not. Because we build a framework treating them as harmonic, and then discover that there's discrepancies which we

can fit to a model. And we can determine from the time dependence what that model is.

OK. So we start out with a molecule in v equals 0. And there is a much repeated truism. Electrons move fast, nuclei slow. Transition is instantaneous, or nearly instantaneous, because it involves the electrons. So what ends up happening is you draw a vertical line. And now, you transfer this wave function to the upper state. You just move-- this is the probability amplitude distribution of the vibration. We transfer that to the excited state. And that's not an eigenstate, the excited state. It's a localized state, localized at a turning point.

Now, you want to know-- so there's the Franck-Condon principle, that is just another way of saying electrons move fast, nuclei slow. And there is Δx equals 0 Δp equals 0. If the nuclear state can't change while the electron is jumping, then the coordinate and the momentum are both constant.

So you're creating a wave packet. And the best place to create it is near a turning point. Because then, you can match the momentum of this guy to that zero point momentum, which you can calculate. You know how to calculate this. Because the potential energy curve is $1/2 k x$ squared. And the momentum is given by this energy difference here. And so you can work it out. It's in the notes. I don't want to write it down.

So you're going to create something which is vertical and is not quite exactly at the turning point. Because you have to have a little bit of momentum to match the zero point momentum here. So you know everything about the initial state. And so you can calculate what it is by taking the overlap of v equals 0 of the ground state with all of the vibrational levels of the excited state. And so we have the coefficients of each of those vibrational levels in the excited state that makes this wave packet.

Now, of course, this wave packet is going to move back and forth, back and forth. And if this were a harmonic oscillator, it would move harmonically. And so the only thing that would appear in the expectation value of x is going to be this motion at ω . Now, this is usually a relatively high vibrational level. And the molecule is not being harmonic here. So there are correction terms called anharmonicity terms.

So we have the energy level expression plus $\hbar \omega e x e$ -- that's one number-- plus $1/2$ squared. So we have a linear term and a quadratic term. And this $\omega e x e$ is on the order of 0.02 times ωe , 2%. So it's a small thing.

But if you're going to be allowing a wave packet to be built out of many vibrational levels, this guy is going to de-phase a little bit. So you go around and come back. And you can't quite have everybody back where they started. And so you'll see a decreasing amplitude here. And that's best looked at by the survival probability. And you'll see characteristic behavior in the survival probably.

OK. But let's go a little bit deeper before I move on to-- what time is it? Oh, I'm doing OK. So let's just say our superposition state, the electronically excited state, is a combination of v equals 10 and v equals 11. So we know immediately that $\psi^* \psi$ -- this probability amplitude-- probability, yes, this probability is $c_{10}^2 \psi_{10}^2 + c_{11}^2 \psi_{11}^2 + 2 c_{10} c_{11} \psi_{10} \psi_{11} \cos \omega t$. That's not very legible.

Now, I'm playing fast and loose here. Because I've done this before. I know what disappears. And I know, if it's harmonic, you just get this. Well, if there's two states, this thing is really just the frequency associated with these two levels. OK.

Now, once we have this, we can also generate the survival probability. Well, the survival probability, capital P of t, that's defined as the square modulus of $\psi^* \psi$.

OK. And you can immediately write what that is going to be. It's going to be c_{10}^2 . And we've integrated so the wave functions go away. And so we have $c_{10}^2 e^{i H \bar{10.5} \omega t} + c_{11}^2 e^{-i H \bar{11.5} \omega t}$.

OK. Why did I made the mistake here? Well, we have a ψ^* . And so we're going to get the complex conjugate of $e^{-i \omega}$. So you end up getting this. Practice that.

AUDIENCE: That whole thing is [$\psi^* \psi$] modulus squared, right?

ROBERT FIELD: Yes. I have that right. Exactly. So and now, lo and behold, we know what to do with this too. And so we're going to get $c_{10}^4 + c_{11}^4 + 2 c_{10}^2 c_{11}^2 \cos \omega t$.

Isn't that neat? So we've got a whole bunch of constant terms. This is constant. Because it's square modulus and it's to the fourth power. And so all of these coefficients are positive. At t equals 0, this is 1. And so at t equals 0, the survival probability is at a maximum. And at some later time, that survival probability will be at a minimum.

OK. And so you can say the maximum will occur at integer when ωt is equal to $2n\pi$. So then the exponential factor is always 1. And we have a minimum when ωt is an odd multiple of π . And all the exponential factors are minus 1.

So we can also now look at the expectation value for x of t and p of t . And I'm going to just draw sketches. So for x of t , we have something that looks like this. This is at the left turning point. This is the right turning point, or near the right turning point. And this is at $\pi/2\omega$. This is at π/ω . So that's the half oscillator point.

Now, it starts out and the expectation value is at the left turning point. And it's not changing. The derivative of the expectation value with respect to t is 0. The momentum, which has a different phase-- the momentum starts out at 0 also. And at $\pi/2\omega$, it reaches a maximum. And at π/ω , it reaches 0 again.

But the important thing here is at t equals 0 the derivative of the momentum is as big as it can get. So what's that telling you? It's telling you this wave packet, as far as coordinate space is concerned, it's not moving at t equals 0. As far as momentum is concerned, it's moving like crazy.

And so this survival probability is changing entirely dominated by the change in momentum, which is encoded in the wave function, which is neat. Because Newton's equation says that the time derivative of the momentum is equal to-- that's the mass times acceleration-- is equal to the force, which is minus the gradient of the potential-- the function of time.

And for a harmonic oscillator, the gradient potential is $-kx$. And so it's telling you that we have this relationship between x and t and p . And we know what the momentum is. And I'm sorry. And so the change in the momentum, which is responsible for the change in the survival probability at t equals 0, is due to the gradient of the potential.

So we're actually sampling what is the gradient of the potential at the left turning point. And often, for any kind of a problem, we want to know what kind of force is acting on the wave packet. There it is, classic mechanics embedded in quantum mechanics. It's really amazing. So if you have some way of measuring the survival probability near t equals 0, it's telling you what the slope of the potential is at the turning point.

OK. Well, if we have an initial state which involves many eigenstates, the Hamiltonian, we still know that there's going to be some complicated behavior which is modulated by ω . So

we have a cosine ωt always.

And so no matter what kind of a wave function we make, if we start out at one turning point, it's going to go to the other turning point. And it'll keep coming back, and back, and back. And so one could imagine doing an experiment where-- let's just draw the excited state and some other repulsive state.

So at this turning point, vertical transition to that repulsive state is within the range of your laser. And at this turning point, it's way high. And so what you can imagine doing is probing where this wave packet is as a function of time by having a probe pulse which creates dissociating fragments.

And now, that is what Ahmed Zewail did. He talked about real dynamics in real time. So when the wave packet is here, it can't be dissociated. When it's here, it can. And you look at the fragments. Very simple. So there are lots of ways of taking these simple pictures of wave packets moving and saying, OK, I can use them to set up an experiment where I ask a very specific question. And I get answers. And I know what to do with the answers.

Now, if it's not harmonic, you can still do Zewail's experiment or some other experiment. And you can ask, OK, the wave packet moved over here. And there's some dynamics that occurs. It dissociates or you do something. And when it comes back, it's not at the same amplitude. And so you can use the time history of these recurrences if it's harmonic. If it's not harmonic, then the recurrences-- even if nothing happens over here, the recurrences will be increasingly less perfect. And so you measure the anharmonicity.

OK. Five minutes. Tunneling is a quantum mechanical phenomenon. And again, you want to use the simplest possible picture to understand the signature of tunneling. And so what do you do? Well, the simplest thing you can do is start with a harmonic oscillator. The next thing you do is you put a barrier in the middle. And you make it really thin.

Thin is because you don't want to calculate the integral. You want to just say, oh yeah, I know that the wave function-- forget about the barrier. We know the magnitude of the wave function at the barrier, OK? And so if you have a state which has a maximum here, well, that means that it's feeling the barrier. And so you know what to do. If there is a node here, it doesn't know about the barrier. So you can do all sorts of things really fast. OK. So and it's harmonic because you're going to want to use a 's and a^\dagger 's.

So v equals 1, 3, 5. They have nodes here. They don't know about the barrier. Or if they do, it's a very modest effect. If you make this thin enough, you won't know about it all. And then v equals 0, 2, 4, et cetera-- well, they're maxima. Well, they have a local maximum here. And remember, this is a harmonic oscillator. So the big lobes are on the extremes. The smallest lobe is in the middle, but it's not 0.

OK. There are also symmetry restrictions. This is a problem that has symmetry. We have even functions and odd functions. And for the even functions, $d\psi/dx$ is equal to 0. And for the odd functions, ψ of 0 is equal to 0. OK. So this is something that-- you choose the simplest problem. And you use symmetry. And bang, all of a sudden, you get fantastic insights.

So let's look at what happens to the even functions. So let's just draw a picture of the harmonic oscillator energy levels. And we have a barrier, which we say maybe goes that high. And so we have 1. And we have 3. And we have 5. They're basically not affected by the barrier. Because they have a node at the barrier.

And then we have v equals 0. What happens to v equals 0? Well, it hits this barrier. And it's got a large amplitude. And it can't accrue more phase as you go through the barrier. So when it hits the other turning point, it doesn't satisfy the boundary conditions. It'll go to infinity at x equals positive infinity.

So it has to be shifted so that the boundary conditions at the turning points are met. And the only way that can happen is it gets shifted up in energy a lot. So v equals 0 is here. Now, it can't be shifted above v equals 1. Because that would violate the node rule. And if you draw a picture of the wave function for v equals 0 in the boundary region, the wave function has to look something-- well, it has to look something like that.

So we have two lobes. And it's trying to make a node, but it can't. It's a decreasing exponential. I mean, if you have a wave going into this region of the barrier, you can have an increasing exponential or a decreasing exponential. You can never satisfy continuity of the wave function with the increasing exponential. But you can with the decreasing exponential.

And so the height of the barrier determines how close this guy comes to having a node. It never will. And how does this compare to the wave function for v equals 1? Well, the wave function for v equals 1 looks like this. The amplitude in this lobe and the amplitude in that lobe are the same. But the sign is reversed.

And so basically, this picture tells you that these two levels have almost exactly the same energy. So v equals 0 is shifted up. v equals 2 is shifted up, but not quite so much. And v 4 is shifted up hardly at all. And so you get what's called level staggering. And this level staggering is the signature of tunneling. This is how we know about tunneling, the only way we know about tunneling.

So we measure the energy levels. And it tells us how are the wave functions sampling this barrier. Now, this is a childish barrier. And there is a real barrier-- molecules isomerize. And they isomerize over a barrier. And the barrier isn't necessarily at x equals 0. But if you understand this problem, you can deal with isomerization.

Now, I'm an author of a paper that's just appearing in Science in the next few weeks on the isomerization from vinylidene to acetylene. There's a barrier involved. So these sorts of pictures are important for understanding those sorts of phenomena.

Now, so I'm done really. So what we are now encountering with the time dependent Schrodinger equation is discovering how dynamics, like tunneling, is encoded in an eigenstate spectrum. Because the encoding is level staggering eigenstates. So people normally have this naive idea that eigenstate time independent Hamiltonian spectroscopy does not sample dynamics because it's only measuring energy levels. Real dynamical processes are time dependent. But the dynamics is encoded in energy level patterns. And that is actually my signature in experimental spectroscopy. I've looked for ways in which dynamics is encoded in eigenstate spectra. And chemists are interested in dynamics much more than in structure.

So that's it for today. I will see you on Wednesday.