ROBERT FIELD: Now if you looked at today's notes, you'll notice that they're very long and very complicated. And that's not intended to be intimidating. It's just to show you the power of perturbation theory. So we have talked about the two-level problem. The two-level problem is one that's exactly solved. It's one of our favorite exactly solved problems, although it doesn't seem to have any physical relevance. It's just a nice numerical exercise.

So we can take a two by two Hamiltonian and exactly diagonalize it. And that's done using a unitary-- or actually, in the case that we looked at, orthogonal-- transformation. And so it's a rotation in state space. And the rotation angle is an explicit function of the parameters in the Hamiltonian.

Now all good things come to an end. We cannot do this for anything more than a two-level problem. But we can take the formalism for the two-level problem and say, oh, well, we can describe a transformation that diagonalizes the end level problem. And it has the same property of being unitary.

But the good thing about it is it's solved by a computer. You tell a computer what the operator is, and it will diagonalize it. And not only will it diagonalize it, but it will give you the eigenvalues and the eigenvectors. It gets those eigenvectors by applying the same two level unitary transformation many, many times.

So if you have a six-level problem or a hundred-level problem, the computer just cranks and cranks on each two by two and does transformations. And it keeps doing that until the off diagonal matrix element is small-- remaining off diagonal matrix element-- is small compared to the difference in energy between the eigenvalues it connects.

And so you tell it, I want this convergence criterion to be a part in a hundred or a part in a million. And it just does this and does this. And eventually, it gives you the transformation and the eigenvalues. So that means that it doesn't matter how big the problem is. You just have to have a computer that's patient or fast. And it will crank out the results. Now you need to know

how to use the t matrices, or the t dagger matrix, because these things enable you to solve basically any problem in time independent quantum mechanics and a lot of problems in time dependent quantum mechanics.

So there is another way, and that's going to solve an n-level problem. And that's the subject of this lecture and the next lecture. It's called non-degenerate perturbation theory. Now our goal-- well, let's ask. I'm a spectroscopist. What do spectroscopists do? Now, there's a silly, stupid answer to that. I want something a little more profound. Yes?

AUDIENCE: Find energy levels?

ROBERT FIELD: Yeah, we record spectra. We get energy levels. And we get intensities. We get all sorts of things. We could also be working in the time domain, and we could we could be looking at some kind of quantum beating system or some decaying system. We make these measurements.

But this is not why we do it. Remember, yes--

AUDIENCE: All spectra have buried information about the physical parameters of the system.

ROBERT FIELD: Exactly, exactly-- that's what's kept me going for my entire career. I use the word encoded rather than buried. But I like that. I might start using buried as well. Yes, we're not allowed to look inside of small things. We're not allowed to determine the wave function by any experiment. But we are able to observe the energy levels and properties of the Hamiltonian.

And we can regard the Hamiltonian as a fit model, a model where there are adjustable parameters which are the structural parameters, like the force constants and the reduced masses and whatever we need to describe everything in this problem.

And today's lecture is mostly going to be on the interactions between normal modes of a polyatomic molecule. Now you might ask, why am I doing this rather than talking about just an ordinary, anharmonic oscillator. And the reason is, I'm going to do that in the next lecture. And it's in your problem sets. You're going to do that. So I'm going to show a little higher order of information.

So we go from what we can observe to a representation of it, which we call the effective Hamiltonian, where in this effective Hamiltonian we have determined the values of all of the important structural parameters. And from that, we can calculate everything, everything that

we could possibly observe, including things we didn't observe.

So it's really powerful. It's a way of taking the totality of observations that you're going to make and saying, yes, I have looked inside this molecule. And I've determined everything that I'm allowed to determine. And I can calculate the wave function. The wave function is an experimentally determined wave function, but only indirect.

This is amazingly powerful. And basically, everybody who deals with spectra is doing this whether they know it or not. And so I want to be able to give you the tools to be able to take any arbitrary spectrum and extract from it the crucial information.

In the last lecture, we talked a little bit about matrix mechanics, and that involved linear algebra. And you have a wonderful handout on linear algebra, which will give you more than enough to be able to do any quantum mechanical problem we're going to be facing in this class. And there is notation. And the notation is unfamiliar, and you have to learn how to use it.

And so we have for example-- the analogy to the Schrodinger equation in matrix language-- where we have the Hamiltonian, an eigenvector, an eigenvalue, and this eigenvector. So it's an eigenvalue or eigenvector equation. And this is the form of the Schrodinger equation and we can pretend that it is the real Schrodinger equation. And we can use the standard approaches, but it's useful to work in matrix notation.

So we can solve for the energy levels, and we can solve for basically all of the eigenvectors. And our friend is this unitary transformation where t dagger is equal to t inverse. And t times t inverse is equal to this thing 1111100, or the unit matrix. I thought I saw a hand up. That was just-- that was not serious.

And so these unitary transformations have this special convenient property. And we use these t daggers and ts to diagonalize the Hamiltonian. Now this is just a little bit of review. So how did we derive the thing that we are going to solve?

Well, we took this equation and we inserted 1 between the Hamiltonian and the vector. And then this is 1. So we don't need to put it over here. And then we left multiply by t dagger, and we put parentheses around things. So this is now what we were calling h tilde. And this is c tilde. And this is now an equation that says, OK, we can transform the Hamiltonian into diagonal form-- E1, En, zeros. And when we have this in diagonal form, we can say, well, this equation is just E1, 100 et cetera. So for any eigenvalue, we have an eigenvector.

Now what we'd really like to know is, well, how do we get these eigenvectors from the unitary transformation that diagonalizes H. We don't calculate this unitary-- yes?

AUDIENCE: Is that i or--?

ROBERT FIELD: This is a 1, this is a 1, this is a 1.

AUDIENCE: I mean in your c tilde, third from the top.

ROBERT FIELD: That's a j. This is a particular eigenvalue, and this is the eigenvector in that. Now it's easy for me to get screwed up, and it's easy for you to wonder, what the hell am I doing, until you've done it. And then it's completely transparent. It's really quite simple. But it's just this extra notation.

And so it's possible to show-- and I don't want to do it. I did it last time. You can show-- and this is important-- that this transformation t dagger c equals c. Do I want?-- above, above. This is telling you that the columns of t dagger are the eigenvectors. They are linear combination of the basis vectors that correspond to each eigenvector. And you can look at this in more detail in the notes.

Now this is great because mostly you want to know what the eigenvectors are for a particular eigenvalue. But sometimes, when you're doing dynamics, you prepare, not an eigenvector, but you prepare a t equals 0, a basis state. This is the most common, doable problem, and it's also something that one does in experiments.

You can set up a problem so that, with a short pulse, you prepare the system at t equals 0 in something that's not an eigenstate. And usually it's a basis state-- it's one of the eigenvalues of an exactly solved problem. But your problems are not exactly solved ones, but your experiment selects that. And this, not being an eigenstate, needs to be expressed as a linear combination of eigenstates so that you can actually calculate this, which will describe how the system is behaving.

And I like asking exam problems like this because it's easy to get hopelessly involved in ordinary algebra rather than just using linear algebra. So if this is the transformation to the eigenbasis, then the columns of t are the transformation back to the 0 order bases. And the columns of t are the rows of t dagger.

Now why should you care? Because you don't know how to calculate the elements of the t

matrices yet, but that's what perturbation theory is for. With perturbation theory, it doesn't matter that the computer could solve for the t and t dagger matrices. But there's no insight. You just get the numbers. I like to say that spectroscopy is not about creating archival tables of observed transitions and observed transition intensities. It's about understanding how things work.

And so depending on whether you're doing a time domain experiment or frequency domain experiment, you're going to want to use either the columns of t dagger or the rows of t dagger. Now at some point in your life, you have to be exposed to non-degenerate perturbation theory because it is really powerful. But it's also incredibly ugly.

So we have a whole bunch of problems-- I'll go over here-- that are related to the particle in a box or the particle in an infinite box or the harmonic oscillator. And so one of the things that you might do is round off the corners because physical systems don't have discontinuities.

Well, that's going to be a very modest change to the energy levels and wave functions. Another thing you might do is have a barrier, and you could put the barrier anywhere. What does the barrier or an extra well do? Or you could do something like this.

So the particle-in-a-box is a whole family of problems that you could solve using perturbation theory by saying, OK, the extra stuff is the perturbation. And we have to work out the matrix elements of the Hamiltonian that correspond to these extra things and then figure out what to do to get the eigenvalues and eigenfunctions.

Now, for the harmonic oscillator-- again, you could put a barrier in the middle or you could make it an asymmetric like almost all molecular potentials are, where this is dissociation and this is two closed cells colliding with each other and doing very hard repulsion. And so that is harmonic near the bottom, but it's not harmonic elsewhere.

And so how do you represent this? And the Morse oscillator is a cheap way of generating something with this shape and then doing the perturbation theory to understand how the nonharmonic aspect of the Morse can affect the energy levels. Or how did the energy levels determine, say, the association energy of this molecule? How is that dissociation energy encoded in the energy level pattern?

Now for polyatomic molecules, if you have n atoms, there are 3n minus 6 vibrational normal modes. Well, how do I know that? n atoms, there's 3n degrees of freedom. There's 3

translations and 3 rotations. And so that leaves 3n minus 6. And all of that is vibrations. So we have many normal modes, and it's not too surprising that, if you stretch one normal mode, it'll affect the frequency of another. And we'd like to know that.

And so perturbation theory is really valuable for polyatomic molecules. And that's the bulk of the examples that I worked in the non-lecture notes for this lecture. But there's also dynamics. So you prepare some initial state of t equals 0 and you want to know how it's evolving. But often that initial state is an eigenstate of one of the exactly solved problems. And you want to be able to re-express that in terms of the eigenstates of the real problem. And so you want to know C J-- I'm sorry. You want to know J, CJ eigenstates.

So once you have this, then you know how to write the time dependent wave function because you are dealing with eigenstates and they have eigenenergies. And so you just write this thing out. It's just mechanical and boring. It's also true that molecules rotate. And when they rotate, there's centrifugal force and their internuclear distances change. And we can then calculate how that will affect the rotational energy levels using perturbation theory.

And then there's the origin of life. Gases are not supportive of life. You need two particles to come together and start to condense into a liquid. That's the beginning. Perturbation theory explains the long range interactions by which all gas phase particles attract each other weakly. So that's important too. And so you'll be able to do all of this stuff.

So here we have non-degenerate perturbation theory. And it is a mind numbing, formal derivation. So we start out with this rotary equation. And we say, well, let us expand the Hamiltonian. And let's put a little thing here. This is our friend. This is an exactly solved problem. This is what's new, and this is what's new and small. And we could probably neglect it. And we do the same thing to the energy levels.

So these are the energy levels for the exactly solved problem. And these are the energy levels-- the first order corrected energy levels. And these are the second order corrected energy levels. And we do the same thing for the wave function.

Now we write the Schrodinger equation with these three term expressions. Now I'm also going to say, we're never going to consider this one either. So life is simpler without them, but in the notes, I included them all. And so what we do is now we write the full equation and we sort it into sub equations corresponding to powers of lambda.

So the lambda to the 0 equation is really easy. It's just H0 psi 0 is equal to E0 psi 0. We could put n's on this. And this is the exactly solved problem. It says, yeah, you build your foundation from the lambda to 0 equation, and it's just what you know already. And what you're going to do is now use the psi n 0 and en 0 to do everything else.

The lambda to the one equa-- well, you might ask, well, what is lambda. It's just a mathematical trick. It has no significance whatsoever. It's a smallness parameter, but it's also something where you can say, these equations will be true for any value of lambda. And so it's just a way of separating the equations into things that have a structure that you can manipulate. People have waxed eloquent about the meaning of lambda, and it really doesn't have any meaning.

So the lambda to the 1 equation-- well, we collect terms on the left hand side that have 1 lambda and on the right hand side. And so the lambda to the 1 equation is going to be, say, H0 psi 1 is equal to E0 psi 1. I'm sorry. There's more to it than that. There's four terms.

We're just collecting the terms that have 1 lambda on the left-hand side and right-hand side. And we've got this equation. What are we going to do with it? Well, one thing we can do with it is multiply on the left. Let's just put some indices here. So we have n, n, n.

We're going to multiply on the left and integrate by psi n 0. So we're going to get a bunch of terms. So we will have psi n 0 H 0 psi n 1 plus psi n 0 H 1 psi n 0. We have integral, integral. And on the left hand side, we have E n 0 integral psi n 0 psi n 1. And we have E 1 psi n 0 psi n 0.

Well, this is kind of an ugly term. It's a psi 0 and a psi 1. But we know that H, when operating on psi 0, gives E 0. So we're going to get E n 0 integral psi n 0 psi n 1-- same two over here. Cancel them. And so we get a simple equation that is just H1 n n is equal to E1 n. So we've gotten now the diagonal matrix element of the perturbation term is equal to the first-order correction to the energy.

And we can continue. The algebra isn't beautiful, but we end up getting the following equations. We have E n 1 is H 1 nm. We have psi n 1 is m not equal to n psi m 0 H nm. So what did I do here? I said, the wave function-- we have completeness. So if we want the first order corrections to the nth wave function, we can write this as a linear combination of the zero order wave functions.

And when we do that, we end up with this formula. This is the mixing coefficient, and these are the state-- now why do I exclude n? Because we already have it. And then we get the second-order correction to the energy, which is m not equal to n h n m 1 H m n 1 over En 0. That's it. That's all we need.

Now it does say non-degenerate perturbation theory. And so it's subject to the requirement that H1 n m over E n minus E m. So if the energy denominator is near 0, we know we're in trouble. But for the vast majority of energy levels, this term is much less than 1. And so that means we can deal with all of the interactions among the non-degenerate levels in one fell swoop.

Now this is an infinite sum, and this is an infinite sum. So we don't like infinities. But we can say, all right, here's the Hamiltonian. It's an infinite Hamiltonian. And we're interested in this little corner of it. And so all of the interactions among these states with all of the infinite others get subsumed into this infinite sum. It's a small number.

And then we're just interested in this little subspace of the energy levels that we're sampling in our experiment. So the molecule more or less tells you how to focus on the part that you care about and to get rid of the stuff that is of no trouble whatsoever. And it just contaminates the wave functions a little bit. And if you wanted to know what that contamination is, you could deal with it.

So this is the tool that you can use to solve, basically, any problem involving molecules with a potential like a harmonic oscillator at the bottom. But it's usable for all problems, but there's a different basis set rather than the harmonic oscillator basis set. So this is your handy dandy key. And you don't need a computer, although when you see the horrible complexity that will result when you start dealing with these sums, you will say, well, I do want to use a computer. But now it's up to me to organize the program so that you can ask the computer to do what you need in a sensible way and you still get good answers.

So in the notes, I'm dealing with a two-mode molecule. There are no two-mode molecules. There's one-mode molecules, and there might be three or four or six or whatever. But the complexity is the interaction between two modes. And so we're going to talk about that.

So we have for a two-mode molecule-- the Hamiltonian will consist of Hamiltonian for mode 1, Hamiltonian for mode 2, and the Hamiltonian for modes 1 and 2, interacting with each other. Well, we know these. These are just ordinary harmonic oscillator. And we've got to do some

work on this. And that's where perturbation theory comes in.

So H12-- and we know, if this weren't here, we know that the energy levels are that some of the energy levels for the two independent oscillators and the wave functions are the products. So even though the energy levels have two quantum numbers, V1 and V2, and the wave functions have two quantum numbers, V1 and V2, if it were only this, we'd have completely solved that problem.

But because of this, there's something else. So these then turn out to be the zero order states that you use to evaluate all the integrals here. And we have these and A and A dagger operators, which are enabling us to-- we have the operator for coordinate x is proportional to A plus A dagger. And this has a selection rule, delta V of plus and minus 1.

So we like these things because we don't have to do any integrals. They're all done for you. And so we're then going to use these sorts of things to deal with the most important terms beyond harmonic. And so there's a cubic and there is a quartic.

And although you haven't really explored this, what happens when you make dimensionless coordinates? You factor out something. And if you have cubic terms, they're 100 times smaller than quadratic terms. And the quartic terms are 100 times smaller than the cubic terms. And so you don't need to go much further.

So the cubic terms for the two oscillators would be 1/2 K 122 Q1 Q2 squared plus 1/2 K 112 Q 1 squared Q2. And you could have Q1 cubed, but we already deal with that in the single-mode problem. So we won't worry about that. So these are the couplings between modes 1 and 2 that are cubic. And then we have 1/4 k 112 Q 1 squared Q 2 squared. There's also a Q1 Q2 cubed, and those terms usually are not important because they mostly are dealt with under here.

So anyway, these are the parameters, and these are the things that you need in order to understand what this molecule is going to do when it's excited. Now when I was a graduate student, there was a great deal of excitement about doing what's called mode-specific chemistry. Ordinary compounds cost on the order of $1 a kilogram. But if you could do mode specific chemistry, you could make things that aren't makeable by ordinary, organic chemistry.

And the organic chemists would love this because it's a load of garbage because these guys make the modes talk to each other. And so even if you could excite a pure overtone or

combinational level, the energy moves around the molecule. And that's called intermolecular, vibrational redistribution. And those there are processes that you could talk about the primary paths for the energy to flow and the rates. And that was a major area of research for the last 30 years. And most people are tired of it.

But it started out being IVR, yeah, anything can happen. It's statistic or whatever. But no, only specific things can happen, and they're controlled by these specific coupling terms. And you could calculate them. Now there's an interesting other thing. I told you that the first-order correction to the energy is equal to a diagonal matrix element of the correction term to the Hamiltonian.

All of the second-order terms involve squares of matrix elements. The second-order terms you don't know the signs. If there is a first-order correction, you get the sine. And sometimes you know you want to know: is the perturbation like that or the perturbation like that? Is there a barrier or an extra well? And this enables you to know that in second-order perturbation theory when you have to square the matrix element, all that information is concealed.

Well, anyway-- so there is a huge amount of algebra that's involved in using these equations. And I don't really want to go through that algebra. You can read my notes. I think the chances of you reading those notes are small. But if I don't lecture on them, it would be slightly greater. It's a complete treatment of a two-mode problem with all of the possible and harmonic terms cubic and quartic. And everything worked out.

Now the trick is, you could easily say, well, the algebra is just so horrible. Why would I bother? But what you do is you take these terms and you sort according to selection rule. So for example, here we have a selection rule delta V1 is plus or minus 1 and delta V2 is plus or minus 2 and 0.

And so there are then six possible selection rules associated with these sorts of terms. And what you want to do is do the algebra that combines all this horrible stuff according to selection rule that leads to simplification of the formulas. And then once you've got everything sorted according to selection rule, then you can calculate what happens.

I can't promise that I will never give you a two-mode problem on an exam, but I can promise I will give you a one-mode problem. And so you want to really know how to do these sorts of things. So non-degenerate perturbation theory works when the energy denominator is large compared to the coupling matrix element.

And accidents occur when you have, say, a situation where omega 1 is approximately equal to 2 omega 2. Now this isn't just blowing smoke. This happens an amazing number of times because stretches are higher frequency than bends. And it's very common for the bending modes to be roughly half or one third the frequency of a stretching mode.

And so you get a resonance. So this is special because now it's violating the fundamental approximation of non-degenerate perturbation theory. But it's a two-level interaction. And so you can say, I know how to do a two-level problem. I can solve that. And these resonances have names. There is a Fermi and there is a Darling-Dennison. The Fermi resonance was discovered and understood by Fermi. And it has to do with CO_2. Omega 1 in CO_2 is approximately twice omega 2. The symmetric stretch and the bend are in Fermi resonance.

So what happens then? Suppose we have a level that involves V1, V2, V3. And nearby there is a level V1 minus 1 V2 plus 2 V3. And because of the energy denominators, these two guys are nearly degenerate. So what happens is one gets shifted up, one gets shifted down a little bit. And they're out of the expectation of smooth behavior.

And it might also be that this state is what we call bright and this is called dark. This state might be connected by an allowed transition from a lower-- an initial state and this might not. So the levels repel because they're interacting and they're out of position. And this guy is supposed to be bright. We're supposed to see a transition in the spectrum. And this one-- well, it should have been somewhere else. But we shouldn't see it because it's dark. It's forbidden.

But because of the interaction between these two levels, the eigenstates have mixed character. And you get both level shifts and extra lines. This is called a spectroscopic perturbation. This is the core of everything I've done for the last 45 years-- spectroscopic perturbations.

And so you can learn about some of these coupling terms because, instead of hiding in the forest of these small corrections, you get a big effect. And it's easy to observe and it's easy to determine each coupling term from these resonances.

And the last thing I want to talk about today is a little bit of philosophy. This is why, among spectroscopists or physical chemists, there are two communities-- communities that like small molecules and communities that like big molecules, because they're really different. For the small molecule community, you have this accidental resonance and you get this sort of thing.

For big molecules, you have a resonance with a dense manifold of levels. All of these levels share, say, the character of the dark state. And so they can all interact with this guy.

And so in this case, you get the main transition in an extra line. In this case, if you have low resolution, you get a broadened line. And if you have high enough resolution, you see that there is a whole bunch of eigenstates under it. And if it's a large enough molecule, you couldn't resolve them anyway.

And so some people are always dealing with fast IVR, fast dephasing of the bright transition into a dark manifold. And other people are always looking at these sorts of things. Now I like these because they really give you a lot of information. Now you can get the information you want from this because the width of this thing is related to the number of dark states and their average coupling matrix element. That's called Fermi's golden rule. We'll talk about that later.

So I think there's a pretty good place to stop because what I try to do is to show you, yes, it can be really complicated. But it's something that you can do, and you can project out the coupling constants that you want in order to determine the stuff that is relevant to your experiment. But then there is this dichotomy between small molecules where the vibrational density of states is always smaller until you get to really high energy.

And bigger molecules-- now they're not very big. Benzene is plenty big for this sort of thing. And there is the question. For example, in some big molecules, when you excite an electronic transition from the ground state to some excited state-- so here's S0, S1. Sometimes you can't see any fluorescence from S1 because the dephasing is so fast that there's nothing.

And so it says, well, tough luck. You can't do spectroscopy in emission. But you can still see the absorption spectrum because then your signal is the removal of photons from your beam as opposed to fluorescence. So there's a huge amount of photochemistry and interesting stuff connected with a large density of states.

And again, when I was a graduate student, there was a huge controversy about non-radiative transitions in medium sized molecules. And there was one community that says, the collisions which transfer population between levels are so fast that, in order to turn off this broadening, you had to go to really low pressure because then there wouldn't be collisions.

And the answer, whenever somebody failed to see sharp spectra, was, well, you're not at low enough pressure. But this has nothing to do with collisions. And that got resolved by two

gentlemen called Bixon and Jortner. Those are two names that any educated physical chemist will know to say, oh, that's the Bixon-Jortner. And they're still alive. They're still doing beautiful stuff. But anyway, that's all I want to say today. I will do details on one mode and Morse oscillator in other sorts of things next time.