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ROBERT FIELD: Last time I talked about LCAO-MO for diatomic molecules. And I didn't finish, but the important point was that this is a toy model. This is based on a little bit of extension from something which is not really a toy model, H₂ plus, to, basically, an interpretive framework that can be applied to, basically, all diatomic molecules.

And the logic is relatively simple. We know this one. We get the molecular orbitals for H₂ plus. There are basically two. There's a binding one and the anti-binding one. Of course, there's many more, but we don't care about them.

And then we go to H₂. And again, there's basically only two orbitals that we care about because the next higher principle quantum number has such high energy that we can just forget about them, because those states that derive from the higher principle quantum number are Rydberg states or complicated things, because they're at such high energy.

And then it's a very small step to go from hydrogen to the AH molecules, because, well, we've got the electronic structure for the A atom, which is complicated-- more complicated than hydrogen. But because hydrogen only can make sigma bonds, because the p orbitals in hydrogen are so high that it's a simpler picture and can easily be understood.

This is in all the textbooks, and it's more or less given to you as something to memorize. But there is a lot more to it than just memorization. And the important thing is that everything in LCAO-MO for diatomics is based on the periodic table. And the periodic table tells you about the ionization energies-- the periodicities of ionization energies.

And so we can say for any non-integer-- Well, if we know what the ionization energy from a particular state is, we can use that ionization energy to derive a non-integer principle quantum number. This is all empirical. And then use that empirical principle quantum number to get the size of the orbital.

And basically, the size is everything. Because everything is based on overlap, And the internuclear distance molecule is based on the relative sizes of the different atoms. And for

different electronic states of the atoms, these sizes are different, because they have the ionization energy from that level implicitly expressed.

So because you know about orbital sizes, and that the different atomic orbitals have different sizes, you can do an enormous amount as far as understanding the electronic structure of all diatomic molecules. Now, this-- when you have two states which have different energies-- We do something like this to describe the molecular orbitals that arise from them. That that's perturbation theory.

So the solid line is the dominant character. The dotted line is the admix character of the other orbital. And this is all qualitative, but you have these different atomic orbital energies. You know them from the periodic table, basically. And so you can say, yes. There's going to be two orbitals arriving, derived from these two states.

And one is polarized towards this atom. The other is polarized towards that atom. And so you get the shape of the orbital. And it's actually useful for saying, well, if I were to do chemistry, which end of this is electronegative, and which end is positive? Or which end of this would attach to a metal surface? Would it attach pointing into the surface or lying down?

And there's all sorts of insights, if you can draw these sorts of pictures. And this is what we do as physical chemists. We take the crudest model, and we say, OK. We understand the important features. And as we discover new, important features, we build them in, or we forget about them because they're too subtle.

And we're always looking for something where the crude picture doesn't work. And we then find the important thing that is needed. And for example, if you were to look at the molecular orbital diagram for C_2 , which is a perfectly legitimate gaseous molecule, you'll see that there's a little bit of ambiguity about which is the ground state.

And this is an important thing. And there was a big controversy about this that was settled by spectroscopy.

OK. So if you can build an intuitive picture for all diatomic molecules, you can also build an intuitive picture for what we could call chromophores. So there are a lot of molecules that are larger than diatomic molecules. But the electronic structure is mostly nothing, except a few atoms that are close to each other, where there's a double bond or there's something special.

And so if you can do LCAO-MO for diatomic molecules, you can also address electronic structure in much larger molecules, because it's really due to a few important atoms or several different groups of important atoms. And so the idea is, in here, enable you to talk about the electronic structure of almost anything.

And one of the things that we care about is spectroscopy. How do we learn about the structure of a molecule? And mostly, you learn about it from doing electronic spectroscopy. You do transitions between the ground state and some higher states. And you want to be able to predict what you are going to see.

And for example-- and I think you may hear about this a little bit more-- if you know the spectrum of nitrogen, it doesn't start absorbing until far into the vacuum UV. And then go one atom over-- the spectrum of oxygen. Well, that defines the vacuum UV. It starts to absorb around 200 nanometers.

And 2 and 1/2 billion years ago, oxygen started to enter into the atmosphere and profoundly changed life on Earth. Because with the vacuum UV radiation, nothing could live on the surface of land, because it would all be killed by this hard UV.

And so everything was underwater at the bottom of the ocean. But all of a sudden, when oxygen appeared, there was protection. And then there's additional protection farther out towards the visible from ozone. It's not such a good shield, but it absorbs between 200 and 350 nanometers. And it protects us, too. But the big thing is oxygen. And why should oxygen be so different from nitrogen? And maybe you should think about that.

OK. I should have mentioned the schedule up there. I'm going to give another lecture on perturbation theory-- one of my favorites, which I thought I wasn't going to get to give on Friday. And then Troy is going to give two lectures on quantum chemistry. And there's going to be significant lab experience. And you'll hear about that from the TAs. And so you will do real calculations. So LCAO-MO could be the organization structure for quantitative calculations. But quantitative calculations are usually huge basis sets, and you lose the LCAO completely.

One could take the results of such a calculation, and then project it onto a LCAO-MO picture. And that's generally what we do. We reduce experiments, we reduce theory, to something that we can intuit. And it's really important to have intuition.

OK. Huckel theory-- Huckel theory is another kind of non-rigorous theory. In fact, it's laughable

in its simplicity. And the idea is that even such a crude theory can make sense out of huge families of molecules and enable you to be quantitative about things without having to do a huge calculation.

Now, you almost always have to diagonalize a matrix. And because usually, in Huckel theory, you're dealing with more than two or three relevant orbitals, it's a big deal. I don't know whether you have experience with matrix diagonalization routines, but there are many of them. And you're going to have experience with them.

But the things you put into them have absolutely nothing to do with a real Hamiltonian. It's a make up picture. It's a picture based on, basically, two parameters-- alpha and beta. And I'll talk about this. And these are parameters that are agreed upon by international committee-- It's not a committee. But people say, OK. This is the value of alpha and beta that we're going to use to describe many problems.

But I just want to make sure you understand that Huckel theory is only a little bit more ridiculous than LCAO-MO theory. Because in LCAO-MO, you really have some semi-empirical sense of how big orbitals are. And once you know how big orbitals are, you know what's going on.

In this, you just have a couple of parameters that says, OK. These are the rules. Let's now apply that.

OK. I'm carrying around too much stuff.

So organic chemists are really wonderful, because they give you an abbreviated way of drawing a molecular structure. And almost everyone in this room is gifted in being able to visualize three-dimensional structures. Physical chemists tend not to be so gifted. But here is something where we don't have any hydrogens-- I mean, there are hydrogens, but they're implied. And we don't put carbons here. We just say, at every vertex, there is a carbon atom.

And so we consider these things. And every organic chemist knows, if I draw something like this, that either I was stupid and I drew something that was impossible or what the structure is.

OK. Now, this is a conjugated system. We have double bonds and single bonds. And that kind of thing is known to be unusually stable. And in order for it to work, it has to be planar. If you have a conjugated system which is not planar, then it's not as stable. So Huckel theory is based on the existence of unusual stability of conjugated systems.

And it can be extended to non-conjugated systems-- to non-planar systems-- and we have rules for how to do that. But the simple rules are, you start with a picture, and you can write down a Hamiltonian. And it's a toy model, but it's still something that the computer has to diagonalize.

So when we're doing a variational calculation expressed in matrix language-- We have a Hamiltonian matrix. We have eigenvectors, and we have eigenvalues. And we have the overlap matrix. And we have something where this is the alpha-- where, here, we can have non-orthonormal basis functions. And this makes them normalized.

So these are the orthonormalized basis functions or basis vectors. And this is the kind of equation we have to solve. It's the generalized eigenvalue equation. And we don't like this, because it doesn't have the simplicity of just a Hamiltonian, where we have matrix elements along the diagonal and somewhere else.

And the idea is, we want to take the secular determinate and make it 0 by adjusting values of the energy differences along the diagonal. But when we have this overlap matrix, it's complicated.

Now, there's a way of dealing with the generalized eigenvalue equations, but one way to deal with it is to say S is equal to the unit matrix. You can do anything you want.

And it's basically saying, there is no overlap between orbitals on adjacent atoms. We're going to neglect it, and then we're going to bring it back if we need it.

But it's a wonderful simplification, because it enables you to write a simple, effective Hamiltonian, which looks just like $H_c \alpha = E \alpha C \alpha$. OK. This, we know how to solve. And we can use the same procedure.

OK. So these are the rules. If we have a planar molecule, we can say there are p orbitals-- one on each carbon atom or one on each atom that's not hydrogen, which are perpendicular to the plane of the molecule. So easy orbitals.

And those are special. They give rise to π bonds. π bonds are bonds where there is one plane of symmetry containing the bond, And then there are p_x , and p_y , and s . And these give rise to σ bonds.

So we have pi bonds and sigma bonds. Never the twain shall meet. And we don't care about the sigma bonds, because anybody can make sigma bonds. But only the special, perpendicular-to-the-plane guys, which are responsible for the fact that the molecule likes to be planar.

And so we're only going to consider these p z orbitals-- one on each atom. So we don't care about no pi-sigma interactions. And we're going to neglect the sigma orbitals, because they take care of themselves.

And we can do anything we want. It's just a question of, if we make too many ridiculous assumptions, we'll get ridiculous results. And this has been time tested, and it gives pretty useful stuff. And it provides a framework for making arguments about molecular structure and molecular reactivity.

In organic chemistry you learn about resonance forms. And this is compatible with generating the resonance forms and saying, what is the relative importance? And what is the charge distribution, and bond strength, and everything like that? So it's really useful using the most primitive tools that organic chemists introduce at an early stage in your education.

And that's one of the reasons why a lot of people become organic chemists, because it's so beautiful.

OK. So our h_{ij} matrix-- So we have a bunch of matrix elements, and we say, OK. h_{ii} is equal to alpha. So every carbon atom has its alpha value. It's the same for all carbon atoms, regardless of who is nearby.

And we have h_{li} plus or minus 1 adjacent atoms, and it's beta. That's it. That's the whole ball game. And it's really a simple-- There's far less here than in LCAO-MO. But it's still a toy. Both are toy models, and they're both very useful

OK. And everything else which is not diagonal or off diagonal by 1-- 0. That's really convenient. And so you can draw the h matrix, regardless of what it looks like, as alpha, alpha, alpha, alpha, et cetera, along the diagonal, and beta, beta, beta, et cetera, beta, along the near diagonal. And if it's a ring, you have a beta here, here, and here.

So that's pretty simple. So we have $0s$, $0s$ -- so that it has a tri-diagonal structure with something up here and there. Never forget this thing here and there, which is present when you have a ring, and it's not present when you don't.

That's it. That's Huckel theory. It's just there. OK. And so now, things can be more complicated. So if we're not content with what we get from the really primitive theory, we can do something like saying, well, we can make beta be dependent on internuclear distance. If the molecule, for some reason, is constrained to have not equal bonds lengths.

So we can add an additional parameter-- some kind of reason for this beta to be dependent on r . But that's already getting sophisticated. And heteroatoms-- In other words, if you have a nitrogen instead of a carbon in a benzene-type ring, you can have-- So, well, nitrogen is different from carbon. It has a different-- In LCAO theory, the distance-- The ionization energy for nitrogen is different from carbon. It's larger.

And so heteroatoms can be included if you use a different value of alpha. And now, alpha and beta are both negative. Now, this is a little bit fraudulent. Yeah.

AUDIENCE: Do you also have to pick a new beta? Or--

ROBERT FIELD: Yes. But the main thing is alpha.

AUDIENCE: I see. Why is that?

ROBERT FIELD: Why is that? Because beta comes from overlap, even though we're neglecting overlap. And so the bond distances between normal and heteroatoms are not usually that different. But the thing is, you put what you need into the model.

And the first thing you do is, you solve the most simple model. And you say, this is not quite what I wanted. And so I allow a couple of extra degrees of freedom. And it's really instructive how these things work. But the thing is, you're not calculating the matrix element of a real operator.

It's all make believe. But it's really powerful, because what you're comparing is families of molecules. And the reality might be really complicated, but the complexity in each member of the family is pretty much the same. And what it's allowing you to see is, what are the differences?

It allows you to see the big picture. I love this. And in fact, at an early stage of my education, I thought Huckel theory was wonderful. And it was what got me interested in quantum mechanics. Because you normally see Huckel theory before you know anything about

quantum mechanics, because it's just a game.

OK So heteroatoms-- You can fiddle with alpha. Now, the ionization energies for carbon and nitrogen are not that different. I'm sorry. They're very different, but the effect on the alpha value in Huckel theory is very small. Well, so it is.

But the more electronegative or the higher the ionization energy, the alpha value becomes increasingly negative. Now, I was starting to say something is fraudulent, and I was distracted by a really good question. Alpha is on the diagonal.

And we know we can determine the sign of a diagonal element. And we know we can't determine the sign of an off-diagonal element. But we say that alpha and beta are both less than 0. And the reason for this is that, when you saw the secular equation, especially-- You get two eigenvalues-- one where you have minus beta and one where you have plus beta.

And so in a sense, beta is present, but it's just a sign choice. And since alpha and beta have to do with stability, we just say alpha is negative. We know that. And beta is chosen to be always negative. There's no, you could have had beta be positive.

And you could do all the theory. It's just a lot more complicated explaining all the cases.

All right. So let's continue with this. And so we can do heteroatoms. So if we have a non-planar system, we can say that beta is a function of the dihedral angle. We can put that in. We can do anything we want.

We have a molecule. We're trying to describe its properties relative to the normal members of the group, which are planar and no heteroatoms. And we can do stuff that will accommodate these interesting differences, which you can impose by you putting the molecule in a constrained environment or doing stuff that distorts the geometry.

So we do this. So when we do this, we get a Hamiltonian. We get the energies of the orbitals, and we get the eigenvector that corresponds to each energy.

And the total energy involves the sum over the energies of each of the occupied orbitals-- the number of electrons in that. And we can also get bond order and charge.

So sometimes, we want to know, what is the charge on each atom if the charge is going to be different from 0? Because that also controls chemistry. Negatively charged atoms are sought

out by certain classes of reactants. Anyway, so you get all this stuff.

And of course, some of it will require a little bit of patchwork, but you do this for your career. And you discover that there are certain things that I know how to handle. And I use my favorite parameters for it. And you get closer to the truth. And you always want to be surprised, because when the crude theory cannot be made consistent with observations, you know you did something special.

You have a molecule, which has a property which is unexpected, and we like that.

OK. So when you're doing quantum chemistry, there are five steps-- or when you're doing molecular orbital theory. And this is one of Troy's rules. We have a five-step procedure. And we define the atomic orbital basis set. And the basis set is one p z orbital per atom.

And so we can have a molecular orbital, which is the sum i equals 1 to n c_i $u_{p z i}$. So this is the p z orbital on the i -th atom. This is the coefficient for this particular linear combination.

OK. So we have a bunch of molecular orbitals. Next step-- compute h and s . But s is 0 because we made this ridiculous assumption. It's convenient. This is called the complete neglect of overlap. And we can do that. It's wrong. But when you include overlap, it leads to greater complexity of the calculation, and not much improvement in the results. And so we normally don't worry about the overlap.

So all we care about is this. And as I said, h has this structure of alpha, beta, beta-- tri-diagonal structure and maybe something up here. That's it. Then we diagonalize the Hamiltonian. And so this gives us the eigenvectors or eigenvalues-- the energies and eigenvectors associated with each orbital energy.

So we fill electrons into orbitals. Now, for benzene, what you would get-- Now, this is important. How many carbon atoms in benzene? Right. And how many orbitals will you get from six primitive orbitals? Right. And so there are six energy levels. And it happens that when you solve the secular equation, you get this pattern.

This is a problem where the number of nodal planes determines the order of energy. And so if you have benzene, you can imagine that the orbitals that you can have will be no nodes-- nodal planes-- one nodal plane. And you could have the nodal planes between the atoms or through atoms-- and two nodal planes or three. You can't have any more with six atoms.

And so you almost don't have to solve this secular equation at all. You can anticipate what the structure is going to be just by saying, no nodes, one node, two node, three node. And you can even anticipate double degeneracies, because if you have two nodal planes, you can put them through opposite bonds or through opposite atoms. And those are examples of the forms that you would deal with.

The only thing you can't do is to know what the order the energies are. But there are tricks for that, too. The tricks for that include-- The sum of the eigenvalues is equal to sum of the diagonal nodes. And so we know that the six orbital energies will sum to 0-- will sum to 6 alpha. The betas go away.

And there are other tricks that you can do, but generally, you solve the equation. You don't want to push your requirements for symmetry too far. So we end up doing that. And then stick diagrams-- We fill electrons into orbitals in energy order. And for benzene, there are six of them.

And so this is, then, the lowest energy state of benzene. This is called the independent electron approximation. They don't know about each other. This is illegal. But it's legal in a sense, if you have two electrons in every orbital, you have nothing but singlet states. The ground state is always going to be a singlet state unless you have something really weird going on-- like in O₂-- But that's not Huckel theory. But it's examinable.

OK. Why does oxygen have a triplet ground state? That's something that every textbook says. You got to know that. And of course, they don't really tell you anything more except something to memorize.

OK. So generally, you have two electrons in each orbital in singlets. Now, if you're going to do spectroscopy you would perhaps promote one of these guys to a higher state. And so you'll have singlets and triplets. But of course the only transition you would see would be a singlet-to-singlet transition. So you might as well forget about triplets. And you might as well forget about having to add [INAUDIBLE].

You can get away with murder, especially with Huckel theory. So we have a stick diagram. We fill electrons into the thing. And then we compute the energy of the many electron problem. And so let's just do this. And you've all seen this.

So we number the atoms. We have our symmetric structure. And psi mu is going to be sum

from i equals 1 to 6. C_i mu p z i. And c mu is c_1 mu c_2 mu to c_6 mu. These are the mixing coefficients.

Well, for benzene, it's pretty simple because you know that if you have no nodes and symmetry, all of these are going to be the same. And so if you put 1s here, you put a $1/\sqrt{6}$ out in front for normalization. And you can figure out the eigenvectors for benzene-- all of them-- just by counting the number of nodes. And that's useful, because if you know the eigenvectors, then you can show what the eigenvalue is by multiplying the original Hamiltonian by an eigenvalue.

So anyway, we have this. And then the Hamiltonian-- we have alpha, beta, and then 0s. And beta, alpha, beta, and then 0s, et cetera. And so we have this tri-diagonal structure. And because it's a ring, we have a beta here and here.

OK. So then, we ask our computer to diagonalize this, or we use clever tricks from linear algebra to find the eigenvalues, but I don't recommend it. I mean, the general problem is going to be something where you have to use a computer. So don't develop tricks unless you want to check to see whether you programmed the computer correctly.

And so when you do this, you get-- E_1 , the lowest energy, is alpha plus 2 beta. E_2 is alpha plus beta. And E_3 is alpha minus beta. I'm sorry. E_2 and e_3 are both this. And E_4 and e_5 are this. And e_6 is alpha minus 2 beta.

Now, we don't really care about these orbitals, because they don't put electrons in them. And so when you put the electrons in the orbitals, you get 2 for this, 2 for this, 2 for that. OK? And so we just calculate the sum of the energies. And we end up getting the energy levels for benzene. The ground state is going to be 2 alpha, plus 2 beta, plus 2 alpha, plus beta, plus 2 alpha, plus beta. Right?

So this gives you 6 alpha plus 8 beta.

Now, this-- You might have guessed it, but you didn't guess it. Your computer told you that. And the computer actually likes numbers rather than symbols. And so you actually obtain this simple structure from the computer-- requires a little bit of manipulation. But you still get 6 alpha plus 8 beta.

And you also get the eigenvectors. And that's the stuff that you know. So c_1 is $1/\sqrt{6}$. 1. 1. All of those. And c_2 is going to be something a little bit more complicated. We

can have the nodal plane going through atoms. And so if it goes through atom one, it's also going to go through atom four, and so we have 0 and 0, 1, 1, 1, 1.

And now, to figure out how to normalize that, we just-- 1 over square root of 4, and so on. We can figure these things out. C 3 is going to be an eigenvector. Now, instead of having the nodal plane going through atoms, it's going between atoms. And so instead of having any 0s, you're going to have something more complicated.

And now I can see that there is something in my notes which is subject to how you'd actually impose the symmetry. But suppose you have something like this-- 2, 1, minus 1, minus 2, minus 1, 1. So why did I use these numbers? Well, I had to have a nodal plane here between atoms two and three. And the corresponding guy will be-- Well, that should have been 2 at the bottom.

Let me just make sure I'm doing this right. No. I had a 2. OK. It's a 1. OK. And so the last 1 is here. So the sign change occurs twice. And those correspond to opposite bonds.

Why were there 2s? Well, the 2s are between two atoms that have 1s, and so it's going to have a larger eigenvector. And you can figure it out lots of ways. You can also say, well, every atom has to be used up. Yes.

AUDIENCE: So should there also be a sign change?

ROBERT FIELD: I can't--

AUDIENCE: Should there also be a sign change in c 2?

AUDIENCE: Yeah. In c 2 eigen c 2 6 should be [INAUDIBLE].

ROBERT FIELD: Did I screw up?

AUDIENCE: Yeah. No, not-- in c 2. Not c 3.

ROBERT FIELD: I'm sorry?

AUDIENCE: The previous one.

ROBERT FIELD: Oh, yeah. Yeah. So opposite sides. OK?

All right. It doesn't matter. The computer tells you. But sometimes you can approach the

problem very quickly, and just say, I know what the eigenvalues are going to be, and I have to normalize them.

But one of the things that you often do if you're trying to be smart and skip steps is to say, OK. We have six eigenvectors. And each of the atomic orbitals gets used up completely among the six eigenvectors. And I do that all the time, because it's a very useful way of making sure I haven't screwed up.

OK. So we get this, and that's perfectly OK. We don't know how significant it is, but say we had three of these-- three ethylenes-- I guess an organic chemist would just do that, right?

But anyway, if we had three of these, when you do this you get $2\alpha + 2\theta$. OK? So we get $6\alpha + 6\beta$. And α and β are both negative. And so the energy for three ethylenes-- did I screw up again?

AUDIENCE: How are those ethylenes arranged with one another?

ROBERT FIELD: They're separate. We could draw benzene. And so we could say, we have three isolated bonds. And since we don't care about the sigma structure, and no bonds are adjacent, you know that they're additive. And so we represent benzene. The primitive structure for benzene is three ethylenes. And benzene is 2 beta better.

AUDIENCE: Yeah.

ROBERT FIELD: That's the resonant stabilization. That's a great thing.

OK. So we get a resonant stabilization. And now, the more subtle and wonderful stuff is, we have these eigenvectors. And we have the energies. And we can do stuff with them. And one thing is bond order. And so we have a formula. The bond order between atoms i and j is equal to the sum for μ equals 1, including only the occupied orbitals, of $c_{i\mu} c_{j\mu}$.

So we have the new molecular orbitals, and we have the adjacent atoms. And this gives you the bond order. And so we can calculate the bond order. And we find that every bond is a pi bond order of $2/3$, which is neat, because the non-resonant structure says, three of the bonds have a pi bond order of 0, and 3 have a bond order of 1.

And so the average is $1/2$. And this is bigger than $1/2$. And it's uniform.

So you can do this, and you can say, OK. The 1, 2 bond order-- the 2, 3 bond order-- you do

the laborious calculation-- always get $2/3$.

Now, you could also calculate the charge on atom i . And that is, again, μ for the occupied orbitals. And that would be $c_i \mu c_i \mu$. And so for benzene, you would expect this to come out to be 0. And it does. So there is no charge.

Let me just make sure that that-- Well, there is an equal charge on each atom, whether it's 0 or $1/6$. That I haven't done. And I am a little uncertain about what this is going to come out to be. But they're going to be equal on every atom in benzene.

And so now, suppose, instead of benzene, you have amylin. Well, you can do stuff. And you could say, well, the amylin out here is going to affect the α value here a lot, and here less and less. And then you do the calculation. And you find when you do this calculation, you get unequal charges.

And you get the normal rules for ortho versus meta. And everything is great. And you also, when you do this, you can actually write resonance structures and you could calculate, well, what is the energy of that resonance structure-- in a Huckel-like theory.

So there are lots of things you can do in order to say, OK. We do Huckel theory to get this 0 in our picture. And then-- I'm way over time. And then we can add special effects, and we know how to parameterize them. And if we're close to being OK, we'll get results that correspond to experiment.

And this is so much better than you deserve, because it's all garbage. But it's empirically-calibrated garbage. And it's calibrated over an enormous number of molecules and a huge amount of experience. And that's good. That's what we do. OK. So I'll see you on Friday with some perturbation theory. One of my favorite problems, too. OK.