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PROFESSOR: Today, since the notes for this didn't exist until last night, I made copies for you. I will do a little more revisions on what appears on the web. But this is a really interesting and important topic. And so I think it's important that I give a little bit of extra guidance.

So we're going to talk about what's in a spectrum. But in a very special sense, we're going to be talking about wave packet dynamics. And how do we understand what to expect in wave packet dynamics? And how do we approach it? And so let's begin talking about this.

So you already know from my lectures earlier, if you have a time independent Hamiltonian, how do you create a wave packet? I mean, after this exam performance, I want some insights.

AUDIENCE: [INAUDIBLE] the individual eigenstates.

PROFESSOR: Yeah. So you use a short pulse. And you create some kind of linear combination. Usually, if you're not making eigenstates, that's a complication. And why would you want to do that? And the reason you do it is because these wave packets are going to move. And particles move. Your instincts are about particles moving. And there are rules for the particles moving, which are mostly what you have in your head. But there are some special stuff that has to do with quantum mechanics.

And so I'd like to build from the bottom. And so I want you to be able to understand wave packets moving on a diatomic surface. And then we'll make a step into slightly more complicated situations.

If we have a diatomic, we have a potential curve. And we have an initial state. And that initial state in V equals 0 gives us access to a range of vibrational levels in the upper state. And if we have a short pulse, we can create some kind of a wave packet involving a linear combination of these vibrational levels.

So suppose you had a polyatomic, $3N$ minus 6 vibrational modes. So what would you do to go from a diatomic molecule to a polyatomic molecule? Initially, you want to do something simple

that doesn't involve anything that's especially new. So what would you say about dynamic diatomic polyatomic surface where there's $3N - 6$ as opposed to 1 vibrational modes? What kind of a wave packet would you do, would you create?

AUDIENCE: [INAUDIBLE]

PROFESSOR: We had Franck-Condon bright modes and Franck-Condon dark modes. So it sounds like you're right on the verge of saying something profound. So say it.

AUDIENCE: You're just going to have lot more coordinates.

PROFESSOR: Yeah. You're going to have more coordinates.

AUDIENCE: [INAUDIBLE]

PROFESSOR: So you will create a wave packet on the Franck-Condon bright modes. And if there's more than one Franck-Condon bright mode, the wave packet will do just like what it would do on a diatomic molecule, except you might have two different frequencies.

OK, well, there's additional complications. And that is, even a diatomic molecule, we don't have harmonic motion. So the wave packet, because of diagonal anharmonicity, will dephase. But the center of the wave packet will continue to move at the average of the vibrational frequencies for all these modes. You know that.

And so in a polyatomic molecule, maybe there's two, maybe there's three Franck-Condon bright modes. And the wave packet will have several different components on the different Franck-Condon bright modes. And they'll be diagonal anharmonicities. And they will dephase and possibly do interesting things.

So now, polyatomic molecules can do something else. Because there are, in fact, $3N - 6$ vibrational modes. And there's anharmonic couplings between the modes. So if you created some wave packet or set of wave packets in a polyatomic molecule, there will be anharmonic interactions between modes. And what you will have is the appearance of wave packets in the Franck-Condon dark modes with their own frequencies.

So this is starting to get interesting. Because you hit this molecule. And it starts revealing its secrets. Where you had Franck-Condon dark modes, they're not going to talk to you. But now, because of the anharmonic couplings, they do.

And then with a diatomic molecule, we might have an excited state. And it might be crossed by a repulsive state or crossed by another bound state. But if you have a wave packet operating on this bound state, it's going to be crossing through this region. What's so special about where curves cross? You know this, too.

If you're in this state and at this point, you have this much momentum. And if you're on this curve at that point, you have the same. So you have two rapidly oscillating things with the same spatial oscillation frequency. And so there's a possibility that the wave packet can leak from this curve, from the bound curve, to the repulsive curve.

And there are all sorts of things of that nature. I'm going to talk about all of that today. And one of the things-- the reason I made these notes is because I've always wanted to say something about the Landau-Zener model for crossing between different potential curves. And we talked a little bit before about driving too fast on a curvy road. Do you stay on it or do you hit the tree?

And that's basically this picture of-- you have two curves that can cross or they could do this. This is the adiabatic representation, which is amenable to quantum chemical calculations. And this crossing curve is the diabatic representation, which chemists like because the electronic wave functions don't change as a function of internuclear distance.

And so the issue is, when you have crossing curves or avoided crossing curves, how do you understand what the wave packet is going to do with those points? And that's the point of this lecture. And there are two experiments done by Ahmed Zewail's research group which illustrate many of the effects of wave packets and avoided crossings.

And so the question is, how do we observe this kind of evolution of the wave packet? What kind of experiments do we do? If we're talking about motion, we're probably not interested in the frequency domain. Although, you can get a lot of information from the frequency domain that enables you to understand what you might see in the time domain.

And one thing about frequency domain experiments-- when you have a molecule, which has $3N - 6$ vibrational modes, like benzene has 30, the vibrational density of states increases rapidly with excitation energy. So rapidly that, above the region of the fundamentals, the highest frequency fundamentals, they're no longer resolvable vibrational levels. The density of states is on the order of a billion per wave number. And you're going to be asking different

kinds of experimental questions to say, do I understand what's going on in even a molecule as small, from your point of view, as benzene, big from my point of view.

OK, so we're interested in mechanism. Why do things happen? What makes them happen? And how do we construct an experiment that reveals mechanism? And how do we interpret those sorts of experiments? And the Zewail experiments are beautiful examples of revealing mechanism, which is more complicated-- well, more revealing than what you might expect.

For example, suppose you excite a molecule and it breaks. Well, how did it break? Did it just break? Or was there some motion preceding the breaking where the molecule arranged itself to receive this photon and do something with it? And it makes fragments. And what are the fragments? What state are the fragments in? There are all sorts of stuff there. And that's mechanism. And it's not just the breaking of a molecule and getting from the width of a spectral feature how fast that breaking occurred. There's things that happen in that time.

OK. So we need to talk about diabatic versus adiabatic. And so if you did a quantum chemical calculation-- and you can. Because you still have access to the Athena cluster. Or is your membership expired?

AUDIENCE: We should always have access to it.

PROFESSOR: OK. Well, you do a calculation using the computer programs. And they're basically clamped nuclei. And that's just because you want to reduce the complexity of the calculation. It's an impossible calculation anyway to do exactly. And if we say, let's keep the heavy particles from moving around, we just solve the electronic Schrodinger equation, well, then we get what we call an adiabatic potential energy surface, or one for each electronic state.

And well, if we clamp the nuclei, molecules don't hit the nuclei clamp. We have to unclamp them. And the effect unclamping leads to some perturbation term, H_1 . And so when we solve the clamped nuclei Schrodinger equation, we don't have vibrations. We don't have rotations.

And so one of the things we don't know about is partial derivatives with respect to nuclear coordinates, which we have the nuclear kinetic energy, which is the second derivative. And when you have a second derivative, you can apply one derivative to the nuclear part of the wave function and one derivative to the electronic part. Or you can apply both.

And so the electronic wave function you get is-- you get a wave function, which is an explicit function of the electron positions and parametrically dependent on internuclear distances or

nuclear geometry. Well, that's there. And this nuclear kinetic energy term, which is present, is going to operate on these guys and lead to trouble. Or maybe not, depending on what the potential curves look like and what their problem is.

But certainly, this nuclear kinetic energy can operate on these functions and give something that we have to at least consider. So this guy has secrets embedded in it that we're going to have to look at. And they're going to be surprises.

So let's think about diatomics. Because with diatomics, most of the things you're going to encounter in polyatomic molecules have examples that you can understand really clearly. So suppose there are two electronic states that cross or do something. And we can have a picture like this.

So the calculation you do will give you these avoided crossing potential curves. Well, why do they avoid each other? If you have two states of the same symmetry, they can perturb each other. The Hamiltonian is totally symmetric. Any kind of term in the Hamiltonian that is totally symmetric can cause interactions between states of the same symmetry.

Now, many of these terms of the same symmetry-- totally symmetric terms in the Hamiltonian-- are excluded when we do a calculation. Because we can. One is spin R.? But there are things that could affect the states belonging to these two potential curves. And so there are going to be interactions between states of the same symmetry.

And this is the place. So you have the ab initio calculation. You get these curves. And you can see that there is some coordinate at which the difference between potential curves is a minimum. Nature tips its hand. These avoided crossings that are really important. And it tells you-- the quantum chemical calculations tell you two things. They tell you the internuclear distance at which the crossing occurs.

And let's call this one-- let's have several names for these curves. OK, I have to-- so we can call this $2, 1, 1, 2$ plus plus minus minus. I have two sets of labels. So let's say that the 2 and 1 describe the electronic character of this state, the kind of thing that the chemists care about. And plus and minus as upper and lower. And that's what you get from quantum chemistry.

And so the quantum chemistry gives you the place at which these two curves have this minimum separation. And they have the plus at RC minus V minus at RC is equal to $2H_{12}$. You know from perturbation theory that, if you have two levels which are degenerate and

they're interacting by some coupling term, the separation will end up being twice the matrix element.

So nature gives you this and this from which you can construct the crossing curves, the curves that chemists like. So even though quantum chemistry doesn't know about diabatic curves, it tells you how you could construct them.

And now, there's two limiting cases. We can have a very weak interaction. And so the curves get really close together. Or we can have a very strong interaction and get something like this. So these are the two limits. And it turns out that the way you would handle these two limits is experimentally and theoretically profoundly different. Why?

This term, the nuclear kinetic energy term, does terrible things here. Because when it operates on the electronic wave function, it says, the electronic wave function is changing rapidly in this region. And so if we're going to try to set up a Hamiltonian that describes the energy levels of these two states, because of this term, there will be enormous couplings between the vibrational levels of the two states.

And as a result, H_0 , the thing that ignores those coupling effects, will bear almost no resemblance to the observed energy level structure. To get from these kinds of curves to the observed energy levels is a lot of work. And it's work that people who use pre-written computer programs are ill prepared to do.

The spectrum will not be predicted in any way by this, unless you do a huge matrix of interactions between vibrational levels of the different electronic states. And when you have a matrix element, which is large compared to the differences between levels, you can't use perturbation theory. You have to diagonalize a matrix. And usually, when you diagonalize a matrix, the eigenvalues are a bit of a surprise.

Over here, the electronic wave function doesn't change very rapidly. And so we have no problem of the interactions among the vibrational levels of these two states. And so the adiabatic representation provides a good zero order picture of the energy levels. And there's a little bit of stuff that you can add to improve the fit.

So when you have what's called a weakly avoided crossing, it tells you that the adiabatic representation is the wrong one. But when you have a strongly avoided crossing, well, it's the right one. Because all of the effects of this repulsion between the two states are included in

your zero order Hamiltonian. Whereas here, none are. And you say, well, I could just go cruising through this region. And I go fast through it. And I don't notice the bad effects. Well, we'll see. OK.

So now, if we had a diabatic representation like this, well, diabatic curves can cross. In fact, that's the whole point. We want them to cross. Because we'd like to keep track of electronic character 1 and electronic character 2. And so I'm just going to use this here.

OK. But the really annoying thing is, when we did an initial calculation, we clamped the nuclei. We said there are certain terms in the exact Hamiltonian we're going to push aside and consider later. But for the diabatic picture, well, it's clearly there's some term in the electronic Hamiltonian that we'd like to turn off. But there isn't one. It's all or nothing. There is nothing you can identify in the electronic Hamiltonian that enables the two curves to cross. So it's not that it's a bad idea. It's just there is no simple way of dealing with this.

Now sometimes, we have the Hamiltonian. And we have, say, the spin orbit Hamiltonian. And this is something we could turn off. But that's gilding the lily. I am a spin orbit aficionado. So I could deal with this. But if we don't say there are specific, named, small terms in the electronic Hamiltonian, there is no way we can get the diabatic limit directly. You have to use a trick.

So let's draw a picture now, which illustrates the trick. And we're almost ready to start talking about Zewail's experiment. So here I'm going to draw. OK. So the adiabatic curves are the ones that don't cross. And The. Dash lines are the diabatic curves. And we know RC and H12. Or at least we know H12 at that internuclear distance. And it's a reasonable thing to say, well, let's let it not change with internuclear distance.

And let's make some other approximation. We can say the diabatic curves are linear in the region of the curve crossing. We can always-- especially when the adiabatic picture is bad, that curve crossing is very, very compressed. And it's not a big step to say, OK, over this relatively small range of internuclear distance and energy, we're going to approximate the diabatic curves as linear. And so we know the exact Hamiltonian, whatever it is, be gotten from.

OK. So here, we have what's available from quantum chemistry. These are the potential curves for the upper and lower adiabatic states. And here we have a potential curve for state 1 and a potential curve for state 2 at H12. And a unitary transformation of this matrix has to be equal that matrix.

Well, we don't know these. But we're going to reduce them to one number, the slope at the crossing. And so we have one number here, one number here. And all of a sudden, we have enough to iteratively determine the difference between the slopes by fitting to the observed adiabatic potentials.

And this is basically how it's done. Now, people who do these calculations for a living have a much encrusted picture of how they do this. But this is basically what's going on. Because people do want the diabatic picture. And a lot of insight is gained from the diabatic picture.

OK. So if we're going to be approaching a spectrum where we have energy levels or an experiment where we learn something about the dynamics, we're going to want to think about this problem with two limits-- weakly avoided and strongly avoided. And completely different methods for dealing with both spectroscopic and dynamical information are appropriate for the two limits.

OK. Landau-Zener-- this is a model for saying, OK, what is the probability of going for one curve to the other? And so we have a formula, which you can derive. I don't recommend it. Because derivations are things you do when you need it. And then you forget them. But I do want to give you a sense of what's in it.

So we're going from one adiabatic state to another. And the probability is $1 - e^{-\pi \gamma}$. The important parameter is γ , right? Everything in this. OK. And so P_{12} is small when γ is-- well, we want this to be 1-- so when γ is small. And P_{12} is large-- now, I just want to make sure that I have it-- yeah, when γ is large.

Now, what's γ ? γ is expressed-- and this is what you would derive if you were going to do this for real life. Because you would never accept somebody else's speculation, you derive it yourself. So V_{12}^2 -- that's the matrix element. That's half the gap between the diabatic curves.

And it's over \hbar velocity $S_1 - S_2$. This is the difference in slopes of the diabatic curves at the crossing point. This is the velocity of the particle going through the crossing point. And you can, of course, get the velocity from the momentum divided by the mass. And so all of this stuff is there. And so γ is small when V is large and when S_1 is approximately equal to S_2 .

Well, if the slopes are nearly equal, that's a strongly avoided crossing, right? And V is large-- well, if you're going through a bend in the road and it's too fast, well, then you're not going to-- yes, you're not going to be able to make the curve. So anyway, this is the physical basis behind Landau-Zener. And it contains the connections to the stuff you have from your picture of the potentials. And this is basically how you organize a Zewail type experiment, which I've got to talk about now.

You have those notes already on Zewail electronically. So I didn't make copies of them for you. So you're going to have to accept what I'm doing without looking at notes for this part, unless you have them already printed out.

So Zewail had the 1999 Nobel Prize in chemistry. And it was really special. Because usually, these things are divided three ways. He got the whole damn thing. And this was because he offered something that we really want. We want to have an idea of, what is the mechanism by which dynamical processes occur? In other words, we're not just getting rate. But we're getting, what are the nuclei doing? And how does the motion of the nuclei affect the rate of the process?

AUDIENCE: I think you want S_1 is very different than S_2 .

PROFESSOR: That's quite likely. And I'm very poor with logic. Let's see. So I want you to decide for yourself, OK? And let me just-- OK. So this is an example of a pump/probe experiment. So the pump pulse at $t = 0$ starts things. And the probe pulse at $t = \tau$ asks the question, has the wave packet gotten to what's called the OCR, the optically coupled region?

In other words, you create a wave packet and you have a probe which can tell you the time at which the wave packet passes through where you're probing it. And this is really neat. And it is, I think, the essence of how Zewail created a really simple experiment using the crude technology that was available at the time to ask the kind of question he needed to ask.

Now, I didn't like this whole experiment when it first came out. Well, because I'm a frequency domain spectroscopist. And I don't really care about dynamics, except how it's encoded in the frequency domain spectrum. So this is completely different. But anyway, so now, I want to describe the essence of what he did, and why it worked, and what it reveals.

All right, and so I want to pick a blackboard. So there are two experiments that he did. One was dissociation of I-CN. And the other was dissociation of sodium iodide. Now, one thing to

notice is we've got a big heavy atom in here. So that means the vibrational frequencies are low. That means that, with a not too short pulse, you could create a coherent superposition.

When you think about what you would need to create a coherent superposition of vibrational levels, different by the canonical 1,000 wave numbers of a vibration, you realize that that experiment was only doable fairly recently when you have on the order of a few femtosecond time resolution. What Zewail did-- he had maybe a 100 femtosecond or maybe only a picosecond. And so he had to have a heavy atom.

For I-CN, the beautiful thing about I-CN is there's CN here. CN is a diatomic molecule that has a very convenient spectrum. And so we're asking the question, how does the presence of the iodine affect the CN spectrum? Because the CN is going to give us the signal in this experiment.

So here is-- it's really neat. This is a triatomic molecule. But we always use one dimensional pictures to describe everything that's going on. And you can do that when the one dimensional pictures are each applicable in separate times or at separate aspects of the experiment. But it's another beautiful example. If Zewail had been attempting to describe the full three dimensional potential, the pictures wouldn't have done anything for anybody. Because you would have to work too hard to understand what the pictures are telling you.

OK. So we now have a repulsive curve. And we have another repulsive curve. OK. So we have V equals 0. And so we're exciting a wave packet. And because we have a few vibrational levels that are accessible with the Franck-Condon principle from V equals 0 and within the necessary Fourier transform of the pulse duration, you get a wave packet starting here.

OK. So this wave packet is going to be toddling along at this energy. I'm sorry it's going to be moving on this potential. But it has a definite energy. OK. And then you can probe it this way, or this way, or this way.

And the important thing is that these three places at which you probe correspond to different excitation energies. It's saying that, as the iodine atom is leaving-- these are transitions between CN. And in here, the iodine atom is close to the CN. And it is affecting the bonding in the CN. Over here, it's gone. And the CN is free. And what's happening is the transition frequency changes with time.

And so if he has the probe pulse here, well, then when the wave packet reaches this point, you

get a response. Before the wave packet gets there, there is no exaltation. So the OCR is defined-- the optically coupled region-- it's defined by the frequency, the center frequency, of the probe pulse.

So if we then look at-- OK, now, what's happening here? When you excite to this state, you have CN electronically excited. When you look at this limit, you have CN not electronically excited. The CN A double pi x double sigma plus transition is one of the most studied things in the atomic molecules. And so it's known. And like all transitions, the intrinsic radiative lifetime is on the order of 10 nanoseconds.

So if we excite to this state, we're going to get a photon out. But the lifetime of that photon is 10 nanoseconds. Are we going to measure dynamics? This is the beauty of the experiment right here. He catches the wave packet at a particular position. And he puts it in the bank.

And then eventually, the CN fluoresces. We don't care anything about when it fluoresces or what frequency it fluoresces at. All we cared about is that-- if you're looking at if the wave packet is in the optically coupled region, it gets excited to this surface. And then when it chooses to say, I got excited, here is my photon, then you can create a plot of-- so versus time.

So you see nothing. And then you get something at the optically coupled region. And you do a sequence of experiments where you vary where the optically coupled region is centered by adjusting the center frequency of the probe laser.

So sorry. I should really say, OK, here is the intensity of the fluorescence. And here is the $1/\lambda$ over the wavelength of the probe. So this is related to the energy of the probe. And so you do a series of experiments. And you discover that the wave packet reaches this. And then you move that. And you get another. And so you get a picture.

So what do I want to say about this? So it basically is telling you that, when the molecule breaks, the frequency of the CN excitation is changing as a function of the distance of the iodine atom from the CN. And so that's mechanism. Now, it's really a very crude mechanism. But because it's reduced to one question, it's a function of one geometry. But nobody's ever be able to say they observed this motion of the wave packet in real time.

And here is where people really get annoyed with Zewail. Because he's looking at real motion in real time. And it ain't real. He's probing one time at a time. But it's still mechanism. It's more

than just looking at when does something break. What's the lifetime of something? There's more than one thing going on.

Now, I really like the next experiment. And the next experiment involves sodium iodide. Now, if I were to ask you, what is the nature of sodium iodide at equilibrium? You'd say, it's probably ionic. But because iodine is at the bottom as opposed to the top of the periodic potential, it's maybe a little bit covalent. So here is the ground state potential. And I just have to make sure I understand what I'm trying to do. And here is an excited state potential.

OK. So what I've tried is crossing curves. Those are the diabatic curves. Now, I've connected-- I should do it with dotted lines. Those are the adiabatic curves. And so the question is, suppose we create a wave packet on this potential. So it's created here. And this wave packet feels a force that way. Because it's the gradient of the potential. It's a particle. It's in a potential. And it's going this way. And then something happens when it goes through this curve crossing region.

But what's going to happen? I should just say this is the ionic. This is the covalent. So this is $Na + I$ minus. And this is $Na + I$. When you dissociate a neutral molecule, you always get neutral atoms. So there is a higher energy limit where you can get ions. And so even if you create this wave packet here, which is below the threshold for making ions, it only can leave by this path.

So what happens is the wave packet is going back and forth, back and forth, back and forth. And each time it crosses through this region, it has to decide, am I ionic or covalent? And if I'm covalent, I can leave. And if I'm ionic, I'm stuck. I've got to go back and try again and again and again.

So this is where Landau-Zener comes in. Because what's happening is the molecule is addressing this ionic covalent curve crossing. And it's deciding each time it goes through, what is the probability of being able to get out? OK. But then, there's something else. And that is, well, what are we probing?

So we probe to an excited state. And so this is where the figures, even for this reduced representation, are confusing. But basically, you're probing by exciting this sodium atom to an excited state, which puts it in the bank. And it fluoresces when it chooses to, which is in 10 nanoseconds. Because sodium's radiative lifetime really is about 10 nanoseconds.

And so how to describe this? So you have a choice of being able to excite at the free sodium transition frequency. And then what you're only seeing is these little packets of sodium that make it out. Or you can excite at a-- well, this is coming out wrong. But if you excite to the red of that, you will only see the sodium atoms while they are still close to the iodine.

And so there are two sorts of signals you get. One is you get a series of pulses separated by the round trip time-- the round trip time is the period. And so the period is related the vibrational frequency.

And so each time this packet goes through the optically coupled region-- I'm sorry-- goes through the curve crossing region, you get a little puff of sodium. If you're exciting so that you can see only the free sodium, well, then instead of this, you see the signal, another signal. So you get little steps. Each wave packet that makes it out dies at the turning point.

And I'm way over time. But this is really the-- so there's two pictures. There is this sampling of the wave packet each time it goes through. And there is the delivery of the goods. And again, the signal is a slow signal. But the pump/probe delay is femtosecond time resolution. And so it can reveal this wave packet propagation. So that's all I have to say on the subject. I think it's really beautiful. I like it more and more the more I understand it.

And the next lecture will be on why gases condense.