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PROFESSOR:

I like this lecture because the first half of my career was entirely devoted to the electronic structure of diatomic molecules. And this is how you make sense of diatomic molecules.

Now in 5.111, 5.112, one of the most exciting thing that attracts people to become chemistry majors is the global interpretation of the periodic table in terms of some simple ideas so that those simple ideas enable you to predict the important properties of all of the atoms. And that's a pretty exciting thing to feel like, yes, it all makes some sense. And then we go on to other topics in chemistry, and we forget about the fact that we think we understand the periodic table completely. We don't use that information.

And one thing that I've tried to do throughout my career is to take the simple insights into the periodic table, and explain molecular properties. And now, this is really a strange thing because we have computer programs that can calculate any of the properties-- any property you want-- of a small molecule. So why would we ever care about being able to predict the properties-- because we can calculate them? And the answer is we want to understand. We want to be able, without a computer, to say this is what we expect for a particular molecule not just a diatomic molecule. What are the things that control the bonding in molecules in general and the properties in molecules in general?

And if you can understand what happens in diatomic molecules, there are very few cases which would leave you at a loss for what will be the properties of this new molecule that you're looking at. Or how would you manipulate a molecule so that you can force it to go into the states that will expose the critical properties that you want? So it's this sort of part of a toolkit that any practicing physical chemist who's worried about spectra, molecular properties, electronic properties would have to master.

And this is really hard because, one, you have a computer-- you can generate the answers completely accurately. And two, you're smart MIT students. And you believe in the truth rather than estimating the truth. But I like to maintain that if you can estimate the truth and find out whether your estimates are wrong or right, that enables you to have confidence to deal with

other properties, other problems.

And so what I want to do today is to give a sense of how you begin to understand the electronic structure of simple molecules. And I want to tell you that a lot of the second-order or complicated patches you put on this simple picture are things that you develop and criticize throughout your career. You say, yeah, well, this works, but that doesn't.

And why doesn't it work? And that's what we do as physical chemists. We look for when the simple picture breaks. And we have our own private simple pictures which we're constantly trying to make better than anybody else's.

OK, so we have the periodic table. We know the properties of atoms. We know, especially, how the ionization energy is supposed to behave. We know how the low-lying electronic states are supposed to be ordered. Excuse me.

We know about orbital sizes. Everything is related to this idea of atomic-orbital energies and shielding. And it's all related to the hydrogen atom. What we got from the hydrogen atom was a framework for understanding electronic properties of atoms. And what we know about electronic properties of atoms should be important in explaining electronic properties of molecules.

So I want you to be able to make toy models, to draw pictures which are crude, but guiding, in your insights. And it's all based on what we saw. And you soon are going to have two lectures from Troy Van Voorhis, which will lead you to use some of the simple computer programs that enable you to calculate electronic property of anything.

OK, so we want to extend what we had for H_2^+ to be able to understand H_2 , AH , A_2 , and AB molecules. And each of these steps involve extensions of relatively simple ideas. And so let's begin.

OK, I told you that I believe the simplest explanation for bonding is when we have two atomic orbitals that overlap in the region where this overlap region can be attracted to both nuclei. Constructive interference causes the density in this special region-- the amplitude to be twice as large, the density to be four times as large. And that's a large, energetic effect.

And the amount of overlap is crucial. You can have too little if the atoms are too far apart-- no bond. You could have too much if the atoms are too close together.

OK, so we need to now look at cartoons of orbitals and learn about the names for these orbitals. So the simplest orbital is gerade-- sigma gerade NS orbital. OK, so "sigma" means there are no nodal planes containing the internuclear axis. "Gerade" means that in the body frame, it's even symmetry.

So we have $ns_A + ns_B$. And that looks like this. We can have an antibonding orbital. Again, we put the predominant atomic-orbital character in parentheses. And for heteronuclear molecules, we also put which atom is more important to that orbital.

And this will be just $ns_A - ns_B$. And that will look like this. And there is no overlap here. In fact, there is negative overlap. And that's an antibonding orbital. And you can say, if there's no overlap, well, then the actual picture will sort of look like this, where the region in the bonding region is actually depleted, and there's less there. And that's part of why it's antibonding. OK.

Now we can also make sigma g np orbitals. And np z-- "z" is the internuclear axis-- $A - B$ and $A + B$ -- well, that gives us something that looks like this-- plus, plus, minus, minus. And the minus sign is needed to turn this around. But this is overall gerade symmetry. And so everything is fine.

And then we can have sigma u star np. And that would just be the plus sign here. And that would be an antibonding orbital.

Now I put a star on these orbitals because when we don't have atomic symmetry, when we don't have g and u symmetry, we still use the star to imply antibonding. But in diatomic molecules, this is redundant. You should be able, just by looking at the orbital character or looking at a picture, to say, yes, it's a bonding orbital, and it's either g or u.

Then we have pi u np. And that would be-- well, let's do it the opposite order. So we'd like to have something that's bonding. So we have to have the phases right.

And that's ungerade because when you reflect through the center of the origin of coordinates, we go from plus to minus. So that's ungerade. But that's bonding. And that's a little trick because you start this think, from sigma, that ungerade is antibonding.

And finally, we have the pi g star np. And that would be plus, minus, minus, plus. And that's gerade.

OK, there are a couple other things that we know just from these pictures. And that is the p-

sigma orbital is much more directional than the s-sigma orbital. That's all you get in sigma for s.

And so the bonding interaction between p-sigma orbitals turns on at longer range than for s. So there's qualitative differences. And sometimes, you have a bond distance determined by favorable overlap between one pair of orbitals. And it makes things not so good for other orbitals.

So usually, you have a ground state. You figure out what the ground state of molecule is. And that tells you something about what the internuclear distance is.

And then you might go to excited states of the molecule or excited configurations. And these excited configurations-- well, if you're going to learn about a molecule, you've got to do spectroscopy. So if you go from the ground state to an excited state, and the internuclear distance of the ground state is wrong for the excited state, well, then, you're going to have a big change in geometry. You'll have Frank-Condon factors, which-- I haven't talked about Frank-Condon factors-- I will-- that say, OK, the transition is going to have a lot of vibrational structure. And it'll tell you all sorts of good stuff about that.

But the important thing is when you start looking at a molecule, you want to know what the ground state looks like and what transitions from the ground state ought to look like when you're ready to know how to use the simple structural information you're getting from these orbitals because there's no point doing an experiment if you don't have an idea about what the experiment will yield. That's what most people do when they do an experiment. They did the experiment because they thought it would yield something, and they wanted to be surprised because they'd like to show that maybe it didn't do what they were expecting.

OK, so we have pictures. And we have notation. And this notation is what is used by professional spectroscopies,

So we care about directionality. And we care about size of orbitals. And this is definitely something that you're empowered from 5.111, 5.112. I'll talk more about that too. How about right now?

OK, in thermodynamics, when we're concerned about the enthalpy of formation of a molecule, we have to set a 0 of enthalpy. And we set it as separated atoms in their most-stable state and energy, or enthalpy, is something where there is no natural 0. We wanted a 0 which is

convenient for all of our calculations and insights.

And so what we do is we say, OK, every particle that we're going to be looking at-- we're going to make a molecule out of two atoms, like A and B and AB star. So we have the energy of A plus electron B plus electron, or AB plus electron. That's a common 0 of energy. So we talk about orbital energies relative to this common 0.

Now in almost every textbook, the orbital diagrams are given to you. There's no discussion of, what's the 0 of energy? If you're going to know anything, you really want to be able to calculate or to say all of the actors in this game are acting in a way related to how far below this ionization energy they are because that determines their size. And the size determines the overlap. And bonding is related to overlap. OK, so we'll play that game.

So for H_2^+ , it was very simple. We just had the 1s at r equals infinity, and over here, the 1s orbital at r equals infinity. And then we solved the minimal-basis variational problem.

And we discovered that we had something like this, where this is the antibonding orbital. This is the bonding orbital. The antibonding orbital is more antibonding than the bonding orbital is bonding. And, of course, this energy difference depends on internuclear distance, also not often talked about. And so we have the starting point at r equals infinity for the separated atoms.

Now as we bring these atoms together, before there's any bonding at all, say, we have 1s on A. We make the internuclear distance smaller and smaller. And the bare nucleus of the other atom starts to penetrate into the-- so as you move the positively charged nucleus towards the static charge on the other atom, that's a favorable interaction. But there's a repulsion between the two nuclei.

And when the bare nucleus of one atom penetrates inside the charge distribution of the other, it sees less attraction and more repulsion. And so this is why you get a potential curve that looks like this. The repulsion occurs at too-short internuclear distance. And from the variational calculation, you can determine the value of equilibrium internuclear distance.

And so a lot of these diagrams are calculated at this particular internuclear distance. It's especially important because the repulsive states don't have a minimum. And so there is no particular internuclear distance that you care about so that if you want a simple picture, everything is calculated at that particular internuclear distance.

OK, so sometimes, you want to have a little bit more insight in this picture. And instead of drawing the starting point at infinite separation, you could say, well, let's schematically suggest what happens as you-- so at shorter internuclear distance, the separated atom energy increases a little bit. And that could be useful. But it complicates things, so I won't do that.

But often, we do like to know what happens as we bring particles together as opposed to starting at infinity and coming into the end point, which is the bond at the equilibrium internuclear distance. So you can put that insight in if you wish. So we know that this bonding interaction is smaller than the antibonding interaction.

OK, we can now go from H^{2+} to H_2 . And the first thing we know is when we go from H^{2+} to H_2 , we can put an electron into the same orbital but with opposite spin. And as a result, we don't have to worry about mysterious things, like overlap repulsion or poly-repulsion because we're putting electrons into different spin orbitals. And that's all you have to do.

If you try to put two electrons into the same spin orbital, that's really bad. And once we get beyond hydrogen-- hydrogen has this neat situation that there is no core. It's just the nuclei. But for anything other than hydrides or hydrogen, we have an inner core, which is filled with electrons of both spins.

So anytime you have an orbital that gets too close to the other atom, there is going to be this mysterious overlap repulsion. And that makes the inner wall of most potentials other than hydrogen extremely vertical. OK, so let me just-- oh, I know what I wanted to say, but I will get to that

When we go from H^{2+} to H_2 , we discover that the equilibrium in our internuclear distance decreases by approximately 30%. The vibrational frequency increases by 90%. The dissociation energy increases by about 70%.

These are big effects. They're not a factor of 2. Naively, if one electron gives a bond or gives some sort of a bonding interaction, two should give twice that much. But this is pretty close to twice that much. Even though that's only 30%, it's a big effect.

And it's because we're allowed to put an electron into an orbital which is bonding. And there is no magic-overlap repulsion. There is just the interelectronic-energy repulsion.

So our picture is-- we're chemists. We believe in bonds. The most important thing is bonds.

And in almost every situation, you want to conserve the number of bonds or know how much you have to pay for changing the number of bonds. That's the course. But we're more sophisticated.

Now in our picture for H_2^+ , we had an effective Hamiltonian or a variational calculation. I like to talk about effective Hamiltonians. But the crucial actors in the H_2^+ problem, or the overlap is a function R , the interaction energy as a function of R , and the orbital energy is a function of R . And these are the actors in almost all further calculations. You're going to want to either know these things or be able to estimate their sizes so you know the consequences.

And we know much of the consequences from H_2^+ . We know that as R decreases, the overlap increases, the increases, and the interaction energy between the two atoms increases. So these are the factors that we put into a calculation.

We know that there is a bonding region. And typically, we can say that the bonding region for H_2^+ and for any molecule is going to be roughly between the atomic-orbital radius and twice the atomic-orbital radius because we've got two atoms. And so they want to see it at twice that radius. And then as we get closer, we get bonding. And as we get too close, we get antibonding. And so this is a critical region.

Now we're ready to take the next few steps. So we want to do H_2^+ to H_2 to A_2 . And so the questions we ask is, how many electrons? That's easy. Feed the energy electrons into lowest MOs. Well, in order to do that, you need to know the energy order of the MOs.

We get a configuration, which is just a list of the number of electrons in each of the molecular orbitals. And these configurations have particular states. And for a diatomic molecule, we know the projection of the electron orbital-angular momentum on the other nuclear axis, λ , we know the spin. And sometimes, we know about this thing, ω , which is the projection of the spin, as well as the projection of the orbital-angular momentum.

And so we have a notation for electronic states, which will be $\lambda 2s + 1 \omega$. And so say we have a triplet. Well, this triplet will be $2s + 1$ is 3. And this is π , say. So the correct way to say that is not "3 π ." but "triplet π ." And we normally don't talk about that in any special notation.

So the splittings of the configurations for H_2^{--} we have the ground state. And that's $\sigma_g 1s^2$, and the lowest excited state, triplet $\sigma_u +$ and that's $\sigma_g 1s \sigma_u$.

So we have these pictures. And this is bound. This has got a bonding orbital and an antibonding orbital. This is a $\sigma_u 1s$. Sorry-- so antibonding. So this is repulsive. Or usually, it's repulsive at all internucleuses.

Then there are higher-energy orbitals that come from $2p$ -- $2p$ pi and $2p$ sigma. And they give rise to many, many states. But we know, for hydrogen, when we go from $1s$ to $2p$, we're at very, very high energy-- $3/4$ of a Rydberg. And that's an energy that's larger than any chemical bond we know.

So the excited states of H_2 are going to be a little bit weird because of this tremendous excitation energy. And because the excitation energy is so high, we're probably not prepared to understand what's going on up there. And in fact, terrible things happen up at high energy.

We get there are some curves that are double minima. There are all sorts of things. And they have to do with-- you could have $H^+ H^-$ ion-pair states. You can have H_2^+ plus electron-- those are Rydberg states as well as the normal valence states.

So normally, we don't want to worry about that. And there are two places we don't want to go without preparation. One is to very high excitation energy. And the other is to very large internuclear distance because things can happen. The weirdnesses are much more important when there is no core.

So since everything is dependent on R , we need to know how to estimate the internuclear distance. And we know, for an atomic orbital, the ionization energy is hc times the Rydberg constant over n squared. And we know that the average r for an orbital is a_0 times n squared over the charge.

And so if we want to relate the size of an orbital to something that we can measure, well, we can simply put in this equation for n squared here. And we get that the average size of an orbital will be a_0 , which is the Bohr radius of the hydrogen atom-- about half an angstrom-- times hcR . The Rydberg is 110,000 wave numbers-- and over z -- I'm sorry-- over l n .

So this ionization energy is measured. And so if you know the ionization energy, you know r . If you are talking about a molecular-orbital diagram, you have r and ionization energy on it. And so you can see how it would make everything relate to each other.

OK, let's do an example. Let's look at the NH molecule. This is not a stable molecule, but it's a

molecule that is important in some chemical reactions. It's easy to make an H by having, say, nitrogen-- N_2 -- and hydrogen and doing a discharge.

And so in order to be able to understand H, you start out with all of the orbital energies. So let's make a little table. We have H 1s. And we have its ionization energy. And its 13.6 electron volts.

We have H 2s and 2p for hydrogen. They're degenerate. And that's 3.4 electron volts-- for nitrogen, 1s.

This is an obscenely large energy. And so it's greater than 100 electron volts. We have N 2s, which is 18 electron volts. We have N 2p, which is 12 electron volts. And we're going to have, at the end, the ground state of NH, which turns out to be a triplet sigma, g minus state. And that's at 13.6 eV.

So one of the things you want to do is ask, OK, all my actors-- where are they below the ionization energy? And the next thing you do is you arrange things in energy order. And so the lowest one is this. And it's out of the picture altogether. The next lowest one is this.

And then we have two. And let's just say this is 3 to 4, and this is 4 to 3. They're roughly degenerate. That's what we're looking for because when the orbitals are degenerate, they have about the same energy. And we know from perturbation theory, if you want to have a mixture of two different things, you want the energy to not measure to be small.

So all the actors-- the simple stuff-- we know what their energies are. We know that if we have two things that have the same, or nearly the same, energy, they're going to be mixed. And so now, with this sort of an annotated table-- the last one is this guy-- we can write down the low-lying configurations. And we can say something about the nature of the molecular-orbital diagram. [INAUDIBLE]

But I stress the most important thing is something that's easily measured for atoms because what we want to do is build on what we think we know for the periodic table to have some sort of insight into molecular-periodic table, although it's a multidimensional periodic table. I know that's probably a stupid thing to say.

OK, so here's the molecular orbital diagram for NH. So over on this side, we have H^+ . Over this side, we have N^+ .

And we put the orbitals on-- OK, so here is minus 3.4, which is the hydrogen 2s or 2p. And down here, we have the hydrogen 1s. And that's at minus 13.6. And over here, we have the nitrogen 2p. And that's at minus 12. So what do we do?

And then down much farther below way down here, we have the nitrogen 1s. The nitrogen 2s. OK, how many electrons do we have? Well, before I do that-- so how many electrons are on nitrogen?

I mean, if you don't do that, you don't know the periodic table at all. How many? Did everybody see that?

Well, then I can't ask you. Yes, it's seven electrons and plus 1 for the hydrogen, right? So we're dealing with eight electrons. And so we're going to put eight electrons into orbitals.

And now on this diagram, basically, I have two orbitals that are roughly at the same energy. And so we know that all the action is going to be that. And so we can draw something like this and something like that.

And now, we use our perturbation ideas. And this guy is higher in energy. And so it's closer to this other orbital. So this one is dominantly nitrogen, and this one is dominantly hydrogen. Make this dotted.

OK, so we have two orbitals. This one is polarized towards nitrogen. And this one is polarized towards hydrogen.

And then there is another orbital here. This is 2p pi. Well, what about 2p pi? There is no pi orbital here. The lowest pi orbital is way up here. So this guy is nonbinding.

So we have a bonding orbital, a nonbonding orbital, and an antibonding orbital. And then up here, we have something that's so high energy, we might call it a Rydberg orbital or just something else.

OK, so now we start putting electrons into orbitals in orbital-order energy. So we have sigma nitrogen 1s squared. That's the lowest one. That's way down here. I erased it. It's at minus 100 electron volts.

And then we have nitrogen 2s. That's pretty far down too. And so these two-- we don't have any doubt. The electrons go into these sigma orbitals. And there's nobody nearby, and so

these are localized on the nitrogen atom.

We've got four more electrons to deal with. We have σ_{NH} σ_{NH} . Well, we'll call this σ .

We got two electrons there. And then we have-- so we got two electrons, two electrons in core orbitals. We have a bond. Then we have a nonbond. Yes.

AUDIENCE: How far apart in energy do the orbitals have to be such that you consider them non-attracted?

PROFESSOR: It's really up to you. I mean, at the lowest-- it's a question of how much detail you want to be honest about. There's always interaction. But the important thing is if the orbital energy is really low or stable, the orbitals are really compact.

And so at equally internuclear distance, which is determined by a bonding orbital, they're just out of play. So it's not 0. But you really care about big effects-- things that are worth, roughly, the energy of a tenth of a bond.

As you get more and more better at this, you could say, well, we'll worry about bonding effects that are worth less than a tenth of a bond or a typical bond. But you want to organize things in the order of how important they are, how careful you have to be, how many subtle effects you have to take into account. And so to avoid craziness, you want to say, I'm not going to worry about this because it's too small, or because their energy difference is too large.

And it's very important to be able to shed unnecessary factors until you're ready to deal with them. Or maybe you never will. OK, so that was a really great question.

All right, so we have the list of-- where did I put it? Oh, here it is. OK, so these are three filled orbitals. They give rise to a singlet σ .

But we have two electrons in a π orbital. And if you care about this stuff, you'll learn how to figure out what two electrons in a π orbital will give you. And they give you triplet σ minus g -- I'm sorry-- no g because it's a heteronuclear-- triplet σ minus singlet δ and singlet σ plus.

And this is actually much easier than for inorganic chemistry or for just figuring out the LS states of an atom because basically, we have σ , π , δ . And you can figure out, well, π^2 is going to give you this. π^3 is going to give you this again, except this-- it's

going to give you this again. So you there's a finite number of things that you don't have to work out the energy levels by an elaborate procedure. And so you can sort of memorize them because there's very few that you actually are going to deal with.

OK, so now Hund's rules apply to molecules. So what's the ground state of NH ? Triplet sigma minus.

So that's nice because you're going to be doing spectroscopy, and you're going to be starting with a molecule in a triplet state and you've got a pi bond. And so you know a typical internuclear distance for a pi bond, or you can figure it out. And we're only going to be seeing triplet states, and we're only going to be seeing triplet-sigma-minus states or triplet-pi states because of the selection rules.

Now I'm telling you this. You could learn that. These are extra things. You've got to know the most-important stuff.

So we have an intentionally naive primitive-molecular orbital diagram. OK, now-- my chance to say terrible things about textbooks.

Every one of you has seen the molecular-orbital diagram for this mystical A_2 molecule. Everybody's seen it. And it's presented either dishonestly or semihonestly with an asterisk. So let's just understand this.

Again we have the ionization energy. We have A^+ and A^+ . And we plot the energies. And naively, we say, OK, here's $2s$ -- same energy $2s$. And here is $2p$ -- $2p$ -- for atoms other than hydrogen, $2p$ is above $2s$.

And so we know, well, we can draw some kind of a diagram like this. So these are the sigma star $2s$ and sigma $2s$. No problem. And then we draw something like this for the p orbitals. And we have something like this. That makes sense.

Now, the lowest-energy orbital has to be the more directional p orbital. So this is going to be the p-sigma orbital. And so we'll have a sigma $2p$, a pi $2p$, a pi star $2p$, and a sigma star $2p$. That's what you get using common sense. And it's wrong.

And most of the textbooks say, well, if we have to correct this-- it turns out that the energy order of these two orbitals is frequently reversed. And most textbooks don't tell you why. They just say, well, this is what you would expect.

And the canonical molecular-orbital diagram for homonuclear diatomics has the pi below sigma except for oxygen and fluorine. Well, that's not something that builds confidence. And that's something you learned in 5.111, 5.112.

The energy gap between 2s and 2p depends on shielding. And so as you start out with lithium, 2s and 2p are-- lithium is more like hydrogen. So 2s and 2p are nearly degenerate.

When you get to fluorine, the energy gap between 2s and 2p is enormous because 2s shields 2p. And as a result, the-- well, the shielding arguments explain this energy gap. And it gets large because 2s is unshielded, and it really gets very stable, whereas 2p is increasingly affected by the shielding by s, and as a charge, increases the orbital energy.

OK, I thought I had a better explanation for it. But I do have one. It's just not handy.

And so what happens? Well, what happens, as you go from lithium, where this and this are close together, you have interaction between orbitals of the same symmetry.

Now the Hamiltonian is totally symmetric. Oh, my goodness. So because the Hamiltonian is totally symmetric, you can have interactions between orbitals of the same symmetry. And as a result, this guy gets pushed up. And this guy gets pushed up. And this guy gets pushed down.

But these are so far out of the picture you don't care. So it's really just the relative energies of these two. And it's all due to the relative energies of 2s and 2p.

And then you get the correct energy-level diagram. And you say, well, maybe as we went across the periodic table, there will be a switch. And there is a switch. And since I've lived most of my early life in CO and N₂ and O₂. I've encountered that. And I thought about it a lot.

OK so that's pretty much all I'm going to say about the molecular-orbital diagram. I think next lecture is on Huckel theory. OK.