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3.091SC Introduction to Solid State Chemistry, Fall 2010
Transcript – Exam 2 Problem 4

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PROFESSOR: Hi, I'm Jocelyn, and today we're going to go over to the Exam 2 from Fall 2009, and Problem 4, Parts (a) and (b). As always, we're going to start by reading the question. Boron exists in the gas state as the dimer of boron 2. Explain how the fact that B₂ is paramagnetic, two unpaired electrons, implies that, in this molecule, the pi 2p orbitals must lie at a lower energy than do the sigma 2p. OK, so what is this question actually asking you to do? Well, it's asking you why the energy of the pi 2p is less than the energy of the sigma 2p, given that boron 2 is paramagnetic.

So the first thing we need to know is what paramagnetic means, and he actually gives that to you in the problem, so it means that you have two unpaired electrons. So this is unpaired electrons. We are asked here then to give a reason why the fact that there are unpaired electrons implies a certain ordering of the sigma and pi 2p orbitals. So the first thing we want to do, probably, is recognize that these are molecular orbitals, not atomic orbitals. Therefore, we probably want to start by drawing the molecular orbital diagram for boron. Now, how do we draw a molecular orbital diagram. Well, the first thing to do is to start with the atomic orbitals. So boron has five electrons, as we can find out from our periodic table, and they occupy the 1s, the 2s, and one electron in the 2p. Again, if this seems unfamiliar to you, you might want to go back to earlier in the course, where we went over electron configuration.

However, when we're looking at molecular orbitals, we actually only care about the valence electrons, because those are what are involved in bonding. The core electrons are much, much lower in energy, so they aren't really involved in the bonding. So we're actually only going to look at the electrons in the second energy level. So we have three valence electrons per boron, and they are in the 2s and 2p, which we remember, there are three p orbitals in each energy level. So now let's draw those in. We have 2s and 2p. Remember to always have a scale here, and we're in an energy space, and this is not to scale, because we're just looking at relative energies, we don't care about the actual difference in energy.

And because we have two borons-- so this is boron one-- I'm going to draw the same thing over here. Make sure they're at the same energy level because they are the exact same atom, and therefore, the same atomic orbitals. So this is, again, boron, and we have three electrons for each. We don't have to fill them in, but I'm going to do so, just to keep track. And again, we're filling according to the orbital filling rules gone over earlier in the class. So now that we have our atomic orbitals, we are going to combine them to, like, molecular orbitals. And we want to remember that s orbitals combine to make a sigma and a sigma bonding and a sigma anti-bonding. Remember that whenever you combine atomic orbitals, you create-- if

you're combining two atomic orbitals, you create one of a higher energy and one of a lower energy, because the net energy stays the same. Oh sorry, that's crooked.

All right, now we'll move on to the 2p, and because the problem told us that we need to explain why the pi bonding orbitals are lower in energy than the sigma bonding orbitals, we're going to start with that configuration. The actual order depends on the molecule, and so without any extra information, we wouldn't really know if the sigma was above or below the pi. So as the question, kind of, hints at: p orbitals make two pi bonds and one sigma bond. This is due to the orientation of the pi bonds, or the p orbitals in space. Then, as always, we need to put in the anti-bonding just to make sure we keep track of all of our orbitals.

OK, so we combined one, two, three, four, five, six, seven, eight atomic orbitals, and we made one, two, three, four, five, six, seven, eight molecular orbitals. We want to make sure we always have the same number of orbitals before and after. So now we can fill in the electrons into the molecular orbitals: that's these in the middle here. And we use the same rules as we do when we're filling atomic orbitals. So we start at the lowest energy, pairing spins, if we only have one orbital in the energy level; but as here, we have degenerate orbitals, so we can actually have unpaired spins. So we have one, two, three, four, five, six electrons, and we have three from each boron atom, and so, we have the same number of electrons in our molecule.

Now that we have our molecular orbital diagram, we can go back to the actual question. Some students stopped here and were like, I made the molecular orbital diagram. I'm done. But we need to remember that the question is asking us why the configuration we drew makes sense because of the unpaired electrons. So if we go back to our molecular orbital diagram, we see that because the pi 2p have two degenerate orbitals, we can have unpaired electrons. If we think about the sigma being below, we would have paired up those electrons, and therefore, gotten 0 unpaired electrons, and it would not be paramagnetic.

So let's just try that out. Move over here, and we're going to draw just the molecular orbitals; since we already did the full process of making them from the atomic. So this is the sigma 2s, sigma star 2s. And now we're just looking at what if the sigma 2p was lower in energy than the pi 2p. And again, we would fill up our orbitals, and we see that because this lowest occupied molecular orbital is singularly degenerate, we pair up our electrons, and so if this were the case, boron would not be paramagnetic. However, because it is paramagnetic, we know that the pi 2p is lower in energy than the sigma 2p. So that's what this question was asking, and if you said all those things, great job, and you answered the question correctly.

Now we're going to move on to Part (b), and it's very related to Part (a), so we're going to use the same diagrams here. So it asks, is the gas molecule B_2^{2-} more or less stable than the gas molecule B_2 . Explain. So here he's asking about the boron dimer that has a negative 2 charge-- that is, it has two extra electrons. So we're still talking about boron; and thus the atomic orbitals that we're combining are exactly the same. I'll write that down. So we have we still have the 2s and the 2p from each of the boron. That's not the same energy level, and they still make the same molecular orbitals, but we have two extra electrons. So when we go to fill up our molecular orbitals, we now have eight instead of six.

So not only is the boron 2 minus no longer paramagnetic, because we don't have unpaired electrons, but we also have a difference in the bond order. So if you don't

remember what bonding order is, it is when-- I'll just put it here-- it's how we determine the strength of the interaction between the two atoms. And because he's asking is the boron 2 minus more or less stable, we want to figure out the strength of the interaction, and that will tell us which is more stable. So the bond order is the bonding electrons minus the anti-bonding divided by 2. Sorry that's a little messy, but I hope you get the idea.

So for boron 2 minus, which we're talking about over here, the bonding order: we have two, four, six bonding electrons, electrons in bonding orbitals. And we have two in anti-bonding orbitals, divided by 2 and that gives us a bonding order of 2. So that's equivalent to saying there's a double bond between the boron 2 minus, the two borons in that molecule. So let's move back to our diagram for the neutral boron dimer, and we have two, three, four bonding, and two anti-bonding, and so that equals 1. So in the neutral dimer, we have a bonding order of 1, and in the charged 2 minus dimer, we have a bonding order of 2. From this, we can see that the 2 minus has more bonding interaction, and so, it will be more stable. So again, you can't just put that it's more stable, we need to have an explanation for why, and this is a way to explain that.

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