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5.112 Principles of Chemical Science, Fall 2005  
Transcript – Lecture 27

At the end of last hour we had just gotten to the point of having developed the molecular orbital energy level diagram for the BH<sub>3</sub> molecule, this trigonal planar entity.

And I had not had time last hour to show you what these molecular orbitals look like in their calculated form.

And so, I am going to start off today by doing that and then will proceed to answer a quadrangle of questions that we can attach regarding diatomic molecules using molecular orbital theory.

Remember that the BH<sub>3</sub> MO problem is a seven orbital problem. And so, we will go through and just look at these seven molecular orbitals in ascending energy from the lowest energy on up.

This one is the lowest energy molecular orbital for BH<sub>3</sub> as calculated using a modern quantum chemical package.

And what you can see is that since we are indicating the phase of the wavefunction by color there is only one phase to be seen. This, of course, is a characteristic property of an s orbital. Remember that?

And what we have here, at the center of the molecule, is the 2s orbital on boron.

And in this molecular orbital theory effectively what is happening is that 2s orbital on boron is reaching out and simultaneously overlapping with the three 1s orbitals on each of the hydrogens. And the way that we have orthogonalized it and normalized it amounts to a single molecular orbital that can, if you will, house a pair of electrons in this orbital that is simultaneously bonding between boron and the three hydrogens.

You have one electron pair in here.

Two of the six electrons in the valence shell of this molecule are in this lowest lying, most tightly held, most electronegative molecular orbital. Let's look now at the next one.

You should be thinking in your mind just what was the next highest lying orbital that we had, and you will realize that this is an orbital formed from one of the boron p orbitals and a linear combination of two of the hydrogen wavefunctions.

And let's see if you can recognize it based on what we did last time.

Maybe I can reorient it to help in that regard. Here is a molecular orbital that can house a pair of electrons, one spin-up and one spin-down, and is simultaneously bonding from that boron to this hydrogen up here.

And then there is a nodal surface here that is coincident with the nodal surfaces of the boron 2px orbital using the same coordinate system that we were using last time.

And so, the wavefunction changes sign as you pass through the boron. And then the opposite phase lobe of the boron 2px orbital is able to overlap with these two hydrogens here. If you will remember, when I wrote down the normalization constants for this molecular orbital we had double the coefficient on the hydrogen up here as compared with the two hydrogens down here.

And they were opposite in sign.

And that leads to a really nice overlap, as you can see here. This is BH bonding here and BH bonding down here. And it involves that boron 2px orbital. One way you can think about this molecular orbital theory is that this 2px orbital on the central atom is reaching out with its intrinsic plus-minus phase combination that is intrinsic to a 2px orbital simultaneously reaching out and bonding with all three hydrogens in the only way that it can, being a 2px orbital.

And so, we created that linear combination with that idea in mind.

And then, if we go up one more in energy, strike that. Not one up more in energy but to the other orbital in the molecule that is at the same energy. What we will find is that we are involving now the 2py orbital.

And it will reach out and interact with hydrogens in the only way it can, given its intrinsic nodal properties as a  $2p_y$  orbital.

Remember that a  $2p_y$  orbital has the  $xz$  plane as a nodal surface. And there is a hydrogen up here on that  $xz$  plane, namely the one that lies on the plus  $x$ -axis. And because it lies on the intrinsic nodal surface of this  $2p_y$  orbital it can contribute nothing to this molecular orbital.

All we are seeing up here at the top is an arbitrary sized sphere just to show the location of that nucleus, the hydrogen nucleus that is on the plus  $x$ -axis.

And then here what you see is the  $2p_y$  orbital oriented along  $y$  and overlapping simultaneously with a plus  $1s$  wavefunction here and minus  $1s$  wavefunction here so that you see a beautiful bonding molecular orbital that is at the same energy as the one we just looked at.

And so, as you step up in energy, looking at the energy level diagram for  $BH_3$  from last time, that is what you see.

We have now six electrons in the molecule, two in this orbital and two each in the two orbitals we just looked at that provide the three  $BH$  bonds that we represent in the valence bond theory as electron pair bonds.

But this is a totally different way of looking at the electronic structure that is very appealing because it just takes advantage of the atomic orbital properties that you would calculate for your central atom.

Now, let's go up one more. The very next one I will skip showing to you for purposes of saving time here, but you know that the next orbital up is simply the  $2p_z$  orbital on the boron, which is our lowest unoccupied molecular orbital, as well as being an atomic orbital in this system and responsible for the Lewis acid characteristics of this species.

And one up above that, one higher in energy than the LUMO is the orbital that I did show you last time, the out-of-phase combination of the boron  $2s$  with the three hydrogens all with the same sign.

It is sort of a round nodal surface intersecting each of the  $BH$  bonds.

And then, finally, orbitals number six and seven are the antibonding counterparts to the ones that I just showed you involving boron's  $2p_x$  and  $2p_y$  wavefunctions.

Here is what these look like. And this one you will see involves the  $2p_x$  orbital. Here is our x-axis pointing up. And the blue lobe of  $2p_x$ , the positive lobe here, as you can see, has squished out and down.

These pictures can be a little bit more complicated than what we are used to looking at from just sketching it out on the board or the qualitative pictures that you sometimes see in your textbook.

But what we do find here that is the important feature is that as we go from the  $1s$  contribution on this hydrogen over here to the positive lobe of  $2p_x$  we are going through a nodal surface. And that is antibonding in character.

And you can see that this deformation of this lobe of the  $p$  orbital, of course, looks like a high energy type of phenomena.

And indeed it is. This is one of the two highest energy orbitals in the energy level diagram for the  $BH_3$  molecule. And then, similarly, here is the other lobe of the  $2p_x$  orbital, the minus lobe. And, as you try to go from it to the adjacent hydrogens, remember in the bonding one we were allowing this to overlap with the same sign on the hydrogens.

Now we have the opposite sign on the hydrogens so that we have a beautiful antibonding node indicated here and here between the minus phase lobe of  $2p_x$  and the adjacent hydrogens.

So, this antibonding orbital has lots of internuclear nodes. Nodes that appear between nuclei and indicate that we are not getting overlapped and bonding but rather we are getting a high frequency orbital that is likewise high in energy.

Finally, I will show you the counterpart to this one that involves  $2p_y$ .

It is a little easier to understand from inspecting it.

And it also evinces the internuclear nodes that you would expect for an antibonding molecular orbital.

And I am orienting so that you will be able to understand it with reference to our coordinate system as introduced last time.

And so, you have the boron and the hydrogen along x up here. Here is our  $2p_y$ . It is sort of bending away from these two hydrogens whose wavefunctions have opposite sign to the lobes that are directed into their vicinity.

You can see that we have here a nodal surface between boron and this hydrogen wherein the bonding counterpart that we looked at had the same sign and a nice bond.

And then over here, once again, the mirror image.

So, this is one of our final orbitals in looking at the  $BH_3$  energy level diagram. It is the case that if you start to put electrons into antibonding orbitals they will cancel the bonding properties of the bonding counterparts.

And we will explore that in quite a bit more detail here shortly.

Let me leave that up there for now and tell you what quadrangle of problems it is that I hope to answer for you today using more MO theory ideas.

First of these will be why  $HE_2$  is so stable?

And so, today's lecture is predominantly devoted to diatomic molecules. And  $HE_2$  will be the first of these. Let's make this unstable. Let's do stable here in just a moment, but first let's say next why does  $O_2$  have unpaired electrons?

Certainly, if we draw the valence bond picture for  $O_2$ , like that, it does not give us any indication that this diatomic molecule would have unpaired electrons.

And so, we are going to see how MO theory can shed some light on this issue. And then the final two questions that I will fold into one line here given the way I am using up space on this board is why is  $N_2$  so stable--

--and CO poison?

MO theory can shed very clear light on all of these questions.

And so, that is what we will work on for the rest of the hour.

In MO theory, there are a couple things you should keep in mind when trying to grasp all the subtleties of a given energy level diagram with which you may be confronted in your textbook or on an exam or just through reading papers in the Journal of the American Chemical Society, wherever you may find these.

You should keep in mind that, number one, interaction is strong.

That is when atomic orbitals interact to form molecular orbitals the AO interaction is strong--

--when there is good spatial overlap.

Overlap is a central concept in molecular orbital theory. The idea is that if you have atoms that are far apart from each other in space then their wavefunctions have dropped off exponentially and are not interacting much and there is not good overlap.

But when orbitals are close in space and if their orbitals are directed in space toward one another then there may be overlap that leads to good bonding.

And also I can echo this first part, AO interaction is strong when, and say two, AOs are close in energy.

When I talk about where atomic orbitals are in energy, I am going to really want you to think about your periodic table and the properties that appear with periodicity and are organized and collated in the Periodic Table.

We are going to be talking about properties like electronegativity as it relates to the energy.

And I will get to that a little bit on the next board, but let's first make a small MO diagram here. And this will be a diagram that we may use both for H<sub>2</sub> or He<sub>2</sub>. This is the simplest of all MO diagrams and one with which you should be quite familiar.

We have a bonding molecular orbital at low-end energy.

And notice that if this is a 1s orbital over here and this is a 1s orbital over here for H<sub>2</sub> or He<sub>2</sub> systems then, when these come together and bond, here are your two nuclei.

And here is a probability density isosurface that I am drawing around that shows in-phase combination of those two 1s orbitals merging with each other giving good overlap and the interacting AOs being of the same energy.

Because the H<sub>2</sub> and He<sub>2</sub> molecules have such symmetry we have a good bonding orbital. And then, up here, we must find there to be an internuclear node in that corresponding antibonding orbital.

And so, it will look something like this.

And, therefore, I am going to associate with this high-lying orbital an asterisk to indicate the antibonding character, the presence of this internuclear node, the change of sign as we go from one nucleus to the other, the absence of bonding character.

Here we have the buildup of electron density in the internuclear region, electrons being stabilized by being held simultaneously by more than one nucleus that is positively charged.

And here, the exact inverse of that, constructive interference and destructive interference in the H<sub>2</sub> or He<sub>2</sub> systems. And then we can ask how many electrons do we have to put into the diagram?

If it is the H<sub>2</sub> case then, to figure out the bond order--

--what we do is populate the diagram according to the same kind of Aufbau principle that you would for generating the energy level diagram for an atom.

And taking into account things like Hund's rule.

If it is H<sub>2</sub>, we have two electrons that we can put in, which in here with a posing spin like that. That is our bonding molecular orbital. We have two bonding electrons.

Zero antibonding electrons divided by two equals a bond order of one. We have an H-H single bond in the case of the H<sub>2</sub> molecule.

But if we have He<sub>2</sub> then in the He<sub>2</sub> system we have two more electrons, and the only place they can go is up here in the antibonding molecular orbital.



We have two bonding minus two antibonding over two is equal to zero for a bond order of zero. And so, the idea is that if two HE atoms collide with each other, when they do so their orbitals may overlap and give rise to bonding.

But, simultaneously you get antibonding.

And the net bond order is zero, and so HE<sub>2</sub> is not bound but these atoms just bounce off each other. There is no stabilization. And you can certainly understand that if we were in the middle somewhere, as we would be if we had HE<sub>2</sub> plus missing one electron up here, then our bond order would be one-half.

It is going to get a lot more complicated than this, but this you have to know because this is a really nice starting point for thinking about bonding in all kinds of scenarios where you may need to consider it.

And so, let's look at some periodic properties. This will be with reference, again, to energy.

And I am interested in how some of the properties of the atoms vary as we go across the Periodic Table, lithium to beryllium to boron to carbon to nitrogen to oxygen and over to fluorine.

And I will stop there. We won't worry about any more of the noble gases today.

As we go from left to right, one of the things that you know from your study of the Periodic Table is that electronegativity increases.

This increases from left to right across the Periodic Table in concert with increasing  $z$ .

That is the increasing atomic number.

That is the increasing number of positively charged protons in our nucleus. As we go across, each time we are adding more protons to that nucleus. The nucleus is becoming more and more positively charged as we go across.

And an important consequence of that has to do with the fact that  $s$  orbitals don't have a node at the nucleus.

Whereas, p orbitals do. Since these elements are in the so-called p block of our Periodic Table, well, lithium in the s block, but we will consider the properties all the way across.

And the energy issue up here that I am going to be concerned with is the energy of the atomic 2s versus 2p orbitals as we go from left to right across the Period Table systematically adding to the number of protons in our nucleus in a way that does not affect 2s orbitals the same way that it affects 2p orbitals.

It turns out that by the time we get over to fluorine where we have essentially our most electronegative element, the 2s orbital has sunk to a very low energy.

And the 2p orbital has gone down in energy as well, but just not by nearly as much.

And so, it is nearly an isotonic function as we go across. 2p is decreasing in energy in response to this increased  $z$ , but not as much as 2s is decreasing in energy having to do with the fact that 2s electrons see much more of the nucleus than 2p electrons do because 2s electrons don't have a node there.

They spend a lot more time in close to the nucleus than do your 2p electrons.

This has a really important influence on that set of diatomic molecule MO theory problems, eight orbital problems that we call homo or heteronuclear diatomic molecules of these elements.

And that has to do with the fact that in between nitrogen and oxygen a fundamental change takes place in the energy level diagram.

And that change that results from the atomic structure of the elements ends up with the result that the MO diagram is much easier to draw for oxygen O<sub>2</sub> and fluorine F<sub>2</sub> than it is for the earlier ones.

And it is much easier to understand for O<sub>2</sub> and F<sub>2</sub> than it is for N<sub>2</sub>, C<sub>2</sub>, B<sub>2</sub>, Be<sub>2</sub>, Li<sub>2</sub>.

So, let's just see what that means.

First of all, when we are going to draw an energy level diagram for a diatomic molecule, if it is a homonuclear diatomic molecule, meaning

the two atoms that are going to be bonded together are the same, that means that the atomic orbitals for the contributing atoms are the same.

Here, on the left, what I am drawing is, let's say, an F or an O atom. We have the 2s and the 2p x-y-z. That is four of the eight orbitals in our problem.

And then over here we have the other identical F or O atom with its 2p x-y-z and 2s orbitals at exactly the same energy as for the counterpart over here.

So, this is another F or O atom. And then we are going to ask how can these atomic orbitals combine to give molecular orbitals in these diatomic molecules?

This is unlike the BH<sub>3</sub> problem because there is no atom at the center of gravity of our system, but the ideas are the same.

And the ideas are very much the same as what we have here for H<sub>2</sub> where also we could make molecular orbitals despite the fact that there was no atom at the center of our system. We can pretend that there is and we can use that pretend atom to identify what linear combinations we should make.

A simpler way to do it, at this point, would be to say that our molecule has the two nuclei oriented along the z-axis.

And then you have x and y perpendicular to z. And so, if we take this choice of coordinate system that the molecule is oriented along z, the two nuclei lie one on plus z, one on minus z.

Then we can immediately classify our atomic orbitals as being either sigma or pi with respect to the z-axis.

I will say AO is sigma or pi with respect to z, which is the molecular axis.

And remember what that means in terms of the nodal properties. If something is sigma with respect to z that means if you view it down z it will look like a cylinder.

It will look like a sphere actually. It will be cylindrically symmetric about the z-axis. If it is sigma then, if you are viewing down z, you see that.

That could be either an s orbital or it could be a pz orbital.

They would look the same if you were viewing right down z. And then pi, viewing down z, would look like this. And that would be a px or a py orbital perpendicular to the z-axis.

And this would be an s orbital or a pz orbital.

What I can say right away is that we can separate out the molecular orbitals that we are going to form from these atomic orbitals into their sigma or pi characteristics relative to the z-axis. And because we are in the O or F atom case, very far on the right-hand side the Periodic Table we have a large gap.

This gap is large.

We can make the approximation that this 2s orbital here, which could in principle form a sigma bond with this 2pz orbital over here, that would be an interaction looking like that.

That that does not occur.

Because remember here I said you get strong interaction when the interacting AOs are close in energy. When you are talking about these very electronegative elements, the s manifold of orbitals is very well separated in energy from the p manifold.

That leads to simplicity in the case of the diagram that we are about to draw.

Because we say that this interacts with this in a sigma fashion giving rise to bonding and antibonding interactions that look exactly like what we have drawn over there.

I will draw the bonding orbital here. Actually, the antibonding orbital here and the bonding orbital here. And I will show the parentage of this molecular orbitals in this way.

And you will recognize that this is our in-phase combination and this is our out-of-phase combination analogous to the H<sub>2</sub> problem.

This is like the H<sub>2</sub> problem built into the F<sub>2</sub> or the O<sub>2</sub> problem. And next what we find is that we can also make a sigma bond by interaction of p<sub>z</sub> with p<sub>z</sub>. This is going to be a nice strong directed bonding interaction that will look like this.

You see we have overlap here in the center, a nice strong bonding interaction in the center with 2p<sub>z</sub> orbitals that are directed at each other.

And this is a sigma bond because you view that down z it is going to look like a round thing.

You are not going to see any nodal surfaces. And then it has up here a corresponding antibonding orbital right there.

So far I have--

--two pair-wise combinations that give us two sigma bonding orbitals and two sigma star antibonding orbitals.

So, that is pretty straightforward. And, once again, I can say that we have the H<sub>2</sub> problem built into this energy level diagram twice with the s interactions, with the p<sub>z</sub> interactions.

The only thing I have left is to do my p<sub>x</sub> and p<sub>y</sub> interactions. And we can make a pair of pi bonds and a pair of pi anti-bonds that corresponds to those pi bonds.

This one is pi. This one is pi star.

And what do they look like? Well, they look like side-to-side bonds between pairs of p orbitals. This is just like what I showed you for the ethylene molecule. The pi bond, in fact, has this nice overlap on one side and up here on the other.

There is your pi bond.

And you have one of those that lie in the xz plane and one of those that lie in the yz plane. You have two of them, and they are at equal energy here. And then up here, what does the pi star look like? Well, the same, except we turn around one of the p orbitals introducing a nodal surface like that.

And we have two of those.

And here is our nodal surface. Now it is an internuclear, between the nuclei nodal surface indicating antibonding character there. That is the easy case because s and p are very well separated.

What you can see, though, is that type of interaction of a 2s on our left atom with a p<sub>z</sub> on the right atom might start to become important as you are over here in this part of the diagram where s and p are pretty close together in energy.

And that is what happens, in fact.

And that is what happens as soon as you go to the left of oxygen and to nitrogen or anything lighter than nitrogen. Suddenly you cannot ignore interactions of s on one side with p on the other.

And so, I am going to draw here the diagram that you would use, say, for N<sub>2</sub>.

And, for simplicity, I am just going to draw the middle part. This part here in the middle is that which corresponds to the molecule. This one is what you would use for O<sub>2</sub> or F<sub>2</sub>.

And let's just go ahead and draw that diagram for the molecule.

This one would be this set of energy levels corresponding to, for example, N<sub>2</sub>. And we have increasing energy on the vertical axis. We are going to find that again we have a sigma and a sigma star.

And then the difference comes right here where we find that as we go up in energy we next get to our pi bonds.

And then the next sigma orbital is slightly higher in energy than the pi system rather than slightly lower in energy.

And then we will encounter up here our pi star. And then, finally, that highest in energy sigma star.

This switch, this sigma going up relative to that pi is really a consequence of all of the sigma orbitals being responsive to the value of the electronegativity of the 2s orbital of the atom.

You can really almost consider the pi system independent from the sigma.

These four sigma orbitals, sigma, sigma star, sigma, sigma star, I can call them one sigma, two, three, four, just to show you that we have, in ascending order, four orbitals of sigma symmetry. That whole manifold, when you can start mixing a little bit of very low energy s into it, sinks down relative to pi.

In the case over here we are basically pulling down the four sigma orbitals relative to pi.

And here, because our s orbitals are higher in energy relative to our p orbitals, they go up a little bit and bumps three sigma up over pi. And what it means is that these orbitals are not so simple anymore.

Any one of them is a linear combination of four atomic orbitals.

This orbital here, one sigma, will not look like it looks in the H<sub>2</sub> problem anymore. This one sigma will have some p mixed into it. And so, one way we can represent that through a simple drawing is like this.

You see the difference between that sigma bonding orbital and the one up there?

We have some extra little nodes in here that are an inherent characteristic of the contribution of 2p<sub>z</sub> orbitals into this.

This is a linear combination of the 2s and the 2p<sub>z</sub> orbitals on the two atoms we have. There are four atomic orbitals that go in with different coefficients to these different parts of the sigma manifold.

And then up here, the other bonding orbital, we can draw it this way.

And this molecular orbital, this one here, three sigma has diminished bonding character in between the two nuclei and enhanced character on the outside.

The part of the p orbital that is contributing to it that points away from the other atom.

And so, while this has bonding character, it also has what we might think of as lone pair characteristics.

In MO theory some orbitals are not that simple. They might be at the same time a little bit bonding and a little bit lone pair in character. Let's look at a couple of orbitals like that briefly.

And here I have done this for the C<sub>2</sub> molecule.

I have done the calculation for C<sub>2</sub>, so now we are over here on the left-hand side of that dividing line where s and p are a big closer together. And I am opening up this orbital, this one down here.

It is a little more complicated than the way I drew it on the board, but what you should be able to see is--

Think back now to the first orbital I showed you today, which was the lowest lying orbital in the BH<sub>3</sub> molecule.

You remember, no matter which way we turned it, we only saw blue, which was the positive wavefunction. It looked like an s orbital everywhere. It had the same sign everywhere and you could not see any nodal properties.

Well, that would be true also for this one down here in the case of O<sub>2</sub> or F<sub>2</sub> because it is not mixing in p character.

Because the atomic s and p orbitals are so far away in energy. But now, when they are closer in energy, this orbital down here, the s over here sees the p over here and they mix in, and vice versa.

And, if I turn this around, what you are going to see are these little negative lobes here that I am indicating that are mixing in. But this is hugely bonding orbital still because look at how much of the orbital is centered in the region between the nuclei.

This is a very strongly bonding orbital in this system.

Let's now visualize the three sigma, the third sigma symmetry orbital as we ascend in energy. And it will look hopefully something like what I drew here. There it is.

You see this is a sigma orbital, because as we look down the z-axis it looks just round.



But it certainly has a lot of p orbital character because as we go from outside the molecule through the nucleus we get a change in sign. And then there is overlap in here, but the amount of the overlap in here is small compared to the amount of this lobe out here that is just nonbonding in character because it is pointing out into space.

It is like a lone pair of electrons at the same time as it is a bonding orbital.

If this molecule actually had enough electrons to fill up through three sigma and no higher than you would recognize that this orbital that we are looking at would be the highest occupied molecular orbital.

And it would be responsible for the basicity and the nucleophilicity of the molecule.

Because any Lewis acid that came in would want to come in on the z-axis to interact with this lone pair electron density out there.

So, that is how our three sigma orbital now looks when we are on the left side of that red dotted line to the lighter elements. I will leave that up there for a moment while we consider a couple of interesting points.

One of the things that you will often be asked to do is to write down the configuration.

And I want to finish these two questions here of O<sub>2</sub>, why does it have unpaired electrons? In the case of O<sub>2</sub>, we are over on this diagram, we have 12 valence electrons.

We can go two, four, six, eight, ten and then 11 and 12, two electrons up here in the pi star manifold.

We are completely filled up through pi. And then we have a half-filled pi star with 12 electrons populating the O<sub>2</sub> diagram.

Let's represent that this way. We have our one sigma with two electrons in. We have our second sigma which is antibonding with two electrons.

Then we have our third sigma with two electrons. And then, as we go up in energy, the next is our first pi orbital bonding.

That accommodates four electrons. And then we have next our second pi type orbital. It is antibonding and has two electrons in it. And then all the other orbitals are empty so I won't indicate them.

This is the configuration for the O<sub>2</sub> molecule.

That means, we come back over here, by Hund's rule of maximum multiplicity we have two spin-up electrons in the O<sub>2</sub> molecule with all these other orbitals down here being filled. That configuration that I wrote down for the O<sub>2</sub> molecule over there is a very shorthand way of representing the MO energy level diagram.

Because I started here at the lowest energy and I went up in energy like this.

And what you can see is sigma star cancels sigma so no bonding there. We have here three electron pairs in bonding orbitals, sigma and 2pi, but we have two electrons that are unpaired electrons responsible for the paramagnetism of the O<sub>2</sub> molecule that cancel some of the bonding down here.

When we want to write that down in terms of our bond order convention, we have six bonding electrons minus two antibonding electrons over two, which is going to be equal to a bond order of two.

That is our bond order for O<sub>2</sub>. While the bond order is what we expect to find based on that valence bond representation of O<sub>2</sub> up there, what we find out is that the representation of O<sub>2</sub> up there in the valence bond terminology would not tell us that the molecule should actually have two electrons that are not paired in the molecule.

That it should have paramagnetism due to the lack of pairing up of all the electrons, spin pairing in the molecule.

And it has to do with this high symmetry of the O<sub>2</sub> molecule. And it cannot distort from high symmetry because it has just two atoms. It has very few degrees of freedom. It cannot bend or something to get those electrons to pair up, and so they are unpaired.

And that is why dioxygen has unpaired electrons. And then, if we go to nitrogen, the order that we write these things down in is a little different because the energy level diagram is different because now s and p are closer together.

And what we have is one sigma with two electrons, or two sigma star with two electrons. And then next we have our one pi with its four electrons.

And then next we have our three sigma with its two electrons.

And that is it. We have two less electrons in the system than we do in O<sub>2</sub>. That is N<sub>2</sub>. And our bond order now is three. That is in accord with our Lewis structure of N<sub>2</sub>, but it is a triple bond.

And it is a triple bond in a molecule that is completely non-polar. And it is one of the strongest chemical bonds known. That triple bond is worth about 226 kilocalories per mole.

And it makes N<sub>2</sub> a very fascinating molecule.

And, of course, it is the major constituent of our atmosphere. And it is very inert due to the stability associated with having this diagram populated up all through the bonding orbitals and then no more antibonding electrons present in the system.

So, that is pretty interesting. And given the time, I think I will leave you after the following.

I just want to show you one more picture as a prelude to where I will start next time. And that has to do with what happens when the two atoms that are bonding are different.

Let's look at the three sigma orbital for the carbon monoxide molecule. It would look like it does for N<sub>2</sub>. It is the same number of electrons. But look here. It is very asymmetric.

And that has to do with the fact that carbon and oxygen have very different electronegativity.

And so, this highest occupied molecular orbital for carbon monoxide, again, an eight orbital problem. And a ten electron system is one where we have a larger coefficient on the lone pair piece that is on the carbon atom of the molecule.

And I will start off with this next time, but that is one of two reasons why CO is a poison.

Have a nice weekend.