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ROBERT FIELD: So in the previous lecture, I told you about many electron atoms. And in order to describe their structure, we have to build a Slater determinant, because that builds in the antisymmetry between all pairs of orbitals. Now, Slater determinants are expanded into a very large number of additive terms. And there are algebraic methods, which I describe in a supplement, which enable you to reduce these algebraic terms, the sum over an enormous number of terms, to something almost identical to what you would get if you didn't antisymmetrize. They're just a few extra things. And so once you know the mechanics, it's not a big deal. It's a little bit more work than just calculating the individual orbital matrix elements, but it's nothing special.

And Henry has produced a beautiful thing, a beautiful handout on Slater-Condon parameters, which is what you get when you evaluate these Slater determinantal matrix elements. And they are the things that you use to describe electronic structure. So electronic structure is a really complicated many electron descriptive thing. But if you can reduce for every atom to a small number of parameters, most of which you understand intuitively how they depend on properties of the atom, like the ionization energy of the individual orbitals, you can say, yes, I understand all of the periodic table. That's where it comes from.

The rules enable you to identify the lowest lying states and to calculate their properties and to be able to intuit their properties and to be aware of when something unexpected happens, which is what we're always looking for as physical chemists. We're always looking for a simple minded picture that breaks. Because then we can go deeper into our understanding of all the pieces. But we're always parameterizing. OK.

So there's a lot of subtleties that I didn't have time to talk about in the evaluation of these Slater determinantal matrix elements. And since whatever problems I give you connected with Slater determinantal matrix elements or Slater determinants are going to be really simple. They're probably going to be 2 by 2 or 3 by 3. You don't really need to know and understand all the rules and all the shortcuts. But you've got the basic mechanism.

So a Hamiltonian doesn't depend on spins. But because of antisymmetry, the spatial part of

the wave function does depend on which spin state you've got. And so the Hamiltonian knows about spins in a peculiar, indirect way, which is beautiful. You've got to admire how clever this Hamiltonian is to be able to capture these spin effects. And of course, you have to capture them too. All right.

So today we're finally getting to molecules. And the simplest molecule is the homonuclear molecule. Two hydrogens with one electron. That's the simplest problem. And because it is representative of all of the qualitative effects and most of the quantitative calculations you do, it's a really great introduction, because it captures most of the important stuff that molecules or small molecules do, that the electronic structure of small molecule.

So the key to being able to describe small molecules using this LCAO, Linear Combination of Atomic Orbitals method, is the variational method. And this variational method says, we're going to throw a whole bunch of basis functions at the problem. A whole bunch of orbitals, which we choose because we like them or because the computer likes them. And we find that the linear combination of coefficients of these orbitals that minimizes the energy.

And you can do this in wave mechanics or matrix mechanics. It's more elegant in matrix mechanics, and you should be comfortable going from one to the other. Now, I'm only going to be talking about a 2 by 2 problem. So you can go easily from one to the other without even taking a breath. But anyway, OK.

In approaching this, you're going to see what's called the general eigenvalue problem where instead of diagonalizing a simple matrix, you have to deal with the Hamiltonian matrix and an overlap matrix, which makes the solution of the secular equation, finding the eigenvalues and eigenstates a little bit more complicated. So you're going to see it first appear here. And it can be solved by a simple matrix equation, which is in a supplement to a later set of lecture notes. But this is the thing that consumes the vast majority of computer time in maybe in the world, but certainly among chemists.

So the crucial thing, and I wrote it all in caps, in dealing with this complicated many body problem, we make a crucial assumption. And that's called the Born-Oppenheimer approximation. It's based on the fact that electrons move really fast and nuclei move really slowly relative to electrons.

And so what we do is we solve the problem with the nuclei clamped. Because that's a good approximation. And then after we solve the electronic problem, we have what we call a

potential energy surface, which is the electronic energy as a function of nuclear coordinate. And it's parametric. But then once we have the potential energy surface, we can calculate the rotation and vibration.

So basically, what we're doing in making the Born-Oppenheimer approximation is we're setting up to treat vibration and rotation by perturbation theory. Now, you never see it mentioned in that way, but that is, in fact, what we're doing. And the reason we can get away with it is the difference in velocity of electrons versus nuclei. But it's a fundamental philosophical point of view that we take about molecular structure that we can clamp the nuclei, get most of the insight, and then allow the nuclei to move and the electrons with them and calculate everything else.

So this is central to chemistry, the Born-Oppenheimer approximation. Without that, we would have a bag of atoms. And that would be a very bad starting point, because we believe in bonds. And a bag of atoms is saying, well, yeah, we could be statistical. We could say every atom is capable of being anywhere and they don't interact in any rational way, and we would have no insight. So this is where most of the ideas that you learn to use as physical chemists and probably any kind of chemist comes from the Born-Oppenheimer approximation. And it's widely misunderstood and misrepresented. But we won't go into that.

OK, we're going to derive two orbitals for hydrogen. H_2 plus. The sigma bonding orbital and the sigma star anti-bonding orbital. This is enough to basically understand how you get bonding and anti-bonding in any molecule. And I like to say that we understand bonding in a very simple way.

If you have wave functions for two adjacent atoms and they overlap in the region between the two nuclei, you get constructive interference, you get twice as much amplitude in the region where the electrons interact with both nuclei, which means four times the probability. So a little bit of overlap leads to a big energy effect because of this constructive interference. And that's really, really important. And all sorts of hand waving arguments about what makes a chemical bond have a lot of currency, even here at MIT, but that's what a bond is. It's constructive interference.

All right, so let's get started. And the lecture notes are extremely long and extremely beautiful and clear. They're written by Troy. I have reduced them to a minimal picture, but I don't want to detract from them. The insight is very rich.

OK, so what we have to do first is to look at a coordinate system. So we have one hydrogen nucleus. Another one. There's a center of mass. And so we say we have R_A , this vector from the center mass to this R_B like that. And up here is the electron. And it's at position R . This is at position R_B . Position R_A . Now, the center of mass can be anywhere in space, and we don't really care. So we tend to not talk about where the center of mass is. But there is another set of coordinates for it.

OK. And now we have this, which is called $R_{sub A}$. And it's a vector. And this is $R_{sub B}$. So we have uppercase symbols for nuclear positions and lowercase for electrons, except they're between electrons and nuclei. OK. And once we have this picture, we can write what the Hamiltonian is, because we're basically looking at the interactions between these three particles. And so we have kinetic energy and we have potential energy.

And the Hamiltonian-- excuse me. --in atomic units is this ∇^2 , which is the second derivatives with respect to whatever we have here, which is little r . And we have $1/2$. It's $1/2$ because of atomic units and because the mass of the electron is treated as one. And then we have a similar sort of term for ∇^2 for nucleus A . And we have a two, because $1/2$ in atomic units. But we have the mass of A . Now, the minus signs, why do we have minus signs here? You know this.

AUDIENCE: This is the Schrodinger.

ROBERT FIELD: Yeah, right. Or we say it's p^2 over $2m$. And p is-- right. OK, but what we're trying to understand stuff, this is negative. That means it sort of leads to a stabilization. And many people talk about bonding in terms of velocity or momentum, but I don't. And then we have $\nabla^2 B$ over 2 and B and then a repulsion term.

A whole bunch of terms that we have. So these are the kinetic energy terms. And then we have the potential energy terms. 1 over R_A vector minus little r vector minus 1 over R_B minus little r . And then the repulsion between R_A minus R_B .

OK, that's it. Now, that's a lot of stuff. And we'd like to make a lot of it go away. But again, we have potential. We have kinetic energy and we have potential energy.

So as I've written it, the Hamiltonian, which is our big problem, is a function of r_a r_b r big R_A big R_B . That's just ridiculous. We don't want to look at a function of all these variables. We would like to be able to simplify it so that we can draw pictures on a two dimensional surface or

just to reduce it now. We like to think in terms of orders of magnitude.

And so it is a very simple matter to say, well, let's simplify this Hamiltonian by clamping the nuclei. They don't move. If they don't move, then the big R s are no longer operators. They're just parameters. And the contributions to the kinetic energy of the heavy particles gone. So there's no rotation and no vibration. Now, it doesn't go away. We have to come back with it. But we come back with it when we have a good representation of the electronic structure for the nuclei clamped. And if we can do it for one internuclear separation, we can do it for all internuclear separations.

And so if you have a grid of say 1,000 points, you do the same calculation 1,000 times, except you don't. Because you know how to extrapolate from one point to another. But basically, you are thinking about this as the problem of finding the electronic wave function at a grid of points. And so that turns all of the big R 's into parameters, not operators, and simplifies the problem enormously.

And so the reduced Hamiltonian becomes-- we'll call it the electronic Hamiltonian. R semicolon r r_b . So r is the variable, and these are just parameters that we sometimes include. And then the Hamiltonian is just $\Delta^2 r / 2 + V_{\text{effective}}$. And this would be as a function of R_A and R_B . But it's because of R approximation, it's just a function of R . So these we pick.

And this is the thing that we're worrying about. And then there's the $1 / R_A - R_B$, which is just a constant. This is the repulsion between two charged particles. So this is a lot nicer. We can also sort of forget about this. I mean, it's there, but it's a trivial thing that we can add in. So we have basically the kind of problem we like. A kinetic energy problem and a potential energy problem.

So we're going to take this approach and we're going to learn how to apply it to the simplest system. And the simplest system is homonuclear. That's better than heteronuclear, because if we had two different atoms, we'd have to somehow represent their difference in properties. But because it's homonuclear, we just basically have an atom, the same atom, repeated, and there's a lot of symmetry that results. And the other is only two electrons. I mean, sorry, only one electron.

Remember, we did hydrogen first, and that was wonderful. We got everything that was--

basically everything is related to anything else. Any property is related to any other property of the hydrogen atom through this orbital approximation. And so one electron makes us feel really comfortable, because we are going to expect that there is some structure, which means not just a random number or random collection of descriptive observations but some relationships. And we don't have to even antisymmetrize. So it's really something we can hit out of a park without getting too stressed.

But there is a problem, and that is, how do we find the wave functions if we take a simple basis set? $1s$ a plus $1s$ b. So these are hydrogenic wave functions. We know them. Now, they may not be the most convenient thing when you're doing a large scale calculation. In fact, nobody uses hydrogenic functions, even though they make a lot of sense, because they're not computationally as easy as Gaussian functions.

So if you need to describe a problem with, say, 10 hydrogenic functions and 1,000 Gaussians, you're way ahead of the game when you use 1,000 Gaussians, because the integrals are trivial. But in terms of understanding, it's really nice to take things we know and do everything in terms of them. OK. And so this is where we get the variational.

So what we do is we say we're going to express the wave function as a linear combination of atomic orbitals. And that means we can adjust the coefficient of each atomic orbital to minimize the energy. And the variational principle or the variational theorem says, no matter what you do, you can't calculate an energy lower than the lowest energy of the system. Even if you don't know what it is, you know that anything you calculate is a little bit higher. And what you want to do, then, is to make the energy as small as possible by doing a min max problem on the coefficients. And so the variational method is basically that.

OK. So basis set. I'm probably not going to finish my notes, even though these are a massively reduced version of what Troy had written, because I have some other things to say that aren't in the notes, and they're really important. When we do perturbation theory, we implicitly are dealing with an infinite basis set and an infinite set of known matrix elements. But we can't ask a computer to diagonalize an infinite matrix.

So we have a tricky way of doing this so that we can use perturbation theory to get a good approximation of almost anything you want. But if your basis set is really terrible, then the perturbation theory is going to be terrible too. I mean, it's going to give correct answers. You're just going to have to do more calculations. The variational method says, OK, let's choose not

an infinite basis set but a physically appropriate basis set or a computationally minimal basis set. And so we are making decisions about form and size.

So we can use hydrogenic orbitals, because we know what they are. We know how to evaluate lots of integrals with them without too much trouble. And how many? Well, we've got two atoms. And so you sort of need one orbital on one atom and one orbital on another to even begin to capture the molecularness of the problem. So we've chosen the simplest possible form but not necessarily the most convenient form. And the size is two. Now, we could use four. We could use 100. And you could use a million.

Most quantum chemical calculations, which you're going to be doing soon, involve not just millions but often billions of basis functions. And the computer does all the work and doesn't complain to you. It doesn't require a trip to the beach or anything like that. It just says, OK, here is what you wanted me to do. I don't know whether you-- it's a stupid question or a smart question, but I'm answering not what you thought you asked but what you did ask. OK. But we're going to show how it works with the simplest possible basis set.

So our electronic wave function will be a function of electron position and parametrically nuclear position. $C_1, 1S A R R$. I'm going to stop including this parametrically dependent on R . But eventually I'll do that. But for now. OK, so that's the wave function. The variational function.

And we need to be able to calculate the average energy, because we know the average energy is going to be larger than the true energy. But if we do a good calculation, the energy difference between the truth and what you get is small as possible. And so you can say for a particular basis that we have, the best possible energies, if you want to do better, you have to use a bigger or smarter basis set.

And so how do we calculate the average energy? Well, we do the usual thing where you say $\int \psi^* H \psi d\tau$ over $\int \psi^* \psi d\tau$. Now, I'm including this because we need it when we don't have orthonormal basis functions. And for this basis set, they're not orthonormal. They can't be. The wave functions for one atom are all mutually orthogonal. But because you have two atoms and there's overlap between them, they are not orthogonal, and they're not normalized. And so we have to do this.

And so the problem is we want to minimize the energy with respect to C_1 or C_2 or C_1^* or C_2^* . Now, this is a subtle point. The complex conjugate of C is linearly independent of C . But they're related to each other. And so you can say that these derivatives are 0, and you can

choose C_1 and C_2 or C_1^* and C_2^* , and you get the same result. And so it's important to understand this.

So this is all by means of introduction. I'm going to start repeating myself. But let's draw some pictures. So the complicated thing is the potential. And so to illustrate the R dependence, I'm going to try to draw things. So we have r small and R large. This is the positions of the nuclei. And the potential will look like this.

So the potential goes to minus infinity at the position of the nucleus, because the electron is attracted to the nucleus. And when the distance is 0, we have an-- it's a forgivable infinity because it-- anyway. So what I should really have done is exaggerated here. So when the particles are close together, the potential in the region between the nuclei doesn't go as close to 0 as it does when we do this. And so that's an important fact. So as the particles are brought together, something happens in this intermediate region. And when they're completely separated, it's as if they are completely separated. They're not talking to each other.

And the wave functions look like this. I missed. And this is what I was telling you. This is a bond. This is why we have a bond. Because we have constructive interference in the spatial region where the electron can be attracted to both nuclei. Whereas here, there is no amplitude in between them or negligible amplitude, and so there isn't much of a contribution from the attraction to both nuclei. And so this is the separated atom or approaching separated atom limit. And this is the molecular limit.

And now it's possible that you can squeeze the atoms too close together and bad things start to happen. Because then what you're doing is you're putting two electrons into the same spin orbital. And we know that that's overlap repulsion or it violates the exclusion principle and there is an energy penalty that you pay in order to get too close. But basically, this is what we're going to be explaining. And we're going to recover this from a real calculation.

OK. So again, we want to minimize the average energy. And the average energy, as I've written somewhere, is given by $\psi^* H \psi$ divided by $\int \psi^* \psi$. And if we are writing these things as $C_1 1S_A$ times $C_2 1S_B$, then we end up getting stuff that we know how to calculate now.

$1S_A$. This orbital is not orthogonal to $1S_B$. It can't be. And so this is something that we had been able to avoid in all of our one dimensional problems. We could always think about a orthonormalized basis set. But the effect that we're really interested in is based on the fact that

these guys aren't orthogonal. You can't just say we're going to write an orthonormal basis set. It's not possible. If you want to construct an orthonormal basis set, there is a transformation you can do.

And it's a simple transformation, and it's done all the time. And you'll see it, but not today. But you still do the calculations on the non-orthogonal basis functions. And then you do a transformation that takes into account the lack of orthonormality. For now just accept it.

And so we're going to have to worry about an integral like this one. $\int \psi_A \psi_B$. And we call this the overlap integral. And this is something that we have to not ignore.

So now we can approach this problem using wave function notation. And it's most familiar. But we can also use these things saying, OK, this is the complete set of the variational coefficients. And this is a step towards the matrix picture. Because it's basically a linear array of mixing coefficients. And you could think of that as a vector. And in fact, that's how you do the vector picture, but we'll use sort of a hybrid notation for the time being.

But we can also say, OK, this means $C_1 C_2 \dots C_n$. And this means $C_1^* C_n^*$. And here we are in the matrix picture. OK, but I will use sort of a hybrid picture until you're ready to take the complete jump. And so the average energy expressed as a function of this set of coefficients is going to be integral. $\int \psi^* H \psi = \int \psi^* C d\tau$ over $\int \psi C^* \psi$.

The reason I'm being hesitant here is because I work in the matrix picture, and this hybrid picture is away from both comfort zones. But it is leading you towards what you need to see, and so we're going to do it.

OK. So in the wave function picture, this thing becomes just $C_1 \psi_A + C_2 \psi_B$, the whole thing conjugated, $\int (C_1 \psi_A + C_2 \psi_B)^* H (C_1 \psi_A + C_2 \psi_B) d\tau$. And the same sort of thing down here, except no Hamiltonian. And so we can now slavishly write down all of the terms that result. And what we get is from the Hamiltonian matrix element. So for H , we get $C_1^* C_1 H_{11} + C_1^* C_2 H_{12} + C_2^* C_1 H_{21} + C_2^* C_2 H_{22}$.

OK, we think we know some stuff. We think this is going to be the energy of the hydrogen atom. But it isn't. Because the orbital one sees both nuclei. And so this is something which we just call this guy. We're calling this ϵ . And that is a function of internuclear distance. But this guy is the same, because it's homonuclear.

And this, well, we can call it V_{12} or V . And these two guys are the same thing. So we've reduced the problem to a simple equation. But I'm not going to go all the way there. But you know how to do this. You know how to do the overlap integral. You're gonna have a similar sort of thing. S_{11} is the overlap of the orbital 1 with itself. And that one is 1. But S_{12} is S .

So anyway, what we end up doing is a lot of algebra. And what we end up getting when we impose the condition that the partial of everything with respect to C_1 star is equal to 0, we get an equation for the average energy. And the average energy is-- oh, I'm sorry. C_1 . When we take the derivative with respect to C_1 , what we get is this equation. C_1 star H_{11} plus C_2 star H_{22} over C_1 star S_{11} plus C_2 star S_{21} .

And so we could also do the same thing, taking the partial derivative with respect to C_2 and setting that equal to 0. But we get another equation. And so that other equation would be E average is equal to-- no, I'm not even going to write it, because I didn't write it in my notes, and I'm operating on batteries. You can write that. And so we have two equations for the average energy. And well, that's kind of good, because we have two unknowns. So we're going to be able to solve for them.

OK. Now, we could also approach this problem using matrix methods. And since that's the way computers think about the problem and that's the way most people think about the problem, you really want to understand the matrix picture. And at risk of repeating myself, we know for this two level problem, we have H_{11} H_{12} H_{21} H_{22} . And we know that the S matrix S_{11} S_{12} S_{21} S_{22} .

So we have an equation C_1 star C_2 star times the H matrix is equal to E average times the C_1 star C_2 star times the S matrix. So this is the H matrix and this is the S matrix. And you can write this down. And when you take the derivatives with respect to C , you get C dagger H is equal to E average times C dagger S .

Now, if instead of taking derivatives with respect to the C s we took the derivatives with respect to the C stars, we'd get a different equation. And that equation would be HC is equal to E average times S then C . This guy looks familiar. It looks like Hamiltonian times something is equal to the energy times-- uh oh. We have something else here. It's not just the energy. We have the overlap integral.

So these two things are examples of the general eigenvalue equation. And so in almost all calculations, the fact that S is present leads to problems of algebra. But in this particular

problem, we know S_{12} is equal to S_{21} . And this epsilon parameter can be-- so we have H_{11} is equal to H_{22} . They're both parametrically dependent on internuclear distance, and they're equal to epsilon of R . So what we end up with is an equation that looks really familiar.

We have a 2 by 2 matrix, which we can diagonalize. We can find the energies. And so what you end up getting when you do that. And I want to spare you my attempting to do a derivation in real time. You can look at the notes and you can see that the results are what you care about and what we're going to interpret. So here we go.

So what you find. The average energy for one of the orbitals that we get. Remember, we got a 2 by 2. We're going to have two eigenvalues and eigenstates. And so for one of those, we get epsilon plus $V_{12} / (1 + S_{12})$. So these are symbols that we've seen. And this tells us now this, this, and this are functions of R . So we're going to have an energy for the sigma orbital, which is a function of R .

And we have another solution, which we're calling sigma star. And that one is epsilon minus $V_{12} / (1 - S_{12})$. So we'd like to be able to know which of these is the absolute-- one of these is-- so we have sigma and sigma star. Both as a function of R . And so if we draw a molecular orbital diagram and we say, OK, well here we have the energy of $1s_A$, which is epsilon as a function of R . And this is epsilon energy $1s_B$, which is equal to epsilon of R .

Normally we choose R as equal to infinity for the separated atom. So these are actually just the energies of the individual orbitals. And what we end up getting is a molecular orbital diagram which, in an exaggerated form, is like this. We get bonding, because it's more stable than the separate atoms, and anti-bonding, which is less stable. And so one question we'd like to ask is, well, one question is why is it bonding? Why is this more stable? And the answer is constructive interference in the important energy region.

But another question is, is this bigger? Is this a larger destabilization than this stabilization? And it's kind of hard to scope that out, because here we have two parameters, which are added, and here we have a difference of two parameters. And here we have a denominator, which is going to be larger for the sigma orbital than the sigma star. And so we don't know whether the plus versus minus V is dominant. But the energy denominator is saying, yeah, this one, the anti-bonding orbital is more anti-bonding than the bonding one.

Now, you can actually do some algebra to calculate what is the difference in energy between the sigma star as a function of R . But evaluated at $R_{sub E}$, which is the minimum-- the energy

where the bonding orbital has its minimum energy. Then if you evaluate at that particular value of R and you make that comparison B_{1S} evaluated at $R_{sub B}$, and you get ϵS_{12} minus-- so I'm doing sigma star, so that's this one minus B_{12} over $1 + 1 - S_{12}$. And for the sigma orbital, I have a similar equation, but I get ϵS_{12} minus B_{12} over $1 - S_{12}$.

So we have the same numerator for these two cases but a different denominator. And so this is saying this simple variational calculation says you're going to get a pair of orbitals, one bonding, one anti-bonding. And the anti-bonding one is more destabilized relative to the separate atoms than the bonding one is stabilized. And this is a kind of general expectation that the anti-bonding orbitals are more destabilized than the bonding ones. But it's not a proof, because it's just a proof for the simplest possible case.

So I'm done. And in the next lecture, we're going to use molecular orbital diagrams like this to describe a series of examples. Homonuclear diatomic molecules, heteronuclear AH, and AB. H is special, and this is more general. And what we'd like to be able to do is without a great deal of thought construct the molecular orbital diagram for basically any diatomic molecule using some insight.

Now, this also transfers to polyatomic molecules. And it's especially beautiful the way it transfers, because electronic structure is usually centered at a particular part of the molecule. And so, basically, you're reducing polyatomic molecules to a diatomic that you understand the bonding and anti-bonding.

OK, so I'll continue on Monday. And your problem set for this week is due on Monday. And the following set for the next week will also be due on Monday. Not that Monday. The following Monday. And that's the next to the last problem set. So you're inside of the home base. OK, have a good weekend.