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**ROBERT FIELD:** Today, I'm going to go over a lot of material that you already know and work an example with non-degenerate perturbation theory. This will give me an excuse to use interspersed matrix and operator notation, and one of the things that you will be doing is dealing with infinite matrices. And we don't diagonalize infinite matrices, but the picture of an infinite matrix is useful in guiding intuition. And so we have to know about what those pictures mean and how to construct them from things that seem to be obvious.

OK, the problem I want to spend most of my time on is an example of a real molecular potential which is quadratic but with a cubic and a quartic perturbation term, and this is a simpler problem than what I talked about last time. The last time I really wanted to set the stage for what you can do with non-degenerate perturbation theory, and this is going to be more of dealing with a specific problem. Now, the algebra does not get simpler, and so it's easy to get lost in the algebra. And so I will give you some rules about what to expect, when you have a potential like this, and how does that come out of non-degenerate perturbation theory?

Now, everything that we know about molecules comes from spectroscopy. That means transitions between energy levels, and so well, how do they happen? And we can lead into that by talking about the Stark effect which is the interaction of an electric field with a dipole in the molecule. And so most transitions are caused by a time-dependent electric field which somehow interacts with the molecule through its dipole moment, and so you'll begin to see that today.

Last time, I derived the formulas for non-degenerate perturbation theory. Now, I'm a little bit crazy, and I really believe in perturbation theory. Most of the textbooks say, well, let's just stop here at the first-order correction to the energy levels, and you get nothing from that except the Zeeman Effect which is kind of important for NMR. But in terms of what molecules do, you need this too, and this is equal to the zero-order energy. I'm sorry, the zero-order energy which comes from an exactly solved problem and then the diagonal matrix element of the

everything that's bad in the world, the first-order Hamiltonian.

And then, we have this complicated-looking thing,  $m$  not equal to  $n$  of  $H_{nm}$  squared,  $E_n - E_m$ . Now, the only thing that you might forget about in this kind of a formula is is it  $n$  before  $m$  or the other way around? And what we know is, OK, here is the  $n$ th level, and here is the  $m$ th level, and the interaction causes this level to be pushed down.

So if the  $m$ th level is above the  $n$ th level, this denominator will be negative, and that causes the pushing down. And so if you remember the idea of perturbation theory-- that things interact, and one level gets pushed down, the other level gets pushed up, equal and opposite-- you can correct your flaws of memory on which comes first. And we can write the wave function as an eigenfunction of the exactly solved problem plus a term,  $m$  not equal to  $n$  of  $H_{nm} \frac{1}{E_n - E_m} \psi_m$ .

Now, the reason this sum does not include the  $n$ th level is, well, if you did, this denominator would blow up, and you don't need the  $n$ th level, because you've already got it here. So these are the formulas, and we had said, OK, we're going to write the Hamiltonian as  $H_0$  plus  $H_1$ , and this is an exactly solved problem. This is everything else.

Now, some people will sort this out into small everything else and big everything else. But it's foolish, because all that does is multiply the algebra in a horrible way, and you don't care, anyway. You just know that this stuff that's not in this exactly solved problem gets treated here, and you're going to know, in principle, how to deal with it, and there'll be some small problems that you know how to deal with. OK, and there is a rule that  $|H_{nm}| / |E_n - E_m|$  absolute value is much less than 1. That's what we mean. Yes?

**AUDIENCE:** Are you making a deliberate choice to put all the badness in the first-order perturbation?

**ROBERT FIELD:** Yes.

**AUDIENCE:** Then, what goes into higher order, if we make that deliberate?

**ROBERT FIELD:** OK, you can say, well, we've got things that are important, that obviously affect the energy levels, and there's things that are smaller, like hyperfine structure. And when you use the word hyper, you generally mean it's small, and so what ends up happening is that you do the big picture, and then you see some more details. But it's only a very small number of people who actually segregate the badness into real bad and not so bad. OK, so this works only when this off-diagonal matrix element is smaller than the energy difference, and that's going to be true.

Now, here is an infinite matrix, and we're interested in a certain space, a state space, which our experiments are designed to measure, and it depends on what experiment you do. This might be here, it might be somewhere in the middle, and the rest, we're not interested, because it's far away. Because the energy denominator is so large that the effect on the energy levels can be ignored, or you can say, well, we're not really ignoring it. We're folding the effect of all these levels through the matrix elements in here into here by second-order perturbation theory. We could in principle do that.

We certainly are allowed to think that we are getting rid of this state space by, in principle, folding it into this block. Now, in this block of levels that we care about-- now I always like to draw these infinite matrices, or these matrices, by just saying, OK, here's the diagonal. And there might be a couple of levels within this state space we're interested in which, because of accident or because of something evil, their energy denominator is small compared to the zero-order energy differences.

But that's usually true for only a few accidentally degenerate states, and we deal with them by using the machinery we obtained from the two-level problem, and so there, we are actually diagonalizing a small dimension matrix. We're not diagonalizing it, our computer is diagonalizing it. You really don't care how it's done, because you have a machine that will solve this like difficulty, and so it's OK for this rule to be violated.

But so what happens, suppose we have two levels, and-- I just want to make sure I use the same notation as in the notes. So here, we have the two zero-order levels, and they interact and repel each other equal and opposite amounts. And these states, which are  $E_2$  and  $E_1$ , are not pure state 2. They have a mixture of state 1 in them.

Now, in spectroscopy, we always observe these levels by transitions. And so suppose we have state 0 down here, and let us say that this transition between the zero level and the zero-order level 1 is allowed. I'll symbolize that by  $\mu_{1,0}$  is not equal to 0. And the transition between this level and this zero-order level is forbidden,  $\mu_{2,0}$  is equal to 0. So we call this a dark state and a bright state, and now these two states interact, and we have mixed states.

So the real eigenstates, you wouldn't have expected to see this level in the spectrum. But you do, because it's borrowed some bright character through the perturbation interaction, and so there's two surprises. One is everything is sort of describable by a simple set of equations, and

then there's a couple of deviations, and there's some extra levels that appear.

That's information very rich, because if it's dark, you can't see it. It's not a ghost. It's there, but you can't see it. Well, the perturbation somehow pulls-- sometimes-- pulls the curtain back and enables you to see stuff you need to know about.

Now, you can imagine exciting this two-level system with a short pulse of light, where the uncertainty broadening of the short pulse of light covers these two eigenstates. What happens then is you get quantum beats, and that's going to be on the exam. OK. So this is a local perturbation, and it's just something in here that spoils the general rule but it's very information-rich, and it also is pedagogically fun.

OK. So now, I'm going to talk about stuff that I've talked about before, but I'm going to go a little deeper and slower, and so let's do this problem. We have a potential, and for molecules, we tend to use  $Q$  rather than  $R$  or  $X$  as the displacement from equilibrium. The harmonic oscillator coordinate, and it's the same thing and so we have-- OK, so this is an exactly solved problem, and this is something extra. And so this is a cubic anharmonicity, and this is a quartic anharmonicity.

In the previous lecture, I talked about anharmonic couplings between different modes of the same polyatomic molecule. Here, this is really a simpler problem, and I probably should have talked about it first. But I didn't, because I want to go deeper here than the big picture, which I described last time. So we're going to have two terms that we are going to treat by perturbation theory, and there are several important things here.

Molecular potential looks like this, not like that. Right? This is bond breaking, and it breaks at large displacement. There is no such thing as a bond breaking as you squeeze the molecules together. So this is a crazy idea, and how do you get an asymmetric potential? Well, it's cubic, and which sign of  $b$  is going to lead to this? Yes.

**AUDIENCE:** [INAUDIBLE]

**ROBERT FIELD:** Right. OK. Now, if we're really naive, we say, yeah, negative is good, but boom, we ignore that. We don't worry that, if we took this seriously at large enough displacement, the potential will go to minus infinity. We don't worry about tunneling through this barrier. We just use this to give us something that has the right shape, and that we can apply perturbation theory to. And we're not going to worry about using perturbation theory to capture this tunneling, at least not

now and not in this course.

OK. So one thing is we have this term, and there is something you know immediately about odd powers. They never have  $\Delta v = 0$  matrix elements, they never have diagonal elements, and so they do not contribute to the energy in first order. The only way you know the sign of this perturbation is from a non-zero first-order contribution, because when you do second-order perturbation theory, the matrix element gets squared, and the sign information is lost.

So there's nothing so far that tells you what the sign of  $b$  is, and the energy level pattern that you would obtain from either sign of  $b$  would be the same. It's just one of the signs is completely ridiculous. Now  $Q$  to the 4th has selection rules  $\Delta v$  of 4, 2, 0, minus 2, and minus 4. So that  $\Delta v = 0$  term does enter in first-order perturbation theory, and so you can determine the sign of any even perturbation which is useful.

Now, what does this do? Well, one thing that  $Q$  does is, if  $c$  is positive, instead of having a harmonic oscillator, it makes it steeper. And if  $Q$  is negative, it makes it flatter. This is typical of bending vibrations, and so bending vibrations tend to have flat bottom potentials, but there there's also something else.

Suppose we have two electronic states. Now, I am cheating, because I'm assuming you'll accept the idea that there is something we haven't talked about yet. But there are different potential curves, and it's mostly true for atomic molecules. These two states can't talk to each other at equilibrium, because a symmetry exists that prevents that. And as you move away from equilibrium, there's a perturbation that gets larger and larger. And as a result, what happens is that this potential does something like that.

So you get either a flattening or an actual extra pair of minima, and this one gets sharper. That's called a vibronic interaction, and that's fairly important in polyatomic molecules. But so we can begin to understand these things just by dealing with these terms in the potential.

OK. So now, we're off to the races, and my goal here is to make you comfortable with either the operator or the matrix notation, and so I'm going to go back and forth between them in what might seem to be a random manner. OK. Now, you know that a dagger. Now, we can call it a dagger with a hat, or we can call it a dagger double underline-- bold, hat, matrix, operator. And you know that this operates on  $v$  to give  $v + 1$  square root  $\psi_{v+1}$ , or in bracket notation, we could write this as  $v + 1$  a dagger  $v$ .

Now this is a shorthand. It's a wonderful shorthand. It's easier to draw this than wave functions. But we have to know, OK, what does this look like in the matrix for a dagger? So here is a dagger, and it's a matrix, and what goes in here?

Well, the first thing you do, this is infinite, so you need some sort of a way of drawing something that's infinite so that you understand what it is. And so the first thing you do is you know that there is no-- all of the diagonal elements are 0. Now, most of the elements in this matrix are 0, and you don't want to draw them, because you'll just be spending all your time writing 0's. So we want a shorthand, and so now this is a matrix element. This is the row, and this is the column, and so where do I put this square root of  $E$  plus 1?

**AUDIENCE:** [INAUDIBLE]

**ROBERT FIELD:** So here, we have the row. I get confused about this, so before I accept your answer, which I want to reject, I have to think carefully about it. So let us say this is 0, and this is 1, so we have the 1-- you're right. OK, and so we have the square root of 1, the square root of 2, square root of  $n$ . And everything else is 0, so we can write big 0's. So that's what this matrix looks like.

Now, if we're using computers, instead of multiplying these matrices to have say  $Q$  to the 13th, or a dagger to the 13th, you can just multiply these matrices. That's an easy request for the computer. It's not such an easy request for you, but you end up getting matrices. When you have integer powers of these, you get a matrix with a diagonal and then another diagonal separated by a diagonal of 0's, and so you know what these things are going to look like.

So you might ask, OK, what does a look like? And there are several ways to say what a is going to look like, because it's the conjugate transpose of a dagger. Well, these are all real numbers, and so all you do is flip this on its diagonal, and now you get a. Then there's another actor in this game, and that's  $n$ , the number operator, and the number operator is going to be a, a dagger or is it going to be a dagger a? So which is it?

**AUDIENCE:** [INAUDIBLE]

**ROBERT FIELD:** This.

**AUDIENCE:** [INAUDIBLE]

**ROBERT FIELD:** Yes. OK, one way to remember this is when you operate with either a or a dagger, it connects two vibrational levels, and the thing you put in the square root is the larger of the two quantum numbers. OK. So what would the number operator matrix look like? So what do I put here? Yes.

**AUDIENCE:** [INAUDIBLE]

**ROBERT FIELD:** But what's the lowest vibrational quantum number?

**AUDIENCE:** [INAUDIBLE]

**ROBERT FIELD:** Right. OK, and so once you've practiced a little bit, you can write these things. And it's not just an arbitrary thing, because you want to be able to visualize what you're doing. Because you're dealing with multiple infinities of objects, and you want to focus only on the ones you care about. And with a little bit of guidance from these pictures, you can do what you need to do.

OK. Well, we know what the operator  $Q$  is in terms of a dimensionalist version of  $Q$ , and that's  $\hbar$  over-- now, I'm going to be using this. OK, this is the dimensionalist  $Q$ . That's what the  $\omega$  twiddle means, and these are constants. And now I'm using  $\omega$  twiddle, because spectroscopists always use  $\omega$  in wave number units, reciprocal centimeter units. Which is a terrible thing, because first of all, wave number doesn't have a unit. It's a quantity.

And centimeters are things that we're not supposed to use, because we use MKS. But spectroscopists are stubborn, and when we observe transitions, we always talk about wave numbers not energy. And so the difference between wave numbers and energies is the factor of  $hc$ , not  $\hbar c$ . So anyway, this is the conversion factor, when  $\omega$  is in wave number units. And we can go further and relate  $Q$  twiddle well, let's just not do that. We can relate this to  $\hbar$  over  $4\pi c u \omega$  square root times  $a$  plus a dagger. OK?

So this is something we did before.  $\omega$  twiddle is  $k$  over  $\mu$  square root  $1$  over  $2\pi c$ --  $hc$ . So this what you're used to, and this is the extra stuff that we have to carry along in order to work in wave number units. OK.

So we have operators that can be expressed like  $a$ ,  $a$ , a dagger,  $a$  or a dagger,  $a$ ,  $a$ ,  $a$  or anywhere you put the dagger anywhere. You look at this, and you say immediately I know two things. I know the selection rule. The selection rule is count up the  $a$ 's and count up the  $a$  daggers, and so this is  $\Delta v$  of minus 2. So is this.

All of the positions of the  $a$  dagger are  $\Delta v$  of minus 2, but the numbers, the matrix elements, are different. You know this from the last exam. So we can have  $v$  minus 2  $v$  and whatever comes in here in one of those forms. So those are the only non-zero elements, and you know how to mechanically figure out what is the value of the matrix element.

Now, in order to simplify the algebra, which is not essential to the physics, you want to take all of the terms that results say from  $Q$  to the 4th and arrange them according to selection rule. And then take all of the terms that have the same selection rule and combining them to a single number. And you use the computation rule to be able to reverse the order of terms. Well, I don't want to do that.

So suppose we have an  $a$ , a dagger, and we can write that as  $a$ , a dagger plus a dagger,  $a$ . And so if we want to convert something like this to something like that, we know that this has a value of plus 1, so we can do that. And that's tedious, and you have to do it. But one of the things that is kind of nice is when you have a problem that's cubic or quartic or quintic, you mess around with this operator algebra once in your life, and you put it on a sheet of paper, and you refer to it. It doesn't matter what the molecule is, what the constant in front of  $Q$  to the 3rd or 4th or 13th is. If you've done the operator algebra, you're fine.

Now, you might say, well, I don't want to do that. I'm going to have the computer do that. Well, fine, you can have the computer do that, and then a computer will tell you what the matrix looks like, and you can do what you need to do.

OK. So spectroscopists call the vibrational energy formula  $G$  of  $v$ . I don't know why the letter  $G$  is always use, but it is, and so this is the same thing as vibrational energy. And the vibrational energy, I'm going to put the tilde on it. You will never find a tilde in any spectroscopy note paper. We assume that you understand that the only units for spectroscopic quantities are reciprocal centimeters, but for this purposes, I have finally caved, and I said, OK, I'm going to put the tildes on.

So the energy levels, now you might ask, why this? This is the first anharmonicity constant. It's not a product of two numbers. It's just what people wrote originally, because they sort of thought of it as a product of two numbers, but it's really only one. And that's times  $v$  plus  $1/2$  squared, and then the next term is  $\omega_e$ , ye,  $e$  plus  $1/2$  cubed. So this is a dumb power series in the vibrational quantum number, and so in the spectrum, one is able to fit the spectrum to these sorts of things.

So that's what you get experimentally, but what you want to know is we want to know the force constant, the reduced mass, the cubic anharmonicity constant, the quartic anharmonicity constant, and whatever. So these are structural parameters, and these are molecular parameters. People like to call them spectroscopic parameters, but that implies something more fundamental. These are just what you measure in the spectrum. And so we want to know the relationship between the things we measure and the things we want to know, and so that's what perturbation theory is for.

OK. Now, to risk boring you, I'm just going to go over material that we've done before. So if we have  $Q$  to the  $n$ , we have this constant out in front,  $\hbar$  over  $4\pi c \mu \omega$  twiddle to the  $n$  over 2, a plus a dagger to the  $n$ . And so we're going to be constantly dealing with terms like a plus a dagger squared and plus a dagger cubed and so on. These are the things I said you're going to work out once in your life and either remember or just become so practiced with it, you'll do it faster. And so these contain the values of the matrix elements and the selection rules.

OK. So I'm going to do an example of the cube, and that's, of course, this thing in constant the  $3/2$  and then a cubed plus a dagger cubed plus a whole bunch of terms which have two a's and one a dagger. So let's just put it a squared and a dagger. This isn't a computation rule. This is just three terms that you have to deal with and three terms that have a dagger squared and a. So that's what you do your work on, because you don't want to be messing around once you start doing the perturbation sums, because it's ugly enough. So you want to simplify this as much as possible, and you do.

And so the purpose is this is  $\Delta v$  of minus 3. This is  $\Delta v$  of plus 3. This is  $\Delta v$  of minus 1. This is  $\Delta v$  of plus 1. You arrange the terms according to selection rules, and so what you end up getting is  $Q$  cubed is equal to this thing, to the  $3/2$  times a cubed plus 3 a  $n$  plus 3 a dagger  $n$  plus 1 plus a.

OK, the algebra is tedious, pretty simple. And what you usually want to do is have the thing that changes the vibrational quantum number after the thing that preserves it, because then it's easy just to write down these matrix elements just by inspection. OK? You could do it the other way around. It's more complicated if you put the  $n$  first and then the  $a$ , but it's up to you. So these then are what you work on, and now we start doing non-degenerate perturbation theory.

The first thing you do is you want to know, well, what is the first-order correction to the energy? And if this is  $Q$  to the 3rd power, then this, that's 0. So you like 0's, but in this case, you're kind of disappointed, because you don't know what the sign of the coefficient of  $Q$  to the 3rd power is from any experiment or at least any experiment at the level we've described. When we introduce rotation as well as vibration, there will be something that reports the sign of the coefficient of  $Q$  3rd.

So now, we're stuck, and we have to start doing all of this second-order stuff. OK. Well, we have this  $bQ$  to the 3rd power, and so we get squares of the matrix element. So we get a  $b$  squared. We get this thing to the 3rd power, because we're squaring the matrix element, so this bunch of constants. And then, you get a matrix element  $v$  prime, some operator  $v$ , then we get an energy denominator.

Now, there's a lot of symbols, but we want to simplify things as much as possible,  $hc\omega$  times  $v$  minus  $v$  prime. So this is matrix element squared over an energy denominator, and what you really want to know is what is the quantum number dependence of everything? OK, so the operator here is either  $Q$  dagger cubed,  $Q$  dagger-- I'm sorry, a cubed, a times  $n$ , a dagger  $n$  plus 1, or a dagger cubed. And so we know how to write all of these matrix elements, trivially, no work. Once we've simplified here, it's really trivial to write the squared matrix element.

OK, so we do it, and so we arrange things according to  $\Delta v$  and we have  $\Delta v$  of plus 3, plus 1, minus 1, and minus 3. And so what we get from the square of the matrix element a dagger cubed, we get  $v$  plus 1,  $v$  plus 2,  $v$  plus 3, and we also have an energy denominator. And we're going to get for this one  $1$  over minus 3, because the initial quantum number is  $v$ , and the second quantum number,  $v$  prime, is  $v$  plus 3, and so we get a minus 3 in the energy denominator. And then the plus 1, that comes out to be-- I've got it in a different order in my notes-- that comes out to be 9,  $v$  plus 1,  $v$  plus 2,  $v$  plus 1 squared, and the energy denominator for this is  $1$  over minus 1.

OK. Then, we have the-- I'm going to skip this one-- we have the matrix element here, and that's going to be  $v$  minus 1,  $v$  minus 2. Remember, we're squaring these things. So that's why we don't have those square roots anymore, and we have an energy denominator  $1$  over 3.

OK, now advice-- you don't like this, and you want to minimize your effort. And so it turns out that if you take the terms with the equal and opposite energy denominators and combine

them, simplifications occur. One of the things you can see is you're going to have a  $v$  cubed here, and you're going to have a  $v$  cubed here. They're going to cancel, because we have a 1 over minus 3 and a 1 over plus 3. So you get an algebraic simplification when you take these terms pairwise and combine them.

Now, you're never in your life going to do this, but if you did do it, this is how you end up with formulas which are simple. They're horrible getting there, unless you know how to get there. So now there's a rule. So if the perturbation is  $Q$  to the  $n$ , then the highest-order term involves  $v$  plus  $1/2$  to the  $n$  minus 1. The reason for that is in the matrix element the highest-order term is  $v$  plus  $1/2$  to the  $3$  over  $2$ , and then you square it, you get to the 3rd power, and then the highest-order term cancels.

So we know that if we're dealing with  $Q$  to the 3rd power, we're going to get a term  $v$  plus  $1/2$  squared. If we're dealing with  $Q$  to the 4th power, well, then we get something from second order from the first-order correction to the energy a  $\Delta v$  of one matrix element. What we've done is square it, and we get  $v$  plus  $1/2$  squared also. OK and the off-diagonal matrix element, we're going to get from the highest order from the off-diagonal is  $v$  plus  $1/2$  cubed.

So one of the things that is great about the algebra is with a little bit of practice, you know how to organize things, and if you do the algebra, you collect the highest-order terms. Then, there's that kind of cascading result, and you get the lowest-order terms in simplified form. So this is irrelevant, but this is how you do it, if you're a professional. So with these results, we can determine the relationship between these molecular constants.

Where did I put them? Oh, probably on this board. No. Oh yeah, it's right here. So we have  $\omega_e$ ,  $\omega_e x_e$ ,  $\omega_e y_e$ , and we have then the relationships between these things which you measure and these things that you want to know. So the stuff you want to know is encoded in the spectrum in a not particularly complicated way-- it's just not a very interesting way, but you have to do it in order to get it.

OK, so I've got just a few minutes left, but I want to get to the really interesting stuff. So if you have some expression for the potential, it's easy to go and get the expression for the energy levels and the wave functions. And you can use the vector picture or the wave function picture. It doesn't matter, and so this is enough to do the spectroscopy. It tells you not only where are the energies, but because some transitions are supposed to be weak because of the dipole selection rule or whatever, it says, well, there are some transitions that have borrowed

intensity.

It also tells you-- suppose we make a coherent superposition state at  $T = 0$  using a short pulse, and suppose in the linear combination of zero-order states, there is only one that is bright. And so then it tells us, if we know how to go from basis states to eigenstates, we can go backwards, and we can write the expression for the  $T = 0$  superposition in terms of some sum over  $\psi_{v0} c_v$ . And if we have this, as long as we are writing a superposition in terms of eigenstates, we know immediately how to get to this, and then we've got all the dynamics.

So the perturbation theory enables you to say, if I want to work in the time domain, I know what to do. You're going to get-- in the time domain-- you're going to get a signal that oscillates, and it oscillates at frequencies corresponding to energy level differences divided by  $\hbar$ . And so what frequencies will appear in the Fourier transform of the spectrum, and what are the amplitudes of those Fourier components? You can calculate all of those stuff. It all comes from perturbation theory.

These mixing coefficients you get by perturbation theory. And remember, if you have a transformation that diagonalizes the Hamiltonian that the eigenstates correspond to, the columns of  $T^\dagger$ , and the expression of the zero-order states, in terms of the eigenstates, corresponds to either the columns of  $T$  or the rows of  $T^\dagger$ . So once you do the perturbation theory, you can go to the frequency domain spectrum with intensities and frequency or the time domain spectrum with amplitude and frequencies. It's all there.

This is a complete tool. It's the kind of tool that you can use for an enormous number of problems, and so you'd better get comfortable with perturbation theory, because the people who aren't comfortable can't do anything except talk about it. But if you want to actually solve problems, especially problems on an exam, you want to know how to use perturbation theory. And you also want to know how to read and construct the relevant notation in the vector picture, because a vector picture and the matrix picture is the one where you see the entire structure of the problem. And you can decide on how you're going to organize your time or what are the important things that I'm going to get from this analysis.

And so it's much better than the Schrodinger picture, because with the Schrodinger picture, you're just solving a differential equation and one problem at a time, whereas with the matrix picture, you're solving all problems at once. This is really a wonderful thing, and so that's why I'm taking a very different path from what is in the textbooks. Your wonderful textbook

McQuarrie does not do second-order perturbation theory.

So nothing you want can be calculated, unless you're dealing with NMR, and you're dealing with magnetic dipole transitions. And then, you can get a lot of good stuff from first-order perturbation theory, and you can avoid second order until you grow up. OK, I'm done. I'll be talking about rigid rotor next time, and I will be talking about it also in an unconventional way.