

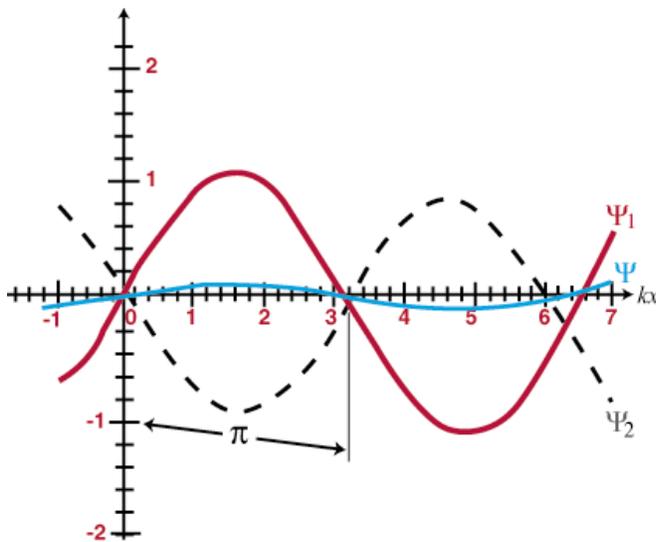
Molecular Bonding Theory: Basics

What is this Molecular Bonding theory? It looks so complicated and confusing! Yep, I whole heartily agree. But really, it is not too bad. Let begin to tackle this bad boy.

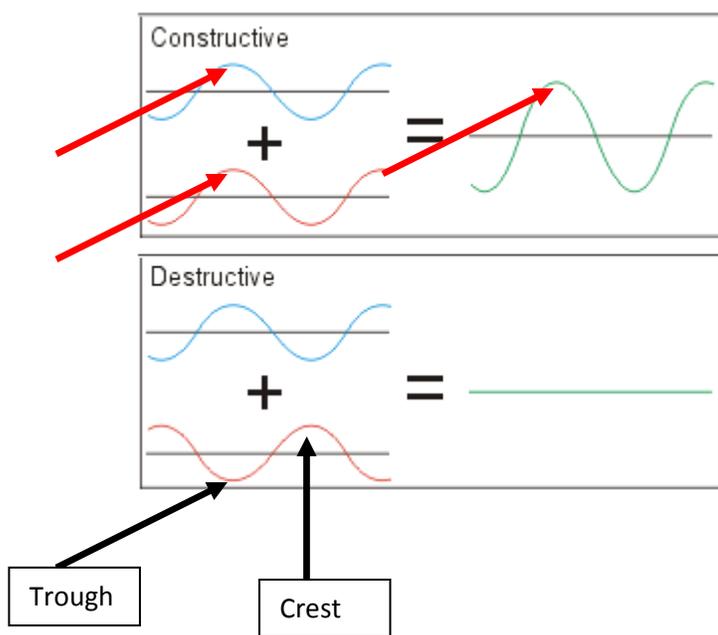
At this point, you probably know your Valence Shell Electron Pair Repulsion and Valence Bond theory very well. Well, that is good. It is good you know them well. Now, I am going to tell you to bonk your head on the wall so that you forget all about them. Well, temporarily anyways.

Molecular Bonding theory is a separate, more complex theory that attempts to use the theory of quantum mechanics to explain bonding. The Valence Bond theory said that two atomic orbitals overlap to form bond that are localized (fixed) between the two atoms. Now, Molecular theory said that two atomic orbitals (AO), instead of overlapping with each other, combine with each other to create brand new Molecular Orbitals (MO).

Ok, you say add or subtract with each other ?! Yep! Allow me to explain why. What are orbitals? They are wave functions right? Yes, and they are represented by the symbol Ψ . If they are wave functions, then orbitals would behave like waves. Which means they will have the following shape: (Red, solid line)



Ok, now suppose you have two atomic orbitals. This means that you now have two waves. Lets play around these two waves. There are many ways of combining them but we are only interested in two situations. The first situation is called destructive interference and the other is called constructive interference.



Here, at the top you see what's called **constructive interference**. It means that the crest of each waves meet at the same time and add with each other to produce a "supercrest". (same for troughs to produce "supertrough") At the bottom, you see what's called **destructive interference**. It simply means that the crest and the trough of each wave meet so that they cancel each other out completely.

Ok, so these two situations are very important because they form the basis of Molecular Orbital Theory. When the two atomic orbitals meet and interfere constructively, they create a molecular orbital. We say this molecular orbital is produced by the addition of atomic orbitals. In other words..

$$\psi_{molecular} = \psi_{atomic} + \psi_{atomic}$$

When two atomic orbitals meet and interfere destructively, they also create a molecular orbital. We say this molecular orbital is produced by the subtraction of atomic orbitals. In other words:

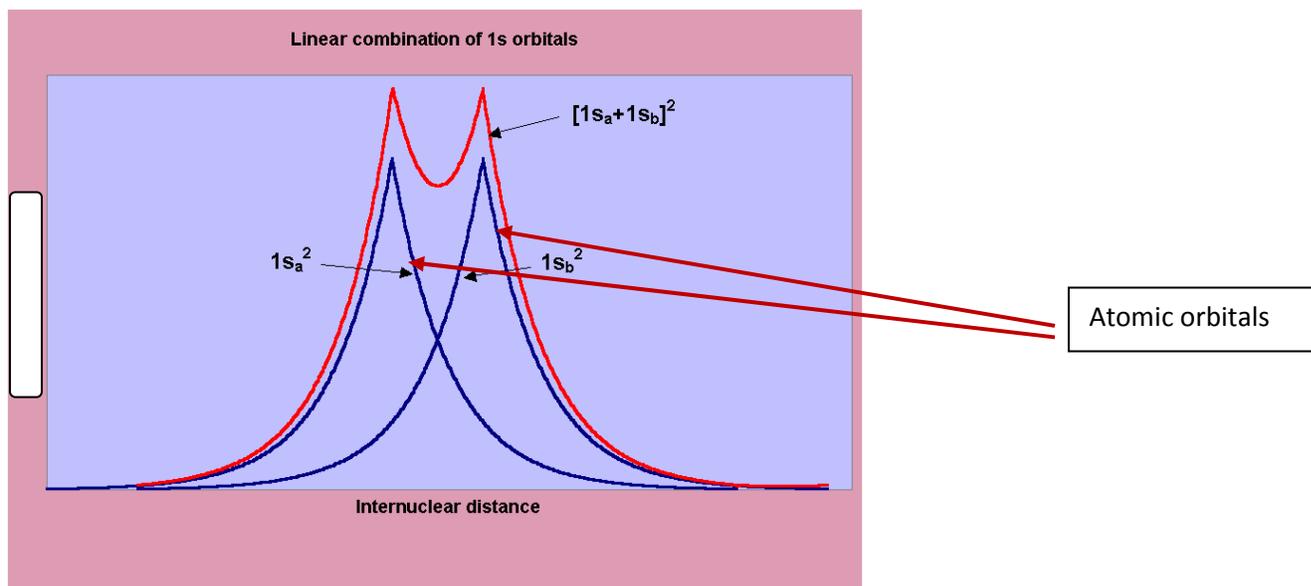
$$\psi_{molecular} = \psi_{atomic} - \psi_{atomic}$$

Thus, addition and subtraction of two atomic orbitals will result in molecular orbitals but these two molecular orbitals are different from each other. We call the molecular orbital (MO) we obtained by adding atomic orbitals **bonding MO** and the MO we obtained by subtracting atomic orbitals **antibonding MO**.

All these molecular orbitals are pretty useless unless we find a use for them right?! Molecular orbitals are created so that we can put valence electrons from each atom onto them. Thus, during bonding, we no longer have atomic orbitals of two atoms overlapping with each other. Instead, molecular orbitals are created and we ripe valence electrons from each atom's atomic orbitals and put them into the molecular orbitals we have just created. It sort of make sense too. Atoms have their atomic orbitals and molecules have their molecular orbitals. The thing to know about molecular orbitals is that they are not localized (fixed) between two atoms; rather, they are spread all over the atom and this is called delocalization. This means that electrons pairs help to bind together the whole molecular and not just an individual pair of atoms. (Molecules are made from two or more atoms)

Bonding and Antibonding Molecular Orbitals

Now let's talk about the bonding MO and the antibonding MO we just discussed. First, bonding MO. If you remember, bonding MO are created from the addition (constructive interference) of atomic orbitals. Now suppose atomic orbitals look like the blue waves below.



Now, they will interfere constructively and what you notice.. A new red wave that's much bigger is formed. You say ok, that's sounds terrific. Yep, it is terrific! You see, when you have a much bigger wave ψ , you ψ^2 is also going to change. We know from 8.10 of Petrucci that ψ^2 is simply the probability of finding an electron at a single point. Thus, as ψ gets bigger, so does ψ^2 . If ψ^2 gets bigger, then there is higher probability of finding an electron at that point. The place where the two waves interfere constructively is between two atoms. Thus, this means that there is a higher probability of finding an electron there.

This high probability means that a pair of electrons on that bonding molecular orbital will spend most of its time between the two atoms. With two atoms keep lock on the pair, the electrons there will have less energy than if they were on atomic orbitals. (Electrons gets pulled closer to the two nuclei, **which results in lower energy for the electrons**) Lower energy on the electrons is great because it means that the molecule (composed of two atoms at this point) will also have less energy. In fact, this lowered energy is the reason why atoms come together to form bonds. The molecule they formed have less energy than the two individual atoms! **Less energy always means more stability.**

What about the antibonding molecular orbitals? Well, these are the bad boys because they make molecules unstable. Lets see why. Antibonding molecular orbitals are formed when two atomic orbitals subtract each other (interfere destructively). Thus, this means there is less chance of finding electrons between the two atomic orbitals (by same logical reason we used above, reduced ψ means reduced ψ^2). In fact, this chance is so reduced that there is a node (a place of 0 probability of finding an electron) between the two atoms. This means that the

antibonding MO is excluding electrons from the very region in which the electrons must occupy to form a bond. Thus, most of the electron probability will be located outside the region between the two atoms. The result is catastrophic! Without the electrons to occupy the region in between the two nucleus, there will be increased nucleus-nucleus repulsion. This increased repulsion contributes to the instability of the molecule and results in the **electrons on the antibonding MO to have much higher energy**. Instable molecules simply do not exist! Thus, the antibonding MO strongly favors against bonding. (Hence the name antibonding).

Wow! You say, this is very fascinating! Yep! Yep!

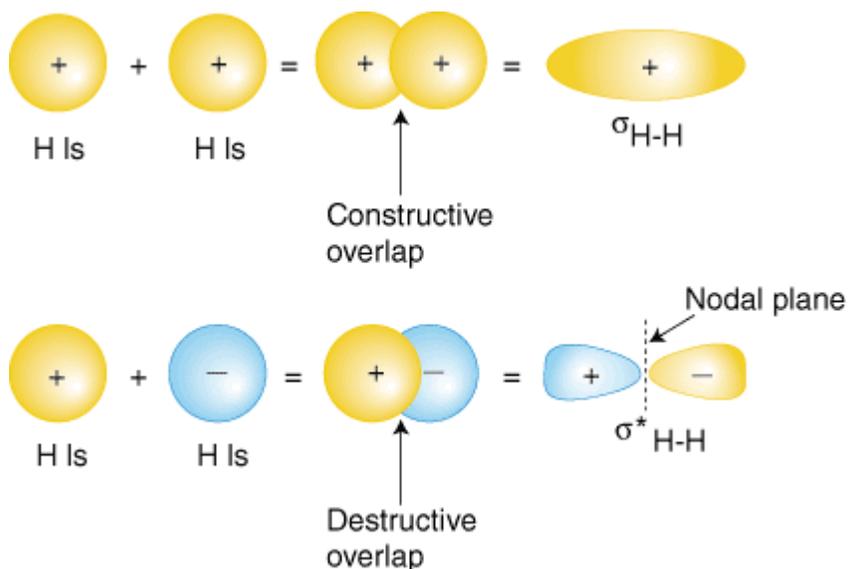
Oh, I almost forget to mention, atomic orbitals combine most effectively with other atomic orbitals of the same energy. Thus, you will see that 1s atomic orbital from one atom will combine only 1s atomic orbital from the other atom. The same applies for 2s, 2p etc..

Ok, now. Lets see some Molecular orbitals kick ass.

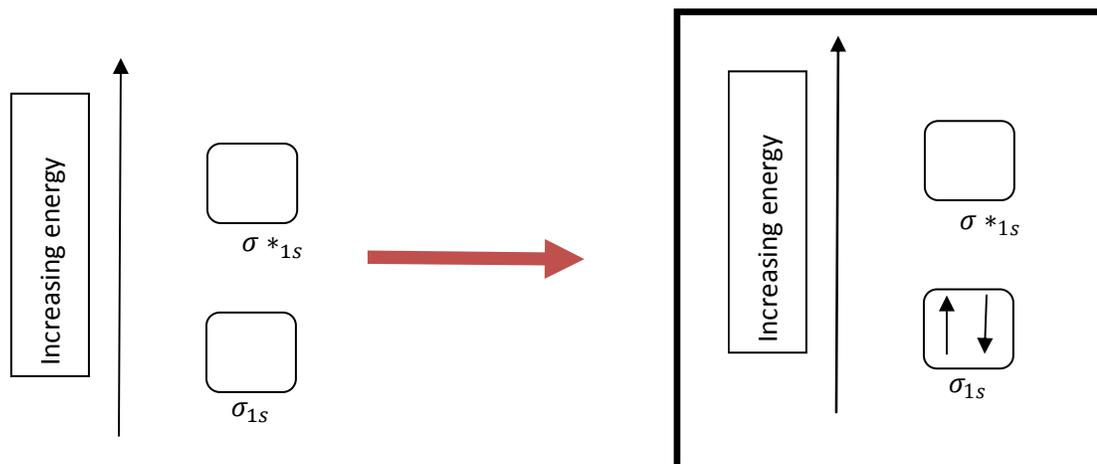
H₂ Compound

The first molecule we are going to look at is H₂. Hydrogen atoms only have 1s atomic orbitals. Since they are two hydrogen atoms, there will be two 1s atomic orbitals. These two atomic orbitals will form **two molecular orbitals**. Yes, two molecular orbitals. This is because the two atomic orbitals could interfere destructively **and** constructively with each other, producing both a bonding molecular orbital and an antibonding molecular orbital. Now, the 1s atomic orbitals are spherically shaped. Thus, they will interact on the line between the two nuclei, producing two sigma molecular orbitals, one bonding, denoted by the symbol σ_{1s} and the other antibonding, denoted by the symbol σ^*_{1s} . (Note the symbol *, it tells us the molecular orbital is antibonding) In general, **number of molecular of orbitals formed = number of valence atomic orbitals that are involved**. $\frac{1}{2}$ of the MOs formed will be bonding, the other half antibonding.

Here is a basic illustration of the process:



Now, although there are two molecular orbitals, only one of them is used. Why? You ask? Well, one of the fundamental properties of molecular orbitals is that they follow the same rules as atomic orbitals. Thus, Aufbau process (fill orbitals from lowest energy to highest), Pauli exclusion principle (only 2 electrons per orbital), and Hund's rule (fill degenerate orbitals singly first before pairing them) must be used. As we said above, antibonding orbitals are higher in energy than bonding orbitals. Thus, if we construct an energy level diagram, it would look like this.



Each of the hydrogen in H_2 have one valence electron. Thus, there are a total of two valence electrons. We put them into σ_{1s} orbital because it is the lowest in energy. So the bonding $1s$ molecular orbitals are occupied. Now you are wondering.. what about the antibonding molecular orbitals? Well, since there are no electrons occupying the antibonding molecular orbitals, the antibonding molecular orbital won't play any role. **Molecular orbitals only has an effect in bonding when they are occupied by electrons.** Now we are pretty much done with H_2 except one little thing.. **bond order.**

In the Lewis/VB theory, we defined bond order to be the number of electron pairs per linkage between atoms. Thus, an compound like $N \equiv O$ would have a bond order of 3 since there are three electron pairs in the linkage between nitrogen and oxygen.

In the MO theory, we define bond order a bit differently but the result is pretty much the same. Bond order in MO theory is defined as

$$\frac{1}{2}(B - A)$$

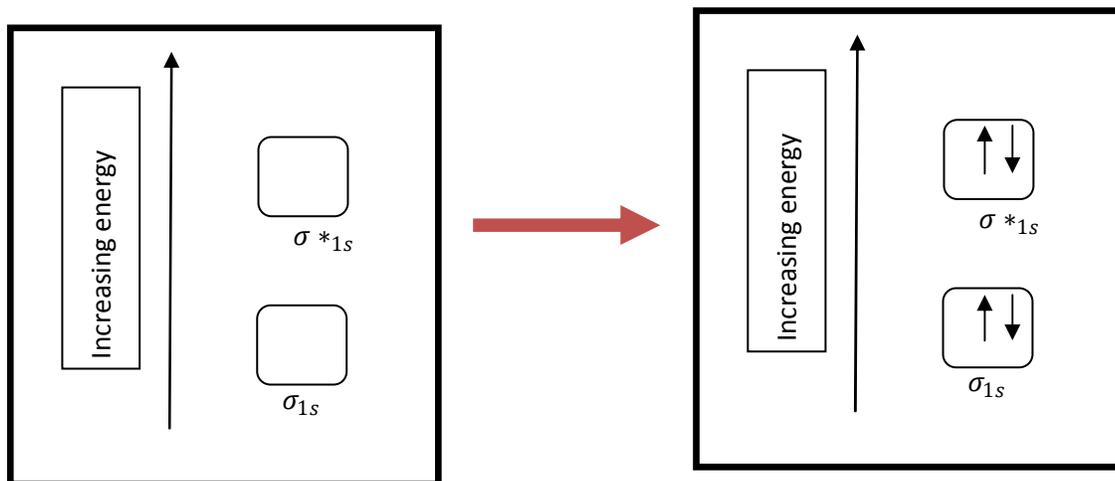
where B stands for # of electrons in bonding molecular orbitals and A stands for # of electrons in antibonding molecular orbitals. This allows for bond orders of $\frac{1}{2}$, $\frac{3}{2}$, or $\frac{5}{2}$, which were not possible with the bond order definition in Lewis/VB theory. Bond order of 0 means that no bond exists.

Thus, if we use the Lewis/VB theory of bond order to look at H_2 , we see that it has a bond order of 1 due to a single bond between the hydrogen atoms. If we take a look using MO theory, then we see that the bond order is $\frac{1}{2}(2 - 0) = 1$. Thus, the bond order for MO theory agrees with the

one from the Lewis/VB theory. This is good! In fact, most of the time, we will see that the bond order deduced from the MO theory will agree with the bond order described by Lewis/VB theory.

He₂ Compound

Hmm, lets examine this big baby. Ok, first thing first. We combine the 1s orbital from one helium atom with the 1s orbital from the other helium atom to create two molecular orbitals, one bonding and the other antibonding. So we have the following..



Now, notice that there are two valence electrons per helium atom. This means when two heliums atoms come together to form a bond, there will be a total of 4 valence electrons in total available for bonding. So, if we fill the molecular orbitals up, we will see that it has the following setup. (Look up)

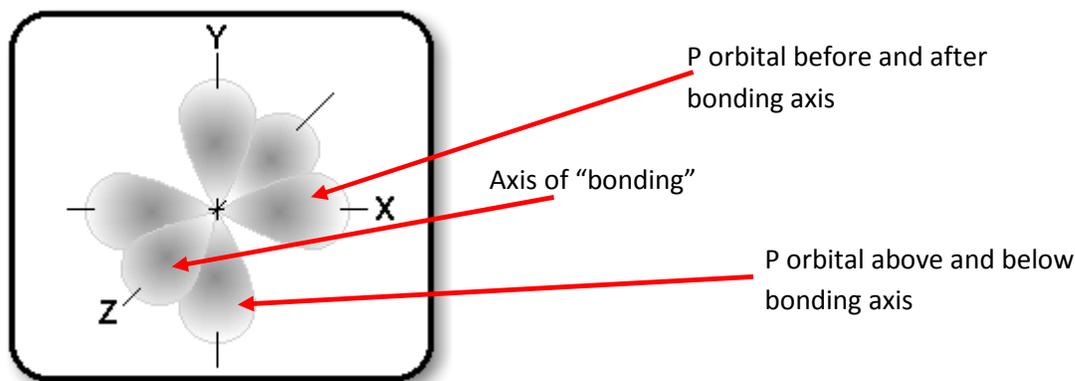
Hmm you say... both its bonding and antibonding molecular orbitals are occupied.. so is there going to be a bond or not? The answer is no, there won't be any bonds. The reason is that antibonding molecular orbitals are highly unfavourable. Thus, when equal number of electrons exists in bonding and antibonding orbitals of a molecule, it would actually results in higher energy than if the atoms that make up the molecule are to be separate. This means that you won't find He atoms bind together. The other way to think about this is in terms of bond order. We said bond order in MO is defined as $\frac{1}{2}(B - A)$. Thus, the bond order in He_2 is $\frac{1}{2}(2 - 2) = 0$, which basically means no bond!

Li₂ and Be₂Compound

Ok, with lithium, we are in the $n=2$ energy level. The electrons in the $n = 1$ plays no more role in bonding since the only electrons that are involved in bonding are the valence shell electrons. Li and Be are in the $n = 2$ energy level so each of them have a single 2s valence atomic orbital they can use to form molecular orbitals. Neither Li nor Be possess 2p orbitals so they cannot be used to form molecular orbitals. Li/Be will form two molecular orbitals, one bonding and another antibonding. Lithium will have similar electron arrangement as hydrogen while beryllium will have similar arrangement as helium. Thus, lithium will have a bond order of 1, creating a Li_2 compound while beryllium will have a bond order of 0, forming no bond at all.

B₂Compound

Hmm, look what we got here... With Boron, we are entering into the 2p orbitals. Sounds fun! There are three p orbitals in total with orientations, p_x, p_y, p_z . These three p orbitals are orientated in such a way that they are all perpendicular to each other. Thus if we choose z axis to be the axis in which two atoms come in to form a molecule, there would one p orbital above and below this axis (p_y) and another p orbital located before and after this axis (p_x).

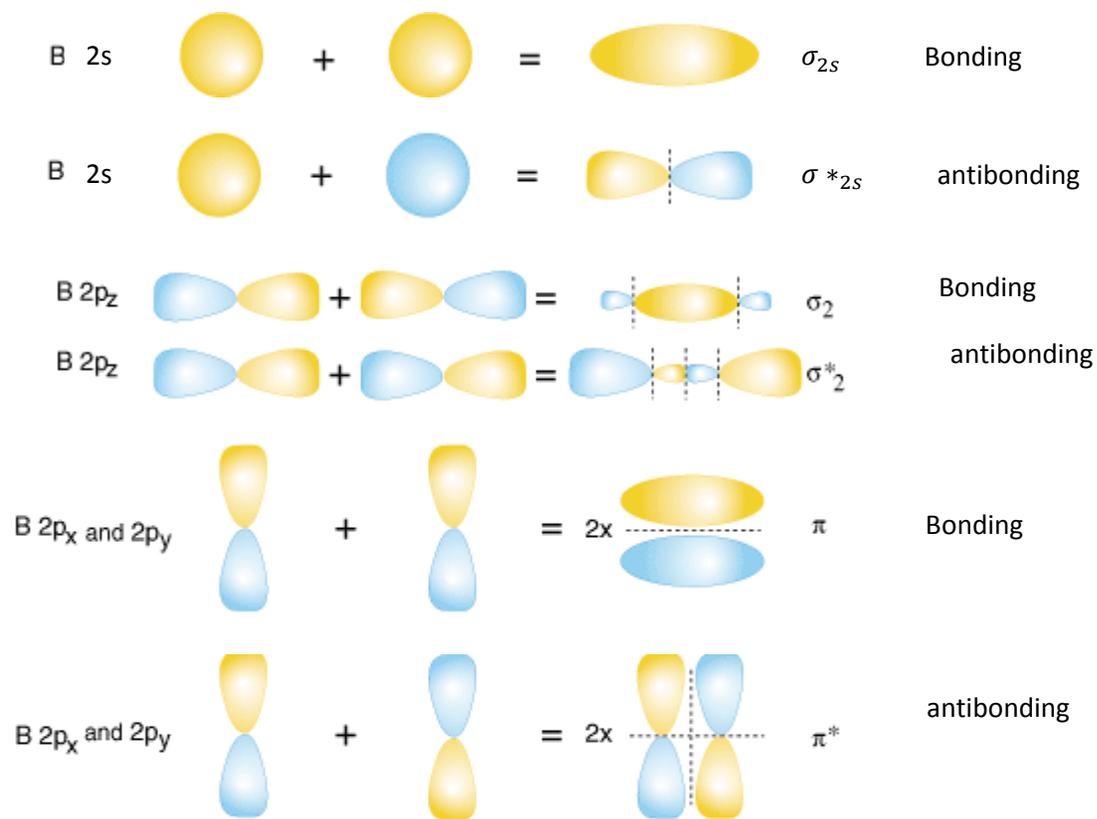


Well, what does this mean? It means that if each of the p orbitals are to form bonds, only one axis, the z-axis will have p orbitals that produce σ bonds since we have defined the z axis to be the "bonding" axis or the internuclear axis. The other two p orbitals will produce π bonds that are located around the internuclear axis. (Remember the definition of sigma (σ) bonds- bonds created along the internuclear axis, and pi (π) bonds- bonds created above and below the internuclear axis)

Similarly, if these p orbitals now combine to form molecular orbitals, the p_x, p_y orbitals will form π molecular orbitals while the the p_z orbital will form σ molecular orbital. Good so far?

Keep in mind that boron also have electrons in the 2s orbital. Thus, it is also able to make molecular orbitals from there.

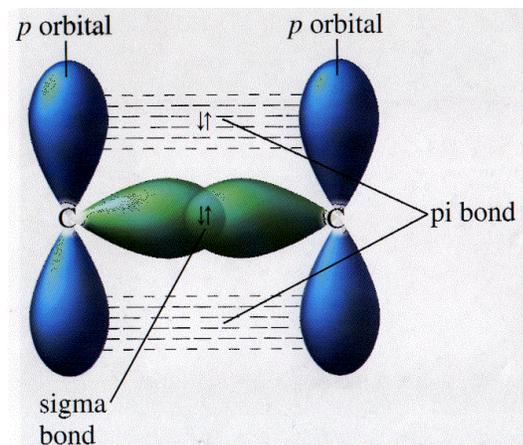
Therefore, when two boron atoms come together, will see that the following orbitals combine to produce new molecular orbitals.



So a total of 8 molecular orbitals have formed, 4 bonding and 4 antibonding. Ok, the next step is to determine their energies so that we can fill these orbitals with electrons.

The 2s and 2p are significantly apart that the σ_{2s} and the σ^*_{2s} are well below in energy than any molecular orbitals formed by the 2p.

The arrangement of molecular orbitals formed by the 2p can be a bit difficult but if we apply the right reasoning, it should become clear. First, we know that sigma bonds are much stronger than pi bonds simply due to better overlap. (Head to head overlap vs side to side overlap) Better overlap means lower energy for the electrons existing in the orbitals.



Thus, we can try to apply the same reasoning to molecular orbitals. The sigma 2p bonding molecular orbitals should have lower energy than the pi 2p bonding molecular orbitals simply due to better overlap when atomic molecules are combined to form molecular orbitals.

So, what we are saying is essentially this:

$\sigma_{2p} < \pi_{2p}$ in terms of energy.

We also know that the antibonding molecular orbitals have much higher energy than bonding molecular orbitals. This energy difference between bonding and antibonding molecular orbitals is greater than the one existing between the 2p pi and 2p sigma bonding molecular orbitals. However, since sigma molecular orbitals are much better overlapped than pi molecular orbitals, we would also expect the sigma 2p antibonding molecular orbital to be higher in energy than pi 2p antibonding molecular orbital. This can be quite confusing but if you think about it, better overlap of the antibonding molecular orbital should increase its effectiveness, which is to increase the energy since antibonding molecular orbitals are formed to increase the energy of the molecule in order to prevent bonds.

Thus, we deduce that the following arrangement in terms of increasing energy is true:

$$\sigma_{2p} < \pi_{2p} < \pi^*_{2p} < \sigma^*_{2p}$$

This is very reasonable but we don't see this trend in compounds like B_2, N_2, C_2 . The question then becomes.. why does this not occur?!

Well, you see, so far in our discussion, we have not talked about one thing, the interaction between the 2s orbital on one atom and the 2p orbital on the other. When forming molecular orbitals, we have assumed that only similar atomic orbitals interact with each other to form molecular orbitals. (i.e. 2s on one atom with 2s on the other) However, the 2s of one atom and the 2p of the other can in fact interact with each other as well to a smaller extent. This effect is not noticeable in compounds like O_2, F_2 and Ne_2 because these atoms have their 2p orbitals raised way above their 2s orbitals. (O, F, and Ne are fairly small. Thus, when you start to add electrons to the 2p atomic orbitals, there are strong repulsions that occur between the electrons that will raise the energy level of 2p well above the 2s. Thus, you get no orbital mixing between 2p and 2s at all since they are sufficiently further apart) However, this effect is present in compounds like $B_2, C_2,$ and N_2 . The result of this effect is that the energy of σ_{2s} and σ^*_{2s} MO are decreased and the energy of the σ_{2p} and σ^*_{2p} are increased. The π_{2p} MOs are not affected.

Yeah, the energy σ_{2s} and σ^*_{2s} MO are decreased.. do we really care? No! The 2s molecular orbitals are already lowest in energy when compared to 2p molecular orbitals. Thus, this doesn't change anything.

However, the fact that the energy of σ_{2p} and σ^*_{2p} are increased does play a role! Well, the σ_{2p} part anyways since σ^*_{2p} already have the highest energy in the 2p molecular orbitals. What does it mean for σ_{2p} to possess high energy? It means ONE THING. Your σ_{2p} is going to have so much energy that it is higher than π_{2p} in energy!! Yep Yep.

So in fact, you have the following energy relationships in compounds like B_2 , C_2 , and N_2 .

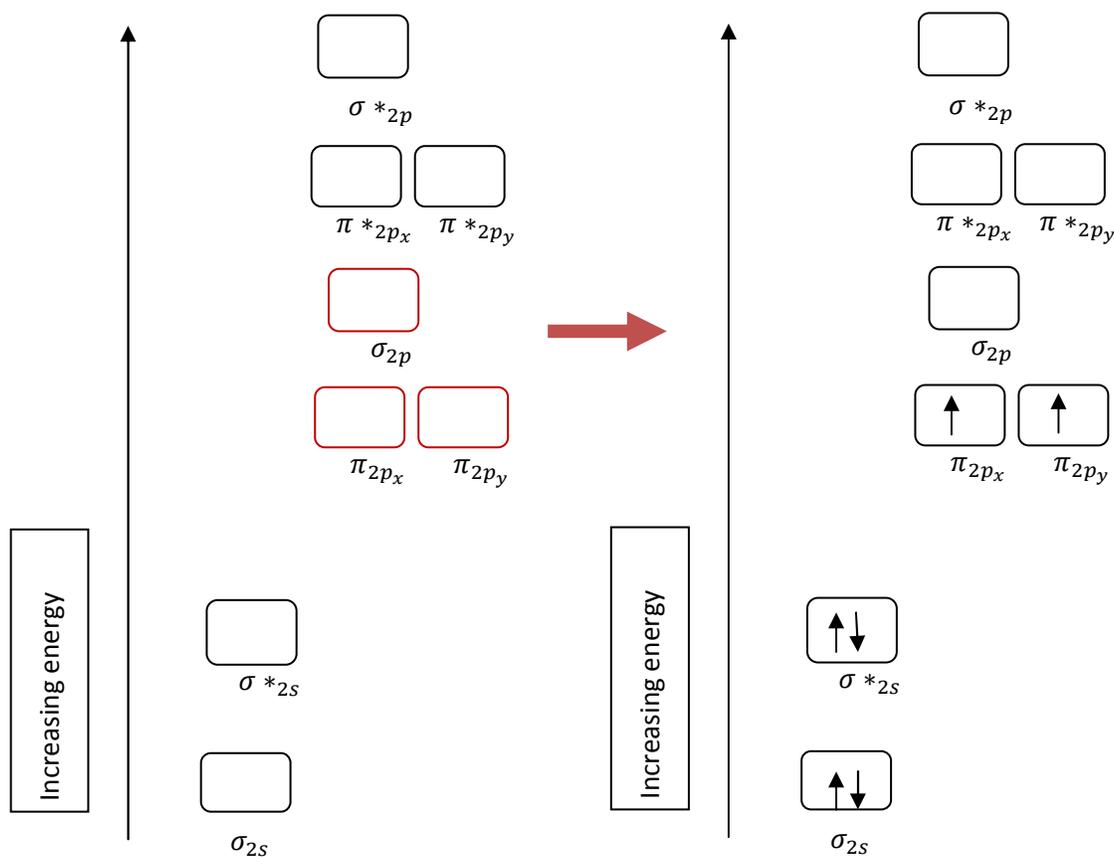
$$\pi_{2p} < \sigma_{2p} < \pi^*_{2p} < \sigma^*_{2p}$$

Rather than the one you expected and which is present in compounds like O_2 , F_2 and Ne_2 .

$$\sigma_{2p} < \pi_{2p} < \pi^*_{2p} < \sigma^*_{2p}$$

Wow, that was a lot of confusing materials to take in. Hope you are still with me.

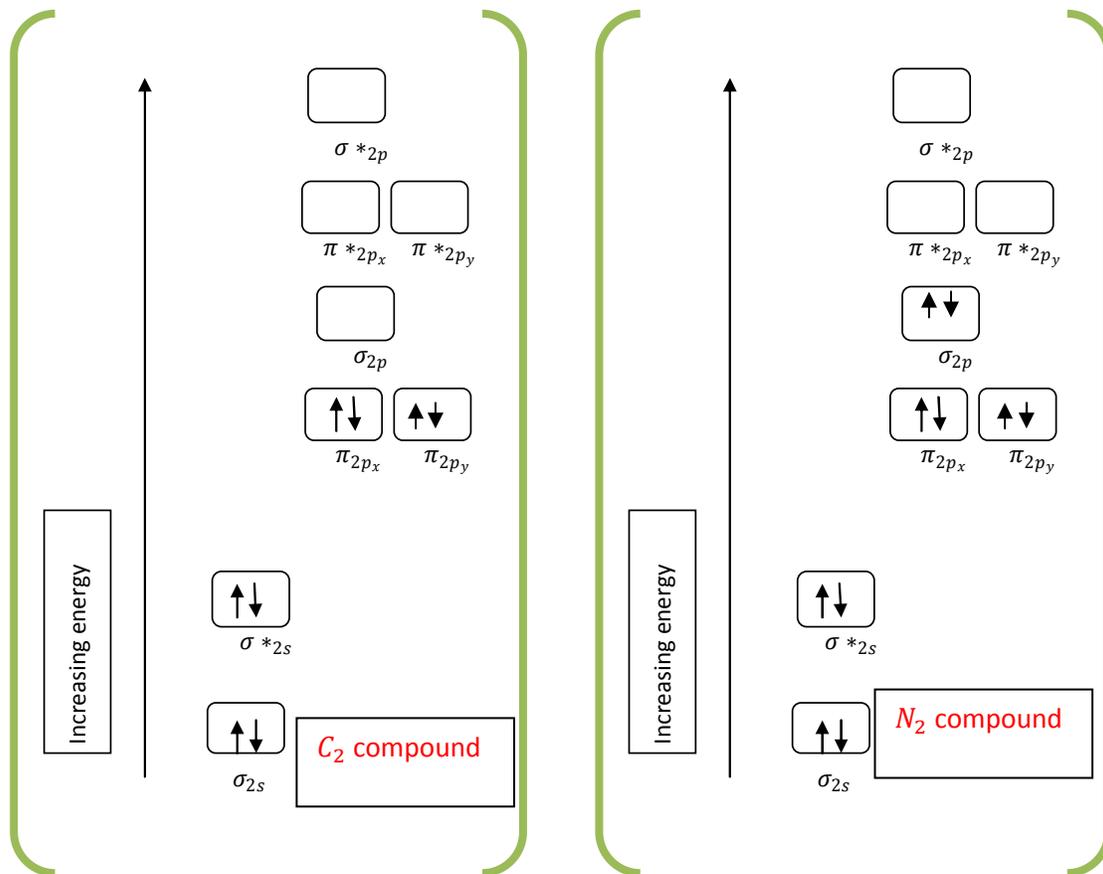
Ok well, why don't we draw the energy diagram for the molecular orbitals on the B_2 compound.



Notice that both the π_{2p} and π^*_{2p} are doubly degenerate. Doubly degenerate means that there are two orbitals of each type that have the same energy. Thus, according to Hund's rule, we put 1 electron into each orbital before pairing them up.

B_2 has six valence electrons in total, three from each atom. Thus, if we start filling the molecular orbitals up, here is what it is going to end up. (Look above). Well, we would predict that the bonding 2s and antibonding 2s roughly cancel each other out (note the word, roughly). Thus, the electrons existing on the pi bonding 2p molecular orbital would hold the molecule together. If we take a look at the bond order, we can see that the bond order is $\frac{1}{2}(4 - 2) = 1$.

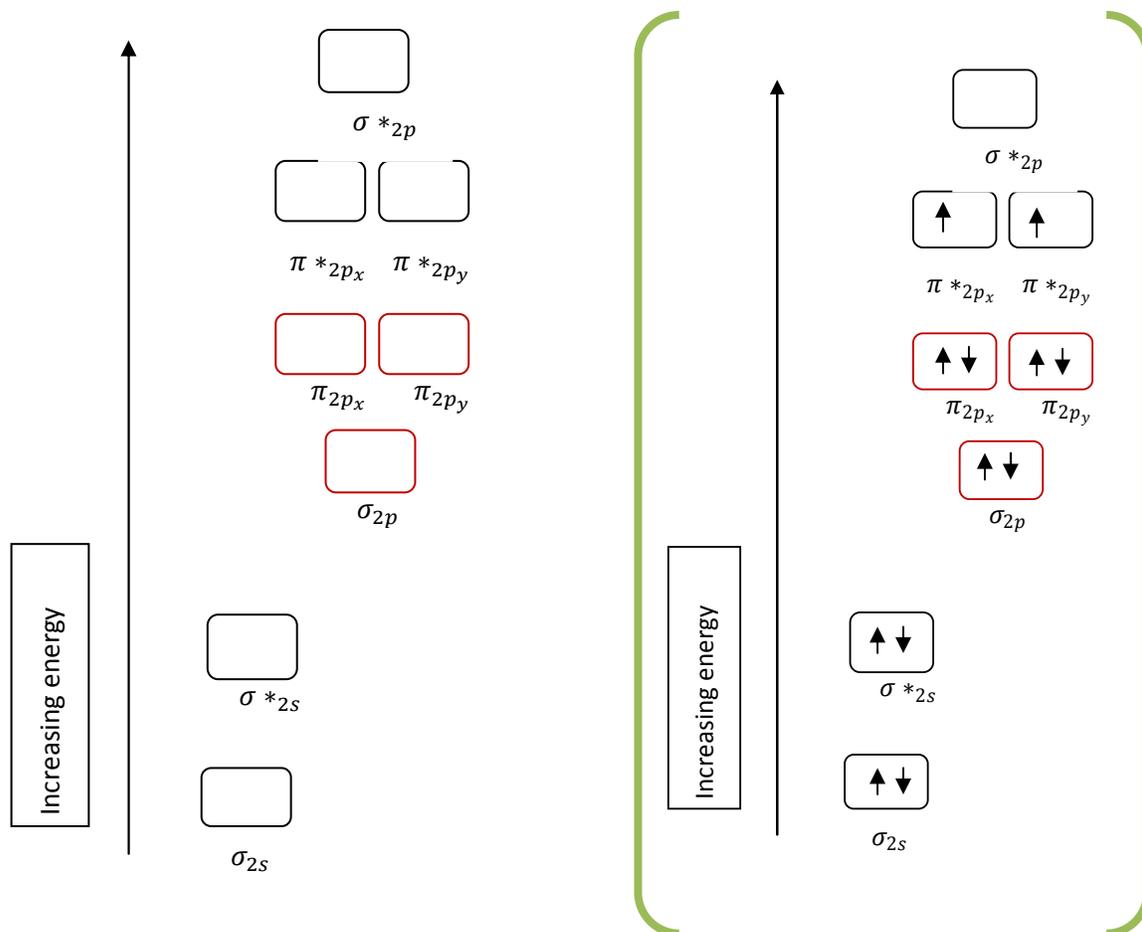
C₂ and N₂ Compound



Bond order in C₂ is $\frac{1}{2}(6 - 2) = 2$ and bond order in N₂ is $\frac{1}{2}(8 - 2) = 3$. If we take a step outside the molecular bonding theory and look at the Lewis/Vb theory, we see that N₂ has the following structure, N≡N with a Lewis bond order of 3. Thus, once again, we see that MO theory agrees with what we have learned so far.

O₂ and F₂ Compound

Now, from here on, we have something different. We have a different energy diagram for molecular orbitals. (Notice the switch between sigma 2p and the pi 2p)



So, for O₂ we have 6 valence electrons per oxygen atom for a total of 12 electrons in the molecule. We fill them up using the rules we have learned. Note again that due to Hund's rule, we don't pair up the electrons in the antibonding pi 2p orbital. This is the reason why O₂ exhibits paramagnetism. It has two unpaired electrons and thus will be attracted to a magnetic field.

The bond order in O₂ is $\frac{1}{2}(8 - 4) = 2$.

In F₂, the bond order is $\frac{1}{2}(8 - 6) = 1$.

In Ne₂ the bond order is $\frac{1}{2}(8 - 8) = 0$. Thus, neon does not exist in nature as a compound.

Conclusion:

Yep, as you can see. MO theory is great for explaining things in period 1 or 2. However, once you get to period 3, it gets way complicated. Also, notice that we have only talked about

homonuclear diatomic molecules (molecules formed from the two same atoms). Heterogeneous diatomic molecules gets more complex. Thus, although MO theory is great, is just too complex for normal everyday use.

Now, we must be wondering. When do we use the MO theory and when do we use VB/Lewis theory?

In general, we use VB/Lewis theory until we can't explain something with it. Then we use MO theory to try to explain it. This occurs mostly with magnetic properties of compounds like O_2 , which we cannot explain using the VB/Lewis theory.

Quick summary:

$$\text{Bond order: } \frac{1}{2}(B - A)$$

For boron, carbon, and nitrogen, the energy level configuration is as follows:



For oxygen, fluorine, and neon, the energy level configuration is:



Filling of molecular orbitals follow the Aufbau, Pauli Exclusion principle, and Hund's Rule.