ROBERT FIELD: When I was really young, I used to go to a television repair store as often as possible to take home one of the dead chassis. And then I would take it apart. And I don't know what I was looking for, but that was sort of the empirical stuff. I had no idea how a television worked, but I was really curious about maybe I could find it if I just did stuff.

And what we've been talking about are ways in which we not just generate numbers, like parts of the television chassis, but insight. And there are we've talked about three ways so far. And one is Huckel theory, where Huckel theory is just a bunch of simple rules and simple ideas for how do you represent a large family of related molecules.

And the Huckel theory is incredibly simple, but it enables you to make really sophisticated conclusions about how things work and what are the important factors. And so it's basically a procedure for distilling insight from random observations. Or maybe not random observations, but observations of many properties of many related molecules.

Then you've seen LCAOMO. Based on the small variations all treatment of H2 plus, we got the idea of orbitals and what makes a bond. And then with the idea that we can describe the size of atomic orbitals by the energy below the ionization limit, we can make similar quantitative predictions based on this minimal basis set.

So we draw molecular orbital diagrams. And these molecular orbital diagrams are especially valuable for isoelectronic and homologous comparisons. So isoelectronic would be, let's say, nitrogen, CO, BF. Molecules with the same number of electrons. And homologous would be something like CO, SIO, GEO, and so on.

And with the concept of orbital size being related to the ionization energy of the atoms, we can make a lot of very useful comparisons. And so we develop insight. Now LCAOMO is a variation of method, and it can be a very large variation of method. And it could become of an issue.

But it's usually not atomic orbitals. It's just Gaussian orbitals or something, which is computationally convenient. And so it can be a procedure to rationalize experience and make

predictions as you go from the same number of electrons but increasing polarizability, polarity.

And these-- this is where you develop chemical insight. And it's really exciting. And it's what was missing when I would take these chassis from the repair shop and chop them up into pieces. And oh yeah, there's a magnet in there and things like that. It's much deeper.

And now perturbation theory is a kind of a different thing altogether. Perturbation theory says we do an experiment. We measure something, and we turn it into something we really wanted.

The Rolling Stones are telling us that if you want to know how a particular property depends on internuclear distance, and you can't directly measure the property as a function of internuclear distance, well maybe you can measure it as a function of vibrational and rotational quantum numbers. And that's what perturbation theory does. It tells you how to get from what you observe to what you really want to know.

And it can be horrible in terms of the algebraic exercises you have to go through in order to get what you really want or from what you-- yes. And today's lecture is going to be an example of not the worst thing you could ever do with perturbation theory, but pretty close to the worst. OK, but all three of the first things are related, are associated with getting insight from either a crude calculation refined against observations or just the observations and reducing those observations to something really neat about how things work.

Then the next two lectures will be given by Professor Van Van Voorhis and it's-- they will be on ab initio theory, where basically you don't assume anything. You don't do anything except solve for the exact energy levels and wave functions. Now this is not possible. Directly you can do this by making approximations, doing an enormous variational calculation.

Now many people think, well why bother with approximate methods when you can get the truth? And the answer is the truth is no more valuable than the parts of a disabled television. It's-- they're stuff. But there's no insight there.

And quantum chemists who do these calculations are not just generating numbers. They're trying to explain how things work. And it's the same business, it's just the tools are different.

The goals are not just getting-- in spectroscopy we can measure things to 10 or 11 digits. And nobody cares. I mean, how many digits? It's a little bit challenging to remember telephone numbers. And having big tables of 10-digit numbers, so what?

But what do the numbers tell you? And this quest-- the same question is asked by good quantum chemists by doing a series of calculations where they turn on and off certain terms in the Hamiltonian. So it's the same thing.

I'm an experimentalist, but many people who are experimentalists think I'm a theorist because I do weird stuff. But I'm not a theorist. Troy is a theorist. And he does weird stuff too, but he's not an experimentalist. And we're both after insight.

And OK, so let's just-- I guess I'll just launch it through the perturbation theory. OK. But you do want to understand the difference in how these different methods, these approximate methods, work, and what they're good for, OK?

So the goal of perturbation theory is to go from molecular constants to structural constants, or structural parameters. Molecular constants are like rotational constant, vibrational constant, stuff that you get by fitting the energy levels you observe to a dumb empirical expression, a power series in quantum numbers. Now there's lots of dumb empirical expressions you could use, and some are better than others. And perturbation theory will often tell you what is the right way to do it.

So you go from molecular constants to things in the potential. So this is the displacement from equilibrium, and we would like to know something about how a molecule works. And there also might be other constants, like spin orbit, and hyperfine, dipole moment.

And so let's just say we have some observable, and it is also a function of coordinate. And we'd like to know what that function is. But what we are able to do is measure energy levels as a function of quantum numbers.

And so the information that we really want, the potential or the internuclear distance dependence of some electronic property, that's all gotten from what we can observe via perturbation theory. It's a very powerful tool. And it's not pretty, but it always works. And it's a good basis for insight.

So perturbation theory is a fit model. The other methods, one doesn't generally do a least-squares fit to the-- of the adjustable parameters in Huckel theory to determine the properties of a molecule. One just says, OK, I'm going to try these because I think that attaching an electro-negative atom to a carbon atom is going to do something that I can predict. And maybe it's going to tell me some surprises about how its influence is not just where it's

attached, but other places in the molecule.

You know this from your first organic courses. You know all sorts of tricks to be able to predict reactivity and things that are related. But Huckel theory is not a fit model.

LCAOMO theory is not a fit model. These are experience-based. And you integrate all sorts of stuff that you learn from comparing molecules. And the comparing of molecules is what makes up for the deteriable lists of the approximations.

And your job is to hone your insight. And so you have nothing to protect you except the truth. You can observe molecules, but you can't be guided to something which is true, because there is no calculation. There's nothing exact and there's nothing complete.

But in quantum chemistry you can get really close to the truth. But you don't know anything about why. And so you're doing the same thing, but from the opposite ends.

OK, but perturbation theory is special because you take a huge amount of highly accurate experimental data of various types and you fit it. And so I want to talk about this. So you have the Hamiltonian. It's a matrix, and it's expressed in terms of parameters.

Let's just use notation p, p of i. A set of parameters. So this is not a quantum chemical, Hamiltonian. It's a thing where we say there are certain degrees of freedom, and each one is controlled by a number of parameters.

And we have the energy levels. And so what you do is you say let's choose a set of these parameters, and calculate the energy levels, and compare them to the observed energy levels. And it's not-- the first try, it's not going to be good.

And then you say, OK, now I've got to do a least-squares fit. I have to vary the parameters in this matrix Hamiltonian to match the energy levels and maybe to match other things that you can observe in the experiment. But it's a complicated least-squares fit, because you have a matrix, and you want to diagonalize it.

How are the parameters related to the eigenvalues and eigenvectors? You don't know. But when you're close, then you can start fitting these things. Then you can say, yeah, I know.

And then once you've done that, you have not just the energy levels, but you have the wave functions. Now again, you don't know that there is something missing in your Hamiltonian. But

you know that from the data you input you can match all the energy levels.

But you didn't put it in all the levels. You put in just the ones that you measured. But you are arrogant. And you think, well, maybe I measured more than I-- I determined more than I measured, that I can extend the measurements to other things.

And I told you at the beginning of the course you cannot observe the wave function. But if you do this, if you do a least-squares fit and match the energy levels, you have a pretty darn good representation of the wave function. And you can use that to calculate other stuff, especially dynamics.

Remember dynamics, at least if the Hamiltonian is independent of time, the dynamics is going to be a function of x and t. But you start with the initial preparation. If you know that, then you, because you know the energy levels, you can calculate the full x of t for all time.

So that's pretty powerful. If you fitted enough stuff, if your Hamiltonian has the important things in it, then you are basically able to do anything you want, whether it's static or dynamic. And if the Hamiltonian is time dependent, you can do that too, I just haven't showed you how yet.

OK, so I really like perturbation theory, because it directly that deals with whatever data you have. And out from that, you get this thing which tells you everything, unless there's something that you didn't sample, that you didn't know you didn't sample. And then you discover that your data and the predictions are not in agreement.

And then that's when you-- you don't go home and say, oh, I screwed up. I got to go take a nap. I don't-- you go home and you say, let's celebrate, because I discovered something that was really missing. And that's what we want to do.

OK, so I have to mess around in the mud here. Because the perturbation theory you've done so far has been, perhaps, ugly, but it's been kind of simple because it's basically vibration. And now we've got vibration and rotation. And we have to combine the two, and we have to see whether there's something special that we can get from the combination. And you bet there is.

OK, so we're going to look at the energy levels of a non-rigid, non-harmonic, or anharmonic oscillator. And we're going to find out how we generate from an expression of the potential energy surface or potential energy curve, because what I'm going to be talking about is diatomics. But it all extends to polyatomics.

And we're going to calculate the relationships between what you observed and what you want to know. So for a diatonic molecule, we have a dumb representation of the quantum numbers. And we can write it.

And I'm just really a stubborn person about spectroscopic notation, so I include this Hc convert wave number unit, the reciprocal centimeter units to energy. But you'll never catch me doing it in real life. But that leads to all sorts of algebraic errors that I don't know I'm making because I'm so unused to doing this.

OK, so we have an expression for the vibrational energy levels. And I can't apolo-- I can't explain why we use four letters to represent one symbol, but that's the traditional thing. And for polyatomic molecules, which came after diatomic molecules, we start using only two letters. Instead of omega XE, we just use XE.

But since I'm a diatomician, I'm going to do this sort of thing. And that's v plus 1/2 squared. And then the next term is omega YE v plus a 1/2 cubed. OK, and so then that's the vibrational part.

And then we have the rotational part. The equilibrium internuclear distant rotational constant minus alpha e times v plus 1/2. Times JJ plus 1. And then minus DE, the centrifugal distortion constant, times JJ plus 1 quantity squared.

And we can have more constants here. We can have additional constants there. But basically we have constants, which are known by multiplying a particular combination of vibrational and rotational constants, quantum numbers.

And so these are the things we can determine, or sometimes we determine some of these and we want to get a prediction of the others because they're outside of our observation. And the potential is going to be dependent on the displacement from equilibrium and the rotational constant. And so there will be terms in the potential, like 1/2 KQ squared plus 1/6 AQ cubed, et cetera.

So we have another dumb power series. And fortunately, we know that as we go up in the displace-- in this displacement coordinate, the coefficients get to be really small. And so we don't need to have a lot of these parameters. But we should have at least two, the harmonic and the cubic one.

And we know for molecules the cubic parameter gives you a potential curve, which resembles

reality. It's hard wall here, soft wall there. Molecules break.

Now this has the unfortunate property of doing that. And so it's got death built into it. But it doesn't really matter, because you basically are looking at increasingly wide regions of the potential. And the fact that it does something terrible in your simple representation is almost irrelevant.

But you have to be aware that you can tunnel through barriers. And when you start being able to tunnel through barriers, and it depends on how close you are to the top of the barrier and how wide it is, then you start seeing effects. And then this term is going to give nonsense. But there is a domain of goodness where you don't have to worry about that.

So we have this, and then we have the rotational constant kind of contributing to the effect of potential, which is HCV of R JJ plus 1. Now here I've got-- here I have coordinates. Here I have quantum numbers. How can I do that?

It's because central force problems can be represented in a universal form. And so we can just integrate over the angular part of the problem. And so now we have a mixed representation.

But this guy is still a function of R or Q. And so this v of R is an operator. It's not just a constant. Some people call it the rotational constant operator. Kind of stupid.

And so our job is now to figure out how to get from this parameter rise potential to the energy levels. Of course, we start with the energy levels. And we're going to want to determine the parameters in the potential. But you've got to have that connection.

So this rotational operator has some constants in front of it. And this is in wave number of units, because I'm a spectroscopist. And we have the vibrational frequency, 1 over 2 pi C. K over mu square root. Also in wave number of units.

Now the first problem is we don't like R, because harmonic oscillators are expressed in terms of displacement from equilibrium. And so we know that Q is equal to R minus RE, or R is equal to Q plus RE. So we want to replace this operator R by this, an operator plus a constant.

So 1 over R squared can be expressed as 1 over RE squared, the equivalent internucleus, plus 1 over Q over RE. Plus [INAUDIBLE] squared. So this is the power series expansion, but we only keep the first term generally.

And so now we're ready to go to work. And we can say we have B as a function of Q is equal to B of E, the equilibrium value 1 minus 2Q or RE plus 3Q squared over RE squared. And there's more terms, but this is enough. You bet it's enough.

By the time this lecture is over, you're going to want not ever to see this stuff again. OK, so we have now a representation of the rotational operator in terms of a constant term, a linear term, and a squared term in Q. And we know how to do matrix elements of Qs, right? So we know we're in business.

And we have the potential as another power series in Qs. So everything is going to come together. It's just going to be will the migraine wipe out your ability to pay any attention to this after we're done.

OK, so I don't want to cover that up yet. So we know that this displacement operator can be replaced by the creation and annihilation operators. And so we have 4 pi C, mu omega E square root. A plus A dagger are friends. These guys, we hardly need to take a deep breath to know what to do with those.

And so we're going to want to express all of the-- all of the actors here, these guys and those guys, in terms of expressions in the creation and annihilation operators. So for the rotational constant expansion, we're going to need something like 2Q over RE. And that, after a little bit of algebra, is 4BE over omega E square root times A plus A dagger.

And we need 3Q squared over RE squared. And that's going to be 3BE over omega E, A plus A dagger squared.

So all of the terms can be expressed, can be reduced to constants that we care about, or that are easily measured, and these powers of As and a daggers. Now this is-- you have notes, printed notes. And I'm following them pretty well, although there are a few typos, which I hope to correct.

And so we do a similar thing for the terms here. And we're only going to keep-- we're only going to look at this. We're not going to go to Q 1/4. But this is bad enough.

OK, and this is part of the zero order Hamiltonian. So we're going to have another term, and that's going to be 1/6 little a Q cubed. OK, so that's-- little a is the anharmonicity parameter.

And what is its sign? Can we know its sign from experiment? You said yes. Why do you say

yes?

AUDIENCE: [INAUDIBLE]

ROBERT FIELD: I'm sorry?

AUDIENCE: It's cubed, so it's odd. So there's [INAUDIBLE].

ROBERT FIELD: The only way you know the sign of an off diagonal matrix element is-- I'm sorry, is if there is a diagonal element of it that can be put into the E, the first order correction to the energy. As soon as you have to square it when you do second order perturbation theory, you've lost the sign.

But here we know the sign because of physical insight. We know that this kind of a potential would be nonsense. So we know that A has a sign and it's negative.

OK, so we have a over 6 times our favorite parameter here to the 3/2 power times A plus A dagger cubed. Now this is something-- you do the operator algebra before you launch into a horrible calculation. And so we know how to do this in principle to reduce this to a simple expression.

And now we take this part, this thing, and we're just going to call it capital A. Because we want it-- we don't want to clutter up what is going to be a terrible thing anyway. And we can always convert back to the little a at the end if we need to.

OK, so now I've set the stage. I'll leave this for a while. That really is-- as you know, I really love revision theory, because it's the tool that I use all the time. And it's a psychological condition that is not curable, all right?

So what do we want? We want E0 as a function of E and J. And that's just the J H0 VJ. And we know that HC will make EB plus 1/2 plus HCBEJJ plus 1.

OK, well this goes in the energy denominators. And so that's good, because we need energy denominators as well as the zero order energies. Right now we need to know the bad stuff, the thing that's outside of the zero order Hamiltonian, which is everything.

And so we have this is HC times BE JJ plus 1 times-- I'm sorry, I have to erase this. Minus BE over 4BE over a big E square root times A plus A dagger plus 3 BE. 3BE over omega E times A plus A dagger quality squared. So that's the rotational part.

And then we have the vibrational power, which we have A, A plus A dagger cubed. OK, so now we look at this thing and we say, oh well, this has matrix elements delta V equals plus or minus 1. And this has delta V equals plus or minus 2 and 0. And this has delta V equals plus and minus 3 plus and minus 1.

We always want to sort things according to the selection rules, because we always combine the things with the same selection rules. And it's best to do that at the beginning rather than somehow trying to do it at the end. Because if you have the same selection rule, you have cross terms. And that's really important. The cross terms are where a lot of good stuff happens.

OK, so we know E0. And we would know E1 if there are any off the-- there are any diagonal matrix elements of this operator. This should be a plus as well.

So this is H1. And this doesn't have any diagonal elements. And this doesn't have any diagonal elements. But this one does.

And it's actually something you encountered, I think, on exam two. I'm not sure, but you've certainly encountered the diagonal element of this. And so if we look at A plus A dagger squared, we get A squared plus A dagger squared plus 2 number operator plus 1. And that's diagonal. So we have a diagonal element, and that gives us E1.

So E1 of E and J is HC6BE squared over omega E times J, J plus 1, B plus 1/2. OK, well that looks pretty good, because this is the coefficient of-- we have an expression for the energy levels, which includes the E minus alpha E, B plus 1/2 of times JJ plus 1. So we have a term that involves B plus 1/2 and JJ plus 1.

And it has a name. Alpha minus alpha. And here we have a term which has those, that quantum number dependents.

And it has a value. And so it's telling us that alpha E, and I'll put on this harmonic oscillator, is equal to minus HC6BE v squared over omega E. One constant.

Now it's also telling you that B of E increases with V. And for a harmonic oscillator, you have an equal lobe at each turning point, the largest lobe. But they're equal in magnitude.

So one can ask, at the inner turning point is the change in the rotational operator, or is it

larger-- is this change in BE larger relative to the equilibrium value, or is this larger? And the answer is we're talking about 1 over R squared. And 1 over R squared gets really large at small r as opposed to getting smaller at large R. And the amount of change is much greater at small r. And so that causes the effective rotational constant to increase.

But we know for a harmonica-- for an anharmonic oscillator, we have a small lobe here and a big lobe here. And so we expect that there's going to be a battle between the harmonic contribution to alpha and the anharmonic contribution. And we expect that this is going to win.

Why? Because every time anybody measures alpha, it's a positive number. And that's why it was expressed in the formula, which I've concealed, with a negative sign, to take into account that alpha is always-- the contribution is always negative, and so alpha is always positive.

Yeah, and these things are-- it's historical. But anyway, so we have a contribution which has the wrong sign. And we know we're going to get another contribution from the interaction between the rotation and the vibration, and that this is going to make things right OK. And it comes from a term.

OK. All right, there's no way I can make this simpler. Just have to bear with me and I will-- so we have delta V equals plus and minus 1 matrix elements from both the A plus A dagger and the A plus A dagger cubed terms.

And we have-- we have this in both the anharmonic expression and in the rotational constant operator. We know what these-- how these things work out. And so delta V equals plus and minus 1 terms from the A plus A dagger cubed V plus 1 and V, V minus 1.

So we can work these things out. And this one is 3V plus 1/2 to the 3/2. And this is 3V plus V to the 3/2. So all of this stuff, you want to simplify it as you go but it. And these come from the A term, the A, A plus A dagger cubed' term.

We don't have a term that's linear at A plus A dagger from the anharmonicity, but we do-- and we do have a squared term, but that's the harmonic correction. So we start here, with A plus A dagger cubed. And then we're going to want to look at the delta V equals plus or minus 2, and delta V equals plus and minus 3 terms.

And there's lots of algebra. You can do all these things. There's nothing challenging here. It's just how do you keep this stuff that you derived that you're going to need in a place that you can find it again, because the pages just get filled with garbage.

OK. So the best way for me to do this is to write the results in the next-to-the-final step, and then in the final step, and show what goes to what. So the second order correction is a function of EJ.

We're going to have terms that involve the delta V equals plus or minus 1. And we're going to get that from the cubic correction through the harmonic oscillator and the linear correction to the rotational concept. So we're going to get an expression that looks like this. B squared minus 2AB plus A squared.

So this is a B term. This is the anharmonic term. We have a cross term. There are going to be three terms in this expression. OK, and so let's do that.

How much time I have? Not very much time. Well that's good, because you won't have to watch much more of this.

OK, so we have the HcBe JJ plus 1. And this guy is squared, because we're doing second-order perturbation theory. This is just the B term squared.

And then we have 4BE be over omega E. And then we have the delta V of 1 and minus 1 matrix elements. V plus 1 over minus HC omega, and V plus V over HC omega.

We have the energy denominators, two energy denominators of opposite side and similar identical magnitude. And we always do that because then the algebra is simple. If we do-- we fail to do that, you might as well just go to a booby hatch right away, because there's just no way you're going to retain your sanity if you don't combine the terms of delta V plus 1 and delta V minus 1.

OK, and this is the first term. And there is the next term in this sum, which is the AB term. And so we have a minus 2 times HCV JJ plus 1.

And it's not squared, because it's one B and one A term. And so we get 4BE over omega E square root. And then the A part. And we get 3B plus 1/2 to the 3/2 times V plus 1/2 to the 1/2, or minus HC omega E. And then the other term, which is 3V to the 3/2, V to 1/2, over HC omega E.

We have to combine these two terms. And the combination is easy. And then there is-- so this term number two. And number three is the squared anharmonic term.

So I'm going to skip it, since I'm basically done. There's just a lot of garbage like this. And at the end, we have an expression, term by term, which simplifies.

And we get the second-order correction to the energy, VJ, is equal to minus HcBe cubed over HC omega. No, not HC. Just over omega E squared times JJ plus 1 squared.

Well this is nice, because we have a term that just involves J, and it's negative, that says as a molecule rotates, the molecule stretches, the rotational constant decreases. This is called centrifugal distortion. And this is a very famous expression that DE is equal to 4BE cubed over omega squared.

I left out a 4. So this is the Kratzer relationship. And that turns out to be of the most valuable ones, because the centrifugal distortion constant is extremely sensitive to contagion.

If there is a perturbation, if there is something missing, this centrifugal distortion constant will have a crazy value. And if it doesn't ever-- if there's nothing wrong, then it will say, well, OK, I can-- if I know something about B and omega, I can determine how the rotational energy levels get closer together as you go up in V. And if you have only a pure rotation spectrum, then you actually-- where you're not sampling anything having to do with vibration, you actually can determine the vibrational constant from the centrifugal distortion.

And I should tell you that spectroscopists come in families, or they used to. Pure rotation, infrared vibration rotation, electronic vibration rotation, electronic. And so the microwavers, who really have only rotation to look at, are kind of deprived.

And they just don't know anything about electronic degrees of freedom. But they know how to get the vibrational frequency from the rotational spectrum, which is kind of nice. Gives them something to do.

And there's more terms. And we're really done, but it's all in the notes. And so what we get is for the constant OAEXE, and center of distortion, and alpha E and beta, which is the vibrational distortion of the centrifugal distortion constant, we get all these in terms of omega and B.

So it's a nice closed set where you get the-- you're able to predict how certain constants depend on the most fundamental ones, omega E and BE. That's kind of neat. And it's both a way of extending your observations and telling well, there's something missing, because these

constants aren't coming out right.

It's also a subject of great consternation. Because if you're a quantum chemist, what you do is you determine a lot of stuff by derivatives at equilibrium. The derivatives, the potential at equilibrium, are basically telling you the shape of the potential at moderately low energy.

And it also turns out to be something with modern quantum chemistry. You can get all these derivatives pretty accurately. The trouble is measuring derivatives here and using the energy formulas gives you slightly different values from what you get from perturbation theory.

So what we have is two communities who are very sophisticated using the same names for different quantities. It's dangerous. And it's also not understood by the two communities.

And so people are struggling and struggling to get agreement between experiment and theory. And it's apples and oranges, but it's a subtle thing.

OK, so that's basically all I want to say about perturbation theory. I will have one more lecture dealing with perturbation theory, and that lecture is on Van der Waals interactions between molecules and why we get liquids. OK.