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CATHERINE DRENNAN: If you haven't clicked in yet, please pay attention to the clicker question, and I'll give you a little bit more time to click in. And I'll give you a 10-second warning. All right. Let's just go ahead and take 10 more seconds.

All right. Does someone want to say how they got this one right? Anyone willing to say how they got it right? We have a American Chemical Society, whatever these are called that hang around your neck and clip things to them. Yes. There's the word. No? Oh, there we go.

AUDIENCE: Thank you. So this molecule is the phosphorus has five valence electrons and then each hydrogen has three so it's per total of eight. So it has three bonding and then one lone pair, which makes it a tetrahedral, but then the lone pair pushed the other bond, so it's less than 109.5 degrees.

CATHERINE DRENNAN: Excellent. Yeah. So I see that some people just decided that there were three things bound to it. And so then they decided either 120 or less than 120, but you really need to do the Lewis structure and see how many lone pairs there are first. So once you do the Lewis structure, then you figure out the parent geometry, Sn forces sum of tetrahedral system. All right. So more practice on these coming up.

All right. So we're continuing on now with molecular orbital theory, and we started the course talking about atomic structure and then we talked about atomic orbitals or wave functions. And then we moved on to bonding, that atoms can come together and bond and talked about the structure of molecules, and now we're going to molecular orbitals. And then we'll also talk more about the structure of molecules based on those molecular orbitals on Wednesday.

So we're really coming all the way around, we're using a lot of the ideas that you've seen before, but now we're applying them to molecules. And then, to me, this is really an exciting part. I love getting up to the molecules and talking about structures and molecules and how orbitals really play a role in those properties that molecules have. And then, to me, the really exciting-- I like reactions.

So after we finish with the structures, we're going to talk more about how molecules react. And so on Friday, we're going to be starting that, reactions of molecules, and getting into thermodynamics. So we're sort of winding our way away from orbitals for a while. We will come back to d orbitals around Thanksgiving time, but we'll have a long time before that where we're talking about reactions. So we're about to do a transition in the type of material.

But before we do that, more orbitals. But these are super cool because these are molecular orbitals. So we're going to talk today about MO theory, MO for molecular orbitals. So molecular orbital theory presents the idea that these valence electrons are really going to be delocalized around these molecules and not just sitting on individual atoms. So to think about this electron delocalization, we need to think about molecular orbitals.

Molecular orbitals, as we've learned, another word for orbital is also wave functions. Wave functions are orbitals. Orbitals are wave functions. You need to consider the wavelike properties of electrons to think about where the electrons are going to be, what is their probability density, how are they going to be arranged with respect to the nucleus.

And so when we take atomic orbitals and we bring them together as atoms come together to form bonds, atomic orbitals come together to form molecular orbitals. So we're going to be adding superimposing, atomic orbitals to form these molecular orbitals. And this is called a linear combination of atomic orbitals, or LCAO. And so we're going to bring those atomic orbitals together and create molecular orbitals. And we're going to create two types of molecular orbitals. We're going to create bonding and antibonding.

And some basic math principles apply here, and that is that you can create N molecular orbitals from N atomic orbitals. All right. So that's really the basis of molecular orbital theory, and now let's apply it to our friends, the s orbitals.

All right. So we're going to think about really simple molecules, bringing together two atoms that are identical with each other and what happens to their s orbitals when this happens. So first we'll talk about bonding orbitals.

So bonding orbitals, again, arise from this linear combination of atomic orbitals, the LCAO. And if it's a bonding orbital, it's going to arise from constructive interference. So we talked before about the properties of waves, and one of the great properties of waves is that they can constructively interfere, destructively interfere. And orbitals are wave functions so they can

constructively interfere and destructively interfere. Bonding orbitals are generated by the constructive interference.

So let's look at two atomic orbitals. And so here we have an orbital. The nucleus is in the middle. It's a little dot. It's a nucleus. And these two atomic orbitals are going to come together. There's going to be a bonding event. And so we have a 1s orbital from atom a and a 1s orbital from atom b, and they're going to come together, and they're going to form a molecular orbital, an ab molecular orbital, and this is called sigma 1s.

So a sigma orbital is symmetric around the bond axis, so the bond axis here would be just a vertical, a line between these two nuclei here. And so this molecular orbital is symmetric around that bond axis. There are no nodal planes for something that is symmetric. There are no nodal planes for our s orbitals, and so there's none for the molecular orbital either. And we can also write this as $1s_a$ plus $1s_b$.

So the atomic orbital from $1s_a$, the atomic orbital $1s_b$ coming together to form sigma orbital $1s$. That is a bonding orbital because it's constructive interference. It's a bonding MO, or molecular orbital.

So now let's consider the wavelike properties and think about these atomic orbitals coming together as waves in what is happening. So here we have the same equation up here. We're bringing together $1s_a$ and $1s_b$, but now let's think about this as a wave function. So there is an amplitude associated with the wave function for $1s_a$, and there is an amplitude associated with the wave function for $1s_b$.

These wave functions come together. Here is one nuclei, here's the other nuclei. And for a bonding orbital, it will be constructive interference, and so the amplitude where these atomic wave functions overlap will be increased when you have constructive interference. So our sigma 1s now has increased amplitude between these two nuclei due to that constructive interference.

So an increased amplitude between these two nuclei, again, this is the bonding axis-- here is one nuclei, here is another-- so an increased amplitude here corresponds to an increased or enhanced probability density. Remember our wave function squared is probability density. It suggests the likelihood of finding an electron in a certain region of volume and if it's enhanced by this constructive interference. So if that probability density is enhanced, you have a greater chance of finding an electron between these two nuclei, which will be attracted by both nuclei.

So now why don't you tell me what you think is going to happen to an electron that is in this region of constructive interference, this increased area of probability density. OK, 10 more seconds. Interesting. OK. So we should have probably not put up the answer there and re-pole.

Yes. So here, if we have an electron that's attracted to both nuclei, then we want to think about whether that's going to be lower or higher in energy than something in an atomic orbital. So if it's attracted to both, it's going to be more stably bound to those, it will be harder to remove that electron, which means that it's lower down in energy. And so we should look at that, and we're going to.

So the answer is it should be lower energy, more stable, harder to remove that electron. It's in a sweet spot. It has two positively-charged nuclei, and it's hanging out right in the middle. It's very happy. It's going to be more stable, and that means lower in energy.

All right. So let's take a look at that. So the electron is lower in energy, and the bonding orbital energy is also going to be decreased compared to the atomic orbitals, and that has to be true if that's where the electron is. So let's look at the atomic orbital from a and the atomic orbital from b. And now, I'm going to put the bonding orbital at a lower energy level. First, I was going to put the electrons on, and now, I'm going to put the orbital at a lower energy.

So remember, this is increasing energy here, so the atomic orbitals would be up here, whereas the molecular orbital is down here. The molecular bonding orbital will be lower in energy. And now we'll put our electrons there. So we have one electron up here and one here, and so when they come together, we're going to have two electrons in this molecular orbital.

So when you have these two electrons and they both occupy the bonding orbital, and this is the case for H₂, each H atom is bringing one electron, H₂ has these two electrons, and that's going to make H₂ more stable. And we saw that before that to associate the H₂ bonds, you have to add energy into the system. H₂ is more stable than free H plus H.

So when you bring atomic orbitals together and you have constructive interference, an increased probability of electrons between those two nuclei, that's a sweet spot. Those electrons are going to be very happy there, and that will result in a more stable, lower energy structure. That's bonding. But whenever there is a positive event like this, there's always a negative event because that's just how life works. So we have bonding orbitals, but we also

have antibonding orbitals.

So antibonding arise from the linear combination of atomic orbitals, LCAO, through destructive interference. So here these are going to be destructively interfering, and that will generate a molecular orbital that is an antibonding orbital. So here are our little nuclei again, and this antibonding orbital is called σ_{1s}^* .

So we can write an equation for this as $1s_a - 1s_b = \sigma_{1s}^*$. That is an antibonding molecular orbital. And let's just think about how this kind of shape arises considering the wavelike properties of these atomic orbitals. So I'm going to now move this equation up to the top. And now, I have my $1s_a$ here, my $1s_b$ here, and now it's destructive interference.

So we have opposite phase of the wave function. And we'll put up a wave function there. Now, the next one has the opposite phase, so they're going to destructively interfere. There is overlap over here, but when you have destructive interference, then the amplitude is going to decrease.

So now, when we consider this destructive interference between these two orbitals, you see that you have what arises between them. Instead of enhanced probability of finding an electron, you actually get a node. So you have decreased amplitude translates to decreased probability density between these two nuclei-- one here, one here-- and that results in a node between the two nuclei.

So in the antibonding orbital, there is a much lower probability that it will be in this sweet spot between the two nuclei that have this nice, positive charge for it's little negative charge, so there's pretty much no shot at being in that nice, sweet spot. And so what that ends up meaning is that an electron and an antibonding orbital is pretty much excluded from that internuclear region, that region between those two nuclei, and that results in a molecular orbital that has higher energy than the atomic orbital. There's just no chance of being in that wonderful spot. It's really very sad for the poor electron that has to occupy an antibonding orbital.

So now, let's put this on our energy scale. So we'll go back to our energy scale. And we saw before that when we had $1s_a$ and $1s_b$ and you had a σ_{1s} , a bonding orbital, that was lower in energy. Electrons that occupy it are more stable compared to their positions in the atomic orbital, but we also now have an antibonding orbital from destructive interference

between the wave functions of the atomic orbitals, and that's higher in energy. And so that's up here.

So this is what our diagram is going to look like that brings two atomic orbitals together to create two molecular orbitals. So the antibonding orbital up here is raised in energy by the same amount that the bonding energy is lowered. And so that gives rise to this diagram. And importantly, as I mentioned, we have N atomic orbitals forming N molecular orbitals. So if we have two atomic orbitals, we generate two molecular orbitals, one is bonding, lower in energy, and one is antibonding, higher in energy.

All right. So let's take a look at some examples. So always start with hydrogen. So hydrogen has how many electrons? One hydrogen, hydrogen atom.

AUDIENCE: One.

CATHERINE DRENNAN: One. So we have two hydrogen atoms, and so we have two $1s$ orbitals, $1s_a$, $1s_b$. And now where do we want to put our electrons? In the highest energy possible, lower energy? Where do we want to put them?

AUDIENCE: Lower.

CATHERINE DRENNAN: Always start with lower energy. So we're going to put them down here. And so this is now the MO diagram for H_2 . And we can write the electron configuration for the MO diagram, which you'll note is a different electron configuration than you were writing when you were looking at the periodic table because now we're not writing it in terms of $1s^2$, $2s^2$, we're writing it in terms of molecular orbitals.

And there are some of these on the problem set, and I tried to indicate example to make sure you know what kind of electron configurations we're talking about. So for MO diagrams, when it says electron configuration we're talking about where the electrons are with respect to the molecular orbitals. So the answer to this would be $\sigma 1s^2$. There are two electrons in the molecular orbital, $\sigma 1s$. Good.

So that means that you can do the same thing for dihelium, and that's a clicker question. So let's just take 10 more seconds. OK, you can vote. All right. So does someone want to tell me-- that is correct-- what's number two for? For hydrogen. What about number three, what was wrong there?

AUDIENCE: [INAUDIBLE].

CATHERINE DRENNAN: OK, everyone's doing really well. Yeah. So all of the electrons were parallel in there, and what does that violate? What would be true in that case?

AUDIENCE: [INAUDIBLE].

CATHERINE DRENNAN: Yeah. And so they'd have the same four principle quantum numbers. This is not allowed. So that one's not good. And what's wrong with four?

AUDIENCE: [INAUDIBLE].

CATHERINE DRENNAN: Yeah, star was on the bottom. So they were flipped around. Antibonding was lower in energy. Great. So we'll just put those in over here, and so we had two electrons. Helium brings two. So two went into the bonding, and two went into the antibonding with opposite spins. And we have the bonding, lower energy; antibonding, higher energy.

All right. So then we can put in the electron configuration here, and we have $\sigma 1s^2$, $\sigma^* 1s^2$, so that's the electron configuration. Now interestingly, you see, you have two at lower energy and two at higher energy, so there's no net loss or gain in energy of H_2 compared to just two helium atoms. And so that raises the question, does helium 2 exist?

So what would molecular orbital theory tell you about whether it exists, and it would actually predict that it does not exist. And the way that molecular orbital theory gives you these predictions is through the calculation of something called bond order. So bond order is half of the number of bonding electrons minus the number of antibonding electrons.

So let's just write out what the bond order for helium would be. So helium 2, our dihelium molecule. So we have a bond order equals $1/2$. There's always $1/2$. And now, the number of bonding electrons, so how many bonding electrons do we have for helium?

AUDIENCE: Two.

CATHERINE DRENNAN: Two. How many antibonding electrons do we have for dihelium?

DRENNAN:

AUDIENCE: Two

CATHERINE Two. And can someone do this math for me?

DRENNAN:

AUDIENCE: Zero.

CATHERINE Zero. Right. So that would suggest a bond order of 0, which means no bond. And let's just

DRENNAN: compare that to hydrogen, H₂, which should have a bond order equal to 1/2. It's always a 1/2. In the hydrogen, how many bonding electrons did we have?

AUDIENCE: Two.

CATHERINE We had two. How many antibonding electrons did we have?

DRENNAN:

AUDIENCE: Zero.

CATHERINE Zero. And the math? Bond order is?

DRENNAN:

AUDIENCE: 1.

CATHERINE 1. So that means 1 bond or a single bond. So MO theory would predict that dihelium, has no bond, i.e. it's not really a molecule without a bond, but H₂ should exist. So let's take a look at what experiment tells us, and it does exist, but only really not that much.

DRENNAN:

So it was not discovered until 1993, which for some of you might seem like quite a long time ago, but since we've been mostly talking about discoveries that were made in the 1800s, it took a long time before someone could prove that dihelium existed. And if we look at the bond association energy for H₂, 0.01, and compare that to H₂, 432, dihelium really doesn't exist very much. 0 is a much better approximation of its bond than 1 would be. It really is not a very good molecule. So I would call this a win for molecular orbital theory. It correctly predicts that our helium 2 is not going to be a very good molecule, but H₂ will be a good molecule, and that works.

All right. Now, let's consider 2s. So 2s orbitals are analogous to 1s except that you have to remember that they're bigger. So we have our 1s and our 2s, but for the purposes of this, it doesn't really matter. So let's look at a diagram now that has 1s and 2s.

So we have lithium. So how many electrons does lithium have?

AUDIENCE: Three.

CATHERINE DRENNAN: Yep. So we'll put on lithium, dilithium. We'll put on lithiums has two in 1s and one in 2s, and so we have one lithium here and one lithium over here. And our 1s orbitals are going to be lower energy, so they're down here. Our 2s orbitals are higher in energy. So that goes for both the atomic and the molecular orbitals that are generated.

So bringing together 1s with 1s, we get sigma 1s and also sigma star 1s. And so we can start putting our electrons in. We're going to start with the lowest energy and move on up. So we have four electrons that we need to put in, so we fill up everything here. And now we go up to our 2s. The 2s orbitals will generate sigma 2s and sigma 2s star. We have two electrons, so they both can go down here.

So here is what our MO diagram looks like. We can write out the electron configuration again, based on this diagram. So we have two electrons in sigma 1s, so we have a 2 there. We have two electrons in sigma 1s star, our antibonding orbital, and we have two electrons in sigma 2s. And now we can calculate the bond order, which is another clicker question.

OK, just 10 more seconds. Excellent. 84%. So if we do out the math here, we always have our 1/2. We have four bonding electrons. We have two down here and two up here. We have two antibonding electrons in our sigma 1s star, and so that gives us a bond order of 1. And in fact, the dissociation energy does suggest there is a bond. It's not a great bond. It's 105 kilojoules per mole, not necessarily enough to power a starship, but still this molecule does exist.

All right. So let's look at beryllium now, do another example. So how many electrons is beryllium going to have? It will have four. So we'll put those up. Now, we're going to start with our lowest energy orbital, and we're going to put some in the antibonding as well. And then we'll do this, and then we'll do that. And we filled up everything. And so we can write out our configuration.

We have two in our sigma 1s orbital. We have two in our sigma 1s star. We have two in our sigma 2s, and two in our sigma 2s star antibonding orbital there. And now there are two different ways that I can calculate the bond order here, and we'll do both of them and show you that they come out the same way.

One way that we can calculate this is to consider all electrons. So if we consider all electrons, our bond order, and that's often just said B.O., is 1/2 of our bonding. And now we can count up

both the 1s and the 2s. So how many bonding electrons do we have? We should have four, so we have two here, two here, so four. How many antibonding? Also four, so that suggest a bond order of 0.

Or we could just consider our valence electrons, so that would be the electrons in 2s, and if we do that, bond order equals $1/2$. It's always a $1/2$, so how many valence electrons do we have in bonding orbitals? Two. How many in antibonding orbitals? Two. And that gives the answer of 0.

So it should always work unless you do something very strange. You should be able to do it both ways and get the same answer. So if this is a complicated problem, you might want to only consider the valence electrons. In fact, on a test, you may only be asked to draw the molecular orbital diagrams for the valence electrons, and you don't have to do the other ones. So that should work both ways.

And we get a bond order of 0, and in fact, the dissociation energy is only 9 kilojoules per mole. It's a little stronger than dihelium, but this is an exceedingly weak molecule. So when you have the same number of electrons and bonding as antibonding, it doesn't lead to a very strong molecule.

All right. That's the orbitals. Now, it's time for molecules that have p orbitals as well. So in this case, now I have my p orbital and another p orbital. And we have our nuclei in the middle, and we're going to bring these together, and we will have constructive interference. And so here we're bringing together $2p_x$ of a and $2p_x$ of b or $2p_y$ of a and $2p_y$ of b.

So just x and y we're considering right now. And if we bring those together with constructive interference, then we're going to form a bonding orbital that has enhanced probability density in both cases and nodal plane along the bond axis because we had nodal planes along there to begin with. So if we think about this and we have both of these, we're bringing them together and they're going to interfere constructively, enhance probability density here, enhance probability density down here, but we still have our nodal plane because we started out with one.

And so if we have a nodal plane, this cannot be a sigma orbital. It has to be a pi orbital, because sigma orbitals are not going to have a nodal plane along the bonding axis. All right. So we could generate π_{2p_x} or π_{2p_y} this way. So a pi orbital is a molecular orbital that has a nodal plane through the bond axis or maybe I should say along the bond axis, so here is

our nodal plane right through the bond axis.

We can also have antibonding, which means destructive interference. So now, I'm going to be subtracting one of these from one of these, and I'm going to get something that looks like this, and it will be $\pi 2p_x$ star or $\pi 2p_y$ star, and it will have two nodal planes. So let's look at this. So this is destructive interference. I'm subtracting one of these from one of these, so the phase has to change. So I'm going to change the phase on one of them and then bring them together.

Now, we're not going to have that awesome, constructive interference increased probability density. These are negatively interacting with each other. And this generates a nodal plane between the molecules. They really look much more like this now, so we have still our nodal plane through the bond. We had that before. We're always going to have that. But now we have an additional nodal plane between the nuclei.

So in one case, we have enhanced density, probability density again. And the other case, in antibonding, we have another nodal plane. All right. So now, let's look at what happens to the energies of these π orbitals. And the diagrams that I'm about to show you, we're only talking about p_x and p_y now. We have for the moment forgotten $2p_z$.

So these diagrams are rated I for incomplete. Warning to the viewer, people come to me and go where are the $2p_z$? Yes, they're not in these diagrams, but when you're asked for a complete diagram, you will always have to put those orbitals in. And in fact, completing these diagrams could be a question you get later.

But for now, we're going to have $2p_z$ here, but it's not forming a molecular orbital in this diagram. This diagram is, thus, incomplete, but we're going to start simple and build more complicated. So only $2p$ orbitals first, and then we'll add the third one. Because this compound doesn't actually need that orbital, so we're good for now.

All right. So we have moved on to the first element that has a p electron in a p orbital. We have boron, and we have two of them. So now I dropped off $1s$ to simplify this. Now, we just have our valence electrons, so it's a good thing we can calculate bond order just using our valence electrons.

All right. So we have two in $2s$ and one in $2p_x$ or $2p_y$. I could have put it in either place. So let's put in where they would go. So we have $2s$ orbitals. They'll go into bonding sigma $2s$ first, then

into antibonding, sigma 2s star, and now we have p electrons, and we're going to put them into our pi orbitals, our molecular orbitals.

I'll put one in, and where am I going to put the other one? Am I going to put it next to it or over here? What do you think?

AUDIENCE: [INAUDIBLE].

CATHERINE DRENNAN: Yeah. So we're going to do that because, again, when you're going to sit on a bus, you want to have if they're degenerate in energy levels as they are here, you're always going to put one electron in each orbital of the same energy first before you pair them up, and they'll have parallel spins. So we're reviewing things we learned before. I love doing that.

So now, let's see what our electron configuration is, and this is just the valence electron configuration. We're simplifying. We're not going to consider the 1s orbital, and we can write this down. So we have two electrons in sigma 2s, and we have two electrons in sigma 2s star, our antibonding orbital, and we have one in pi 2px and one in pi 2py. And I can put a 1 or not put a 1. If I don't put anything, for a 1, 1 is assumed.

And we can calculate our bond order as well. So we have 1/2, and again, we're just using our valence electrons, but that's OK. We have four now who are bonding, two down here, two up here, these are bonding orbitals, and we have two that are antibonding. And notice for our pi orbitals, this is what we saw before bonding are lower in energy, antibonding are higher in energy.

With the bonding orbitals, we had constructive interference, enhanced probability of the electrons near the nuclei, and so that's lower in energy. But in our antibonding ones, we have a nodal plane in between our nuclei. So we don't have any probability that electrons are right in between there because there's a nodal plane, so those are higher in energy.

So here is our B2 diagram. So now let's try the same thing for carbon, C2, and that is a clicker question. All right. Let's just take 10 more seconds. So let's take a look at that over here. The easiest thing to do to answer this question was to fill in the diagram in your handout. And so if you did that, you would have put two down here and you would have put two up here. Then you would have put one here, one there, another one there, and another one there.

So now we have used these up, and so our configuration is sigma 2s 2, sigma star 2, pi 2px 2, pi 2py 2. And the bond order is 1/2. There are six bonding electrons-- 1, 2, 3, 4, 5, 6-- and two

antibonding electrons, and so that adds up to a bond order of 2.

And so sometimes on a test, they'll be a simple question what is the bond order, but to get there you have to draw your whole molecular orbital diagram and figure out how many bonding and how many antibonding, so these are not really that fast questions. And it's nice. Sometimes we give you like a little space, and you see this whole little molecular orbital diagram fit in there to answer the question.

All right. So let's just compare these two diagrams for a minute. So in both cases, we had 2s orbitals, two atomic orbitals for 2s, and they both generated two molecular orbitals, a bonding and an antibonding. The bonding is lower in energy, and the antibonding is higher in energy. We also had two 2px atomic orbitals. They generated 2 pi 2 px orbitals, one bonding, one antibonding.

And the same for our two atomic orbitals for 2 py. We had two of those, and they generated one lower energy bonding, pi, bonding and one pi star antibonding. So you always have N atomic orbitals generating N molecular orbitals.

So the stability of the resulting molecules in these cases depend on how many of the electrons are bonding, how many are in energy lower as a result of formation of the molecule, and how many are at higher energy as a result of formation of the molecule. And if the net result are more electrons in lower energy, more electrons in bonding orbitals, then that molecule is more stable. If there's a very slight or no difference, then that's not a very stable molecule.

So now let's just compare these two and think about which of these is going to be more stable. So we have our configurations again. So in the case of B2, how many electrons are in lower energy or bonding orbitals?

AUDIENCE: [INAUDIBLE].

CATHERINE DRENNAN: Yeah, we have four-- 1, 2, 3, 4. How many in higher?

AUDIENCE: Two.

CATHERINE DRENNAN: Two. Up here. For carbon, we had six-- 1, 2, 3, 4, 5, 6-- two in higher. And so the bond order here was 1, the bond order here was 2. Which is more stable? Higher dissociation energy, which one do you think?

AUDIENCE: [INAUDIBLE].

CATHERINE DRENNAN: Carbon. Right. Has a bond order of two. It has more electrons in lower energy orbitals. So it cannot really well out of this bonding deal, and the dissociation energy for B₂, 289, whereas, for C₂, 599. So when molecules come together such that more of the electrons are in lower energy or bonding orbitals, you form a nice, stable molecule. When molecules come together such that more of their electrons are in antibonding or higher energy, that's not a happy molecule.

So I'll just and with one way to think about this. In this cartoon molecular, break up lines, sometimes two atoms just have an incompatible number of valence electrons. And there are just too many-- just here this molecule saying, I'm sorry. Too many of your electrons are in my antibonding regions. I don't know how many times we've all heard that, but it's time to dissociate, but our atomic orbitals, well, they can still be friends.

OK. See you on Wednesday.

Take a look at the clicker question. All right. Let's just take 10 more seconds.

All right. Let's just go through this one. So this is a review of where we were last time. So the correct answer is 1. So sigma orbitals are cylindrically symmetrical. Let's quiet down a minute. You can hear the answer. So this one is true.

The second one is not true. A bond order of zero doesn't mean that you just have antibonding orbitals. Whenever you bring together two atomic orbitals, you have to make two molecular orbitals. So it isn't that sometimes you make bonding orbitals and sometimes you make antibonding orbitals. Every time you bring together two atomic orbitals, you make two molecular orbitals, one that's lower in energy, and that's the bonding orbital, and one that's higher in energy, and that's the antibonding orbital.

So that is not what that means. A bond order of zero means that you have equal numbers of electrons in your bonding and antibonding orbitals. So there's no net stabilization due to the formation of these bonds. So here bonding occurs when you bring together two atomic orbitals to make two molecular orbitals that are both of lower energy.

No. Every time you make the two orbitals, one is lower energy, one is higher that energy. You can't make two that are both lower in energy. And bond order of 1 means constructive

interference is generated at one bonding orbital. That's not what a bond order of 1 is.

And again, every time you generate a bonding orbital, you generate an antibonding orbital.

And 1 means that you have twice as many electrons in your bonding orbitals as antibonding orbitals because the formula is $\frac{1}{2}$ the number of bonding minus antibonding. But that's good, and it's important to remember that sigma orbitals are symmetric around the bond axis.

All right. So we had these diagrams for boron and carbon, just talking about the interactions of the p_x and p_y , and so we had forgotten about our p_z . And you can't do that on a test. You get into trouble, so I'm always telling people for these two handouts, you must include the molecular orbitals that are derived from p to z .

So on a test, you need to put them even if they're empty. Even if they don't have anything in them, they need to be part of your molecular orbital diagram. We didn't have them in the diagram because we hadn't talked about them yet, so now we're going to talk about them.

So two p_z orbitals, again, this is on Monday's handout. You have this linear combination of atomic orbitals. And all are p orbitals. They all look the same as each other, they're just different in orientation. You have one along x , one along y , one along z , but they're the same. So now we're going to bring our two p_z orbitals together, and we're going to do it along the bonding axis.

So we've defined this as the bonding axis in the class, so we'll bring them together, and they'll be constructive interference with our bonding orbitals. There's always constructive interference that generates bonding orbitals. And so we're going to create an enhanced amplitude as the wave functions come together, and it's going to be cylindrically symmetric. So what type of orbital do you think this is going to be, sigma or pi?

AUDIENCE: Sigma.

CATHERINE DRENNAN: It'll be sigma because it's cylindrically symmetric. So we do not have any bonding plane along the bond axis, and it's symmetric around. And we have enhanced probability density, and we have the wave function squared enhanced probability of having an electron between the two nuclei. And so this is a sigma $2p_z$. So p orbitals can form sigma molecular orbitals.

So we do have nodes passing through our nuclei. Here are our nuclei again. We do have them. They were here before in our p orbitals. There's the nodal plane in our p orbitals, but we

do not have, in this case, a node along the bond axis.

So that is our bonding. So whenever you generate a bonding orbital, which is going to be lower energy, we're going to have our increased amplitude between the nuclei, again, our increased probability density and therefore, lower energy. So whenever you have constructive interference generating a molecular orbital of lower energy, you got to create something of higher energy. That's just how life works. So we also are going to have antibonding orbitals, which are generated by destructive interference. And again, these orbitals can be thought about as wave functions, and a property of waves is that they constructively interfere and destructively interfere.

So now we can subtract our two orbitals, which we're going to switch the sign and they're going to be out of phase. So they'll destructively interfere, and that's going to look like this. So now, you're going to generate a nodal plane between the two nuclei, but it's still symmetric around the bond axis. So this is a sigma $2p_z$ star, so it's an antibonding orbital.

So again, it's sigma, so it's still cylindrically symmetrical with no nodal plane along that bond axis, but you do have a new nodal plane that's generated. So nodes pass, again, through the nuclei, but also now between these two orbitals. So we have a new nodal plane that's generated that's between these nuclei, and that's a result of destructive interference. Generates that nodal plane.

You have decreased probability density for an electron being found there. And so that poor electron is shut out of that sweet spot. The electrons like to be between those two nuclei where they have the two positive charges of the nuclei and then their little negative charge, and they can sit right there and be very happy in a low-energy state. But here there's really lower probability density, lower likelihood the electron will be found here, and that generates a molecular orbital that's antibonding or higher in energy.

All right. So now, we have to go back to our MO diagrams and figure out where to put these new molecular orbitals onto our nice diagrams. And it's not as simple as it was before because where we put these new sigma $2p_z$ molecular orbitals depends on what z is. So it depends on the value of z .

So if z is less than the magic number of 8, then we have our pi $2p_x$ and $2p_y$ orbitals are lower in energy than our sigma $2p_z$ molecular orbital. But if we are equal to or greater than 8, then the sigma $2p_z$ orbital is lower energy than the pi $2p_x$ and $2p_y$. So less than 8, pi is first. It's

lower in energy as you go up your energy scale. And if z is equal to or greater than 8, pi is second and sigma is first.

So how are you going to remember this? There could be many different ways one can remember it, but I'll tell you how I remember it. And my life revolves around my daughter and my dog. And so at Thanksgiving, we always have the question, can I eat pie first?

So if you are under the age of 8, you always want your pie first. So if z is less than 8, pi comes first. Pi is lower in energy and sigma is higher. However, when you mature to the grand age of 9, say, or 10, if you were a kid, 10 is like the oldest you can possibly imagine being, very mature. And you can eat your Thanksgiving dinner and wait for pie.

So that is how I would remember it, under 8 pi is first, equal to 8 or greater, you can wait till after dinner to have your pie, pi comes second. Note that the ordering of the antibonding orbitals is the same, so all you have to remember is down here depends on z , is pi first or is pi second?

So let's take a look at an example. Let's look at our friend molecular oxygen that has a z equal to 8. So oxygen is at the old, mature age of 8, and so it's going to have its sigma 2pz first. It can wait for its pi orbitals until later. So let's start putting in our electrons.

So we have each oxygen making up molecular oxygen, or O₂. Brings two 2s orbitals to the Thanksgiving dinner table, and two of them go down in energy into the bonding sigma 2s orbital and two go into our antibonding, sigma star 2s orbital. Now, we have four electrons in our atomic pz orbitals, four from each molecule, so we need to put all of those in.

So we always start with the lowest energy orbital. So we'll put two in there, then we'll go up. We have two more here, two more here. We'll put them in singly with their spins parallel, and then we'll pair them up in the lowest energy orbitals. And then we have two more left, so we're going to have to put those up in our antibonding orbitals. So they go into pi 2px and pi 2py star orbitals up here.

All right. So now we can calculate the bond order for oxygen, and that's a clicker question. All right. Let's just take 10 more seconds.

All right. So let's take a look over here. So bond order, again, is $1/2$ the number of bonding electrons minus the number of antibonding electrons. And we have eight bonding-- 1, 2, 3, 4,

5, 6, 7, 8. And we have four antibonding-- 1, 2, 3, 4. So that gives us a bond order of 2. And the bond order equation is one that you do have to memorize. That will not be given to you on an exam.

And with a bond order of 2, we have a pretty big number for dissociation energy. Again, that's energy you have to put into a bond to break it, to dissociate it, and that means it's a pretty strong bond if it's a big number. If you need a lot of energy, that's a strong bond.

Another thing that you can see from this diagram is that O₂ is a biradical. It has two lone pair electrons, so two unpaired electrons, which also makes it paramagnetic, or attracted to a magnetic field. So whenever you have unpaired electrons, you will have a paramagnetic species, and diamagnetic means they're all paired. And so there are some questions on problem sets and on exams, so you need to know the definitions of those.

All right. So we talked about this when we were doing Lewis structures, if you recall. And we drew a beautiful Lewis structure of molecular oxygen that had two lone pairs on each oxygen and a double bond. But I told you that that was not really a complete description of molecular oxygen, that molecular oxygen was actually a biradical, but you would not get a hint of that from the Lewis structure. So if you draw the Lewis structure as a biradical, then you have a single electron here and a single electron there and a single bond. But we also see the bond orders 2, so this one describes the biradical nature, but doesn't really describe that double bond character that it has.

So neither of these Lewis structures really completely describe molecular oxygen. And we need our molecular orbital diagram to really help us understand the properties of molecular oxygen, that it's pretty strong bond between it, it has double bond character, but it also is very reactive. It's a biradical. So this is just a bizarre molecule. And really that is why this diagram right here really tells us why our life, our planet is what it is, right here, that describes it. It's because of oxygen that we have the life forms that we did.

Life was very different on this planet before molecular oxygen came about. You did have microbes that lived anaerobically without oxygen. But when oxygen came, everything changed.

And so if I say, can you explain life to me? You can draw this, and there it is. This explains life as we know it because life as we know it exists because of this crazy molecule that is O₂, nothing else really like it. It is an amazing molecule that allows us to live. So there you go. I

was going to say you don't learn anything in chemistry. This diagram I just explains life as we know it to you, right there.

All right. It's not just oxygen, there's a few other elements that, yeah, are pretty important, and one of them is nitrogen. We wouldn't really be much anywhere without nitrogen either. Oxygen is, no, nitrogen is pretty special too. This also helps. Maybe these two molecular orbital diagrams really sum up life as we know it.

All right. So let's look at molecular nitrogen, N_2 . So we have two electrons in our 2s orbitals, so we're going to bring them together. We're going to put two in the lower energy orbital, our sigma 2s, and two in our antibonding orbital. And then we have three in our p orbitals from this nitrogen, three electrons from this nitrogen, and so we'll put them down here. We'll put in 2, 3, 4, 5, 6. So we didn't need to use any of these antibonding orbitals, and this is a z less than 8 case. So here we have our pi orbitals first because it is z less than 8.

So let's look at the bond order here. And the bond order is $1/2$ of 8-- 1, 2, 3, 4, 5, 6, 7, 8-- eight bonding electrons and just these two antibonding electrons, so $1/2$ of 8 minus 2 is 3. And you have a really big number for your dissociation energy, 941. This is a very stable molecule, and you can draw the Lewis structure of this without much difficulty. This one works quite well, and you get a triple bond and two lone pairs.

So this would be a diamagnetic molecule, no unpaired electrons, no radicals here. But this is a crazy, strong bond. It's really hard to split nitrogen because of this triple bond. And molecular orbital theory tells you it should be its triple bond. It should be really, really strong interactions between these nitrogens.

And so this is a very hard thing. We want to do is industrially, and we'll talk more about this when we get a chemical equilibrium. How do you split the nitrogen bond. This is actually, currently, a big area of research, how you break that bond because we need nitrogen for life. And so how do you split it? There's lots of nitrogen N_2 in the atmosphere, but we need it here, and we need it usable, so we need to break that bond to use it.

So we'll come back to this in chemical equilibrium and how people are able to split the nitrogen bond. So forget man of steel. We should have man of nitrogen. That's strong. Nitrogen is strong. Forget steel. Man of nitrogen.

One more thing to do before we move on to today's handout and this is really fast, you can

also be asked to draw molecular orbital diagrams where both atoms are not the same. So if you were asked to do that, you can use the following rules. If z is less than 8 for both atoms, π is first. If z is not less than 8 for both atoms, it's hard to know what to do, so you don't need to know what to do. And that's it.

So we might tell you something about it and then you can do it, but otherwise, just worry about things when z is less than 8. So that's molecular orbital theory.