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PROFESSOR: Today's lecture is on intermolecular interactions. And it's really one of these favorite topics where I can say, well, this is the origin of life. How do gases actually condense? And we can build a really, really simple theory for how gases condense based on what we know, based on second order perturbation theory, based on some hand-waving stuff.

And it really is something from nothing. But it's also an example of what we do in physical chemistry where we explain one phenomenon by taking something that seems to be unrelated and building a model around it, and explaining this surprising thing. And that's what's going to happen today. We'll talk more about that.

OK, now last time we talked about wavepacket dynamics. And so with wavepacket dynamics, there is first the pluck. How do you start the system in some superposition of eigenstates?

And then there's the evolution of the pluck, which is usually some kind of particle-like state that follows Newton's laws. The center of the wavepacket follows Newton's laws for the position and the momentum.

But if you make a wavepacket in a real molecule, the molecule is going to be not a harmonic oscillator. There will be anharmonic effects which causes the wavepacket to de-phase, but the center of the wavepacket continues to move as if it were in a simple potential. And it can de-phase, and rephase, and all sorts of complicated stuff. And that can be very interesting.

Now, when you take this step from a diatomic molecule to a polyatomic molecule, you have $3n$ minus 6 oscillators cohabiting in the same house. And they're going to interact. And so if you start a wavepacket on one Franck-Condon bright mode because of anharmonic interactions handled by perturbation theory, between modes you start to get this wavepacket leaking out into other modes.

And so the expectation value is going to exhibit an oscillating time dependence associated with the bright mode and some of the dark modes that are anharmonically coupled to the bright mode. And it can get pretty complicated. But you can understand all of it because you have

perturbation theory.

And so you can say, OK this time the wavepacket-- some amplitude of the initial wavepacket is transferred to a different mode. And when does that happen? Stationary phase. It happens at a particular geometry.

And so you can be asking, OK, when is this excitation transferring? How strongly? This is a very, very complete picture. And it's very much like classical mechanics because it's localized.

Then we talked about Landau-Zener. And the Landau-Zener is basically a simple idea that you also understand from real life. And it has to do with how does a wavepacket jump from one potential surface to another?

And again, it's stationary phase. At the internuclear distance of the curve crossing, the wavepacket has to decide which curve it's going to follow. And it depends on the velocity of the packet at the curve crossing and the difference in slopes of the two paths it has to choose between. And all of this is very simple.

Now, I am trying to create an exam problem which is related to Landau-Zener. And this is hard. But if I succeed, then you can expect to see it. The last thing I talked about the last lecture was the Zewail pump-probe experiments.

And this is a beautifully graphical picture of how do you create something and then probe what's happening. And again, I hope that I can come up with something pictorial for the exam on the Zewail pump.

OK, now before I talk about intermolecular interactions, I want to do a little bit of tying up loose ends. You know about non-degenerate perturbation theory. Now there's another kind of perturbation theory called degenerate perturbation theory.

And this is when non-degenerate perturbation theory fails because $H_{ij} / (E_i^0 - E_j^0)$ is greater than one. Well then you've got a problem. You can't use ordinary perturbation theory. You have to diagonalize. You diagonalize it two by two or you diagonalize all of the little cases where this is violated. That's called degenerative perturbation theory.

And there is a little bit of extra recipe for how do you put information about remote states into the part of the Hamiltonian you diagonalize? That's called a Van Vleck transformation, and I'm not going to talk about it.

But basically you fix things up by diagonalizing two by two or three by three. And then do ordinary perturbation theory.

And then there's variational. The variational model is something we've used mostly in a minimum basis set for talking about the atomic molecules. And in the variational model, we minimize energies by optimizing mixing coefficients.

Now, perturbation theory is implicitly an infinite basis. Usually the infinity doesn't matter because the interesting stuff comes in from relatively low-lying levels. And the infinite number of very far away levels just modifies the energy levels a little bit, and you don't have to worry about it.

The variational method, you choose your own basis set. Now, the choice of basis set is frequently dictated by convenience. And the basis set is often not very large or not orthonormal. And so there are problems with how do we deal with basis functions which are not orthonormal, especially not orthogonal to each other?

And there is a transformation that you can do to make that work out. I mean, the problem is basically-- the secular equation is this for the variational method. And this is the overlap matrix.

And the overlap matrix is not the unit matrix. We have what's called the generalized variational calculation. And there are methods for handling that. And I have often introduced those methods on a final exam. Those are just statements.

OK, so variational is not guaranteed to give the exact answer. And it can't if you don't use an infinite basis. Perturbation theory implicitly uses this infinite basis. And you should feel confident that you're getting close to the right answer. And you can know what sort of errors you're making.

OK, yes?

AUDIENCE: When you go to very high orders in perturbation theory, your convergence is not necessarily better--

PROFESSOR: That's correct.

AUDIENCE: --on the real solutions.

PROFESSOR: OK, but that's--

AUDIENCE: [INAUDIBLE] when to cool it?

PROFESSOR: This is-- the problem there is that you cannot include correlation in perturbation theory. And so there are things that are outside of the network of things that I've described. And so correlation effects where the particles can move in some way that they know about each other. That's very difficult to build in via perturbation theory.

But when we don't have correlation, length perturbation theory makes an error. And you know how big that error is.

OK, and then we know that we can diagonalize the matrix by some kind of unitary transformation. And the columns of T dagger are the eigenvectors. And the rows of T are the inverse-- rows of T dagger or the columns of T are the inverse.

And so if you want to make a wavepacket where you have some additional state to equal 0, you want to express that as a linear combination of eigenstates. And this sort of transformation provides that information if you know how to use it.

And you can get approximations to all of these elements of T dagger from non-degenerate perturbation theory. And on the second exam that was one of the things you didn't do very well on. And so you can see that again. All right.

OK, so now we're going to talk about intermolecular interactions. And up until now, we've been talking about isolated molecules. And you have a lot of insights about how isolated molecules work, or at least what kind of stuff you need to be able to make predictions about isolated molecules.

And perturbation theory is a very important tool in building that insight. In almost every problem which is not an exactly soluble problem, perturbation theory gives you at least a hand-waving argument for what's going on.

Everything we did with LCAO-MO is really based on perturbation theory, or at least the interpretations, especially when you go from homonuclear to heteronuclear. And when we talk about what various orbitals look like and why they look that way.

OK, so perturbation theory can also be used to talk about-- we have two particles, A and B.

And we have the origin of coordinates. And so this is the coordinate for A, and this is the coordinate for B. And this is the interatomic coordinate.

And so we're interested in what happens as a function of this interatomic distance. And can we use perturbation theory to be able to say something about that? And the answer is you betcha.

Because basically we understand how these two molecules work. And so we have to somehow build in some insight into what is the interaction between these, and then use perturbation theory to quantify it.

OK, now this is a situation where we're going to say atoms A and B are our field shell, or whatever you want to call it. They don't need to make another bond. They're not going to bond to each other. There's no covalent bond between A and B. There is no charge on A and B. There is no donor/acceptor.

All of the things that we can understand by looking at individual systems, they are all turned off. These molecules do have energy levels. And so if we could find some way to talk about the weak interaction between them, well then we have the basis for perturbation theory. Because we have weak and we have energy levels that we know for the two molecules.

And so if we're going to do perturbation theory it'll be second order perturbation theory because we are going to be interested in how interaction of A with B causes excited states of B to mix into B, and vice versa.

And so one of the things you know about perturbation theory, if you're talking about the ground state of a system and you do perturbation theory, what happens? What happens to the energy levels?

I mean, you have-- for second order perturbation theory-- I'm sorry?

AUDIENCE: Everything gets-- things can increase or decrease. The H term gets squared.

PROFESSOR: Yes.

AUDIENCE: Some [INAUDIBLE] information. But depending on whether a level that's lower--

PROFESSOR: But if we're talking about the ground state--

AUDIENCE: If it's that ground state it has to go down.

PROFESSOR: Right. And so that's the key. We know that if we're going to do second order perturbation theory and we're going to be asking questions about molecules in their ground state, they're going to be stabilized by interaction with other molecules.

It doesn't matter, as long as there's no bonding interactions, or very strong short range interactions, this sort of a problem is guaranteed to give stabilization of the ground state of the system.

And that's really a surprise, because--

Yes?

AUDIENCE: You're treating the system as though it has like a ladder of energies and everything is already at its lowest?

PROFESSOR: Yes. Well, OK-- you know, I'm not allowed to talk about statistics. I can't, actually. Because we do it-- we now do some statistical mechanics in 560. So you know a little bit.

And you know that the molecules like to be in the lowest energy levels. And so we have these ground state molecules in a gas. And we understand they're isolated properties, or we could understand. And what happens here? Somehow there's interactions between them.

And now first order perturbation theory, you're allowed to have a sign. But you're allowed to have a sign for diagonal elements of the perturbation operator. OK, so we'll just continue with this.

So we want to talk about Hamiltonian for the system, which is the Hamiltonian for particle A, the Hamiltonian for particle B, plus some interaction term between A and B.

OK, now the typical interaction between two particles is a dipole-dipole interaction. If molecules have dipole moments, then we already know something about what they want to do with each other. And from electricity and magnetism-- we know this isn't quantum mechanics-- we know that we can write a general formula for the dipole-dipole interaction.

So that's the general formula for the dipole-dipole interaction. And it's a little more complicated than you would like because there's two terms. And this one is kind of a puzzling term because you're projecting a dipole on the interatomic axis.

And so we'd like to be able to simplify this. And we can simplify it by simply drawing some vectors corresponding to the dipole moment.

And so we have the dipoles oriented like that. Or we have the dipoles oriented like this, or like this and like that.

Now, this is a reduction. You know, these are the simplified terms where these guys are irrelevant or at least you don't have to worry about the projections.

And we know that this is an attractive interaction, this is an attractive interaction. This is repulsive and this is repulsive. And we know also by plugging into the formulas, we know that the energy for this one is minus $\mu_A \mu_B$ over two $\pi \epsilon_0 R^3$.

And this is minus the same stuff, except a four in the denominator. So that means it's less attractive than this one. Minus means attractive.

And then we have two terms that resemble these except they're repulsive. So there's four terms.

So there's two terms that are attractive and two terms that are repulsive. And they come in pairs, one positive and one negative. And so you might naively say well, you can't win. If the particles are randomly distributed and randomly oriented, there will be no stabilization, even with dipoles.

But that's not true because the molecules try to find an orientation which is more stable than the sum of the energies without the dipoles. And so maybe we could draw a picture and try to figure out, well, how that would be.

So does anybody want to give me guidance to a picture showing, let's say, four dipoles oriented in the corner of a square? And what would be the stable arrangement for four dipoles oriented on the corners of a square?

OK, right? So we have two attractive interactions, two more attractive interactions, and then there are repulsive interactions this way.

But we have nearest neighbors. And they're stronger than the repulsive interactions. And so for one layer, that can win. Now, we have another layer of four dipoles. And if that layer is-- so we have another layer, and there will be four of them. And what would happen? What would

be the stable arrangement if I have a dipole above this one? Is it going to be this way? Right.

And so the next layer, all the dipoles are reversed. And so you can conceive of an arrangement where the dipoles would adopt a more stable arrangement. And statistical mechanics, or whatever you want to call it, guides that.

And so we can say, all right, the ensemble of dipoles interacting with each other can arrange to be energetically stabilizing. And so we can reduce the problem to just one picture, say this type or that dipole-dipole arrangement, and do second order perturbation theory.

And that will be an overestimate of the stabilization. But it will be proportional to the stabilization. And so we can get what we need for a very complicated infinite number of particle problem.

OK, another thing that I want to ask you, suppose you have two particles and they come together. And so they come together with some kinetic energy.

And they can't get rid of that kinetic energy, so they come apart. Now, if you have three particles, if something drives them together by mutual attraction, then one particle can take away the excess energy. You can end up leaving the two particles together. That's how you make liquids.

So the driving force for the attraction between atoms or molecules is somehow related to what we're going to drive here. And that is the only way you make liquids from gases.

And it's really strange because we're going to be talking about energy levels and interactions between molecules, and somehow coming up with a picture that leads to universal attraction between molecules that are not charged, not reactive, not anything. And they will always attract each other. And that's the first step towards making liquids.

OK, now the important thing in all of this is that the interactions are small compared to the energy levels of the individual molecules. And so that's why we're doing perturbation theory.

OK, so in perturbation theory we have an H_0 . And the H_0 is-- I've got to make sure I use consistent notation. Well, I already see I have inconsistent notation in my notes.

But anyway, OK, so we have the Hamiltonian is the individual system Hamiltonians, the sum of the two. And the first order term is VAB .

And so whenever we can separate a system, we know that the zero order wave functions are products of the eigenfunctions of H_A and H_B . And the energy levels of 0 [INAUDIBLE] energy levels are sum of the energy levels for H_A and H_B .

So we know that we can write $H_0 \psi_A \psi_B$. So this guy-- H_A operates on ψ_A and treats this as a constant. H_B operates on ψ_B and treats this as a constant. And when you do that, what you discover is that we get--

OK, so these are our energy levels. And these are our basis functions. And we are off to the races. So this is E_0 . And this is ψ_0 for the system.

OK, now the first thing we do in perturbation theory is we say, let's look for the first order correction of the energy. That's the diagonal matrix element of the H_1 term, this.

So suppose we do have dipole moments on both particle A and particle B

So that's the first order energy. Well, this is just the dipole-dipole interaction. And so we can take the reduced formula. We're just going to regard V_{AB} as $\mu_A \cdot \mu_B / R^3$.

And so the energy is minus one over two pi epsilon 0 R^3 . I left out the two pi epsilon 0 on this formula. And so skipping a couple of steps, we have $\mu_A \mu_B$, the expectation value of these.

So if there's a dipole-dipole interaction, there will be a first order correction term. And keep in mind that these guys can have signs. And that sign does appear in the first order correction to the energy.

But that's basically these pictures we drew here. We have a dipole pointing this way, we have a dipole pointing that way. That's repulsive. And that's all-- so there's no surprises here.

OK, but the important thing is that the energy-- If we have two molecules with dipoles, we get an interaction energy that we can calculate. But the interesting thing is going to be when we have molecules where at least one of the molecules doesn't have a dipole. Then we're getting into territory that we didn't think we understood. But we're continuing with the problem where we do have dipoles.

I just want to make sure that-- yeah, OK. So for the second order correction to the lowest

energy level, we have the sum over m , which is two quantum numbers. And m is not equal to the 0-0 state. α is not 0, β is not 0 sum over everything except the ground state.

And what we have is an integral of $\psi_m^* \langle V \rangle \psi_0$ $d\tau$ squared over then $E_0 - E_m$.

Standard formula for second order variation theory. This is the ground state. This is some excited state. This is negative. This is squared. And this is squared. So this overall correction is negative.

Now we can unpack all this and we can write the various terms in more instructive form. And what we'll have in the denominator will be $E_0 - E_A - \alpha + E_B - E_0 - E_B - \beta$.

Now we can rearrange that so we have $E_0 + E_B - E_A - \alpha + E_B - \beta$.

So we have the ground state energy and the known excited state energies. And there is the difference between these. So that part is simple. And the matrix element also simplifies to the product of the dipole moment.

OK, now suppose-- I just want to make sure that I'm doing this in the order it appears in the notes.

Suppose μ_A is not 0 and μ_B is equal to 0. OK, well then all these formulas go out the window because nominally we think well, this B doesn't have a dipole moment.

But suppose we have a particle B in an electric field. The electric field will polarize B. And if we have molecule A, which has a dipole moment, near B, it will also polarize B. And second order perturbation theory tells us how to handle that.

And so we get a formula, a second order correction to the energy E_B . And we call this E_B^{ind} . And that's going to be μ_A^2 over $4\pi\epsilon_0 R^3$ times the sum over $\beta \neq 0$ of the squared matrix element $\int \psi_B^* \mu_B \psi_0 d\tau$ squared over $E_B - E_\beta$.

Now, I just told you that the dipole moment-- the permanent dipole moment for particle B is 0. But this is not the expectation value of the dipole moment. This is an off-diagonal matrix element of the dipole moment. This is the transition dipole.

Transition between v equals 0-- well, between the ground state of B and some excited state, the beta, excited state of B. Well, we can write something like that because we know for all molecules there are transitions, which are electric dipole allowed. Now they could be between the ground state and an electronically excited state or the ground state and a vibrationally excited state.

So we know something about these: we know the rules for when they're not 0. And this is a perfectly reasonable thing because it says this is related to the transition of-- the intensity of the observable transition.

And this should really start to make you a little bit appreciative of perturbation theory. Because we're taking something which you can observe, a transition strength, and using it to describe an interaction between two molecules.

So it's a relationship between two apparently unrelated phenomena. Physical chemistry is full of that. You build a model. And the model is telling you that certain things are related.

And how are they related? Well, they're related by one over R to the sixth. They're related by the strength of the dipole on one, the permanent dipole on one, and some transition intensity-derived quantity on the other. Isn't that neat?

And since the dipole-- we say well, this is a dipole-dipole interaction. And the μ_A , the dipole on A, is inducing a dipole on B. It's not inducing anything. It's using transition dipoles. But it's creating something that looks like a permanent dipole.

And you have dipole-dipole interaction. But the only difference is that it's one over R to the sixth because it's an induced dipole.

OK, so we're using transition-- well, electric dipole transition moments. (There used to be two erasers!)

So these electric dipole transition moments play the role of producing a dipole that can interact with the other dipole. And so-- well, do we need this? Well, we don't really. If you had dipoles, then the interaction would be one over R cubed.

But if one of the dipoles is 0, then the interaction is one over R to the sixth. And it's one over R to the sixth times the permanent dipole of one and this thing from perturbation theory, which is

the induced dipole of the other.

Suppose μ_A equals 0 and μ_B equals 0. Will the particles interact with each other? Will they attract each other? And the answer is yes. And it's going to be an induced dipole-induced dipole interaction.

Which, now since most people who write for general science have no clue about what quantum mechanics is, they will talk about all sorts of fanciful things-- you get an institute-- an instantaneous fluctuation on one particle which creates an instantaneous fluctuation on the other particle, and bam, you've got stabilization. Well, yeah, maybe. But you know, this is a simple perturbation theory.

And so I don't really need to actually write out everything. Because one, you do that and you include the second order perturbation expression for particle A and particle B, you get a term that looks just like this. It has one over R to the sixth.

But it now involves transition moments, particle A and particle B-- nothing new. You don't have to induce anything more. You don't get another factor of one over R cubed. You've already got the one over R to the sixth.

So I'm going to skip a lot of steps because the notes are really clear in there. And we don't have a whole lot of time. And so I'm just going to write down the result.

And now the name of this term is called dispersion, or London because a fellow by the name of London invented this. And the energy level formula for this correction term is one over four pi squared epsilon 0 squared R to the sixth.

And then this sum of alpha equals one beta equals one to infinity. In other words, not alpha equals 0, not beta equals 0. And then--

Sorry about that. So we have a numerator, which is the squared transition moment between the 0 level of particle A and the alpha level and the 0 level of B and the beta level. We have the energy of the ground state and we have the energy of these excited states.

All of this stuff, you know or at least you can parametrize it in terms of this strength of our transition. And there is an explicit formula that relates the dipole moment to the intensity depending on what kind of experiment you do.

So I'm not going to take you through that. But you know you can measure the intensity, the molar absorptivity, or whatever you want that is related to this.

So these are experimentally observable. These are experimentally observable. And usually this infinite sum is dominated by the lowest allowed transition from the ground state. And that can be an electronic transition or a vibrational transition.

So for our homonuclear molecule, there isn't going to be an allowed vibrational transition. So nitrogen and oxygen cannot talk to each other through transition dipole-- vibrational transition dipoles because the dipole moment is not dependent on [INAUDIBLE] but they have electronic transitions. And so there is this electronic-- as opposed to a vibrational polarizability of the two. And that's what gives rise to attraction between N₂ and O₂, or N₂ and N₂.

So everything is knowable and predictable. And even though the perturbation's sum is infinite, and even though we've made a gross approximation and say, well, we're just interested in this sort of an interaction or this sort of an interaction, and we know that the true interaction will be less because there will be an average over all of the random orientations.

But there's going to be a lowest energy picture. And you can get that from statistical mechanics. And so you can do the configurational average over all possible orientations of all of the interacting particles. And you can calculate this.

So that's beyond the level of this course. But the engine of the calculation is this formula.

So molecules are polarizable. They react to an external electric field. And there are several ways you can describe the defined polarizability. One is to say well the polarizability-- let's call it α -- is equal to the second derivative of the energy with respect to the electric field.

But the polarizability, you know, you also get from perturbation theory. And so each of these terms or the energy is associated with the interaction of a dipole with an electric field is the electric field times the dipole. And so we have electric field squared. We take the second derivative of that. And we've got back to this.

So now here we come with intuition. If I asked you to tell me the van der Waals or the dispersion interaction between helium and helium, and compare that to xenon to xenon, would you be able to tell me? So which one is stronger? Which one-- which pair of inert gases is stickier?

AUDIENCE: Xenon.

PROFESSOR: Xenon, right. Why? Because the energy denominator for the first excited state is much lower for xenon than for helium.

OK, what about large molecule versus small molecule? Do I need to provide a hint? $3n$ minus six. The more vibrational modes, the more transitions are available for polarization.

And so again, now we're talking about molecules which can be floppy. And the floppier the molecule-- that means they have low frequency vibrations-- you can polarize the daylights out of them. And so large molecules are really sticky, stickier than inert gases. Because you have this dispersion interaction that brings them together. And once they're together, then they can do magic.

But the thing that drives the condensation, or the formation of droplets, or whatever, is this dispersion interaction. And it's universal. Every pair of molecules or atoms is going to attract each other. And the strength is something that you can rate in terms of what you know about atomic and molecular properties.

And isn't that neat? Because you're saying the viscosity, or whatever it is, the property of a gas, all of those things are related to the properties of the individual atoms or molecules embedded in perturbation theory. This is why I think perturbation theory is so wonderful, because it enables you to relate different things.

And even if you're not going to evaluate the magnitudes of the terms, you can make comparisons which are always going to be right. And that's kind of wonderful. I mean, you don't have to use the equations.

Or you just know that these particles will attract each other and the driving force is either a permanent or an induced dipole. And the induced dipole will be strong if you have a strong transition to a low-lying state, or a lot of strong transitions to a lot of low-lying states as you have in big molecules.

OK, so I'm not positive what I'm going to talk about on Friday. It's probably going to be photochemistry. But I may panic and do something else.

OK, I'll see you Friday.