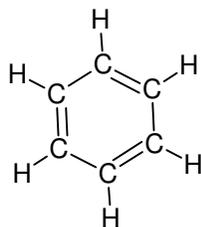


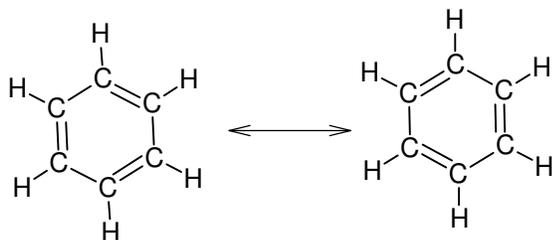
11.6 Molecular Orbital Theory: Benzene (Resonance)

Now that we got the basics of MO theory down, we can use it to explain more complicated examples. Consider for example, the molecule benzene, which has a formula of C_6H_6 . We can draw the Lewis structure for it, which is really this:



Wow, this is one complicated structure! Yep! Welcome to the world of organic chemistry! Benzene here plays a very important role in organic chemistry and will become your best friend next year (or whenever you are taking Organic Chem)

Hmm, if we look at this monster of a molecule, we see that **it exhibits resonance structure**. Very interesting!

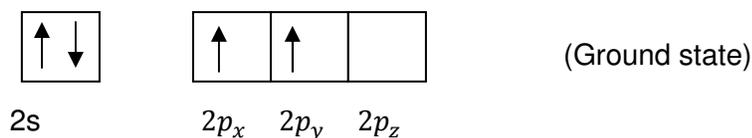


So, using what we have learned so far, how do we explain resonance structure? In fact, let's ask this question instead, how do we explain the bonding of molecules that contains more than two atoms?

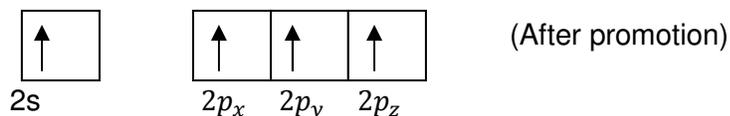
There is one feature of molecular orbital theory that I have not mentioned before. Molecular orbitals are delocalized, meaning that they are not restricted to the space between a given pair of atoms. The molecular orbitals belong to the entire molecule. This means that if you have a molecule made up of more than two atoms, molecular orbitals will affect all of them. This idea was unnecessary to mention in 11.5 because we only dealt with two atoms per molecule there. Thus, this feature didn't do much there. Now, as we will see, this idea becomes very important.

Ok, let's take a detailed look at our benzene friend here. Let's **try to see this molecule in terms of VB theory first**. We have resonance structure, which means that the correct structure of benzene is a combination of the two structures listed above. This also means that we need to save a 2p atomic orbital on each carbon atom so that we can use it for the π bond in the "double bond" that forms between pairs of carbon atoms. (Double bond is in quotes b/c it is not exactly a double bond, it is something in between a single and double bond.)

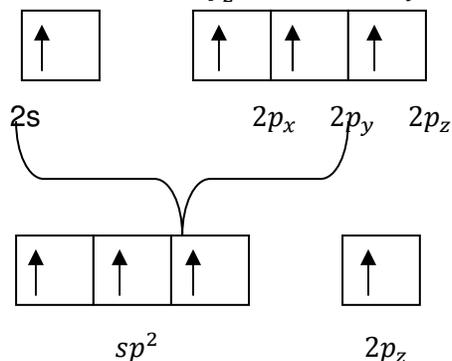
So we have the following ground state electronic configuration for a carbon:



Time to promote an electron up..



Lets save the $2p_z$ orbital and hybridize the rest into sp^2

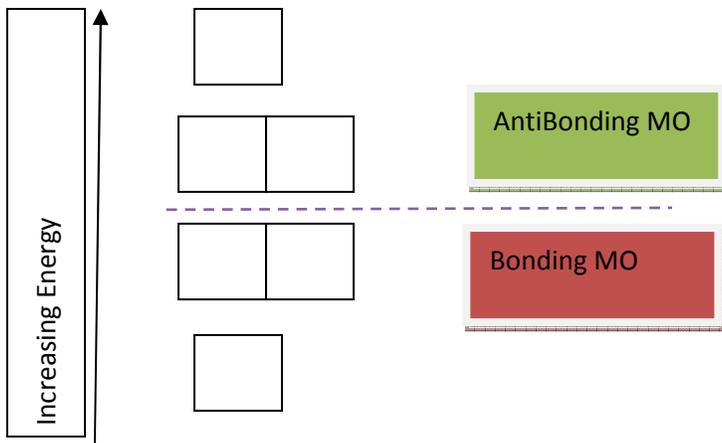


Ok, now we will use the sp^2 to form σ bonds with the two adjacent carbon atoms and the hydrogen atom. One all the carbon atoms in benzene have done this, we have formed what's called a σ network.

So far so good. Valence Bond theory explains it well. However, we know that Valence Bond theory does not explain resonance at all. (It assumes that electrons are localized (restricted to the space between two atoms) so it would be very difficult to explain 1.5 bond (combination between single bond and double bond, the bond that actually exists between carbon atoms in benzene) in terms of that.) . So, how about we stop using VB theory now and use Molecular Orbital theory (MO) instead?

Now you are probably like.. dude how can you mix up the two theories?! Well, first of all, because I can. Secondly, remember that theories are just theories-predictions of what might happened. There nothing in nature that says you can only use only one theory to explain one thing. I can mix up a number of theories to explain something and if that works, then it works. Nothing wrong with that.

According to MO theory, the $2p_z$ orbital from the 6 carbon atoms would combine with each other constructively/destructively to produce 6 molecular orbitals. Now, in compounds with only two atoms, which we took a look at in 11.5, it is very straightforward since you only had 2 atomic orbitals to work with. You either have constructive interference (forming bonding MO) or destructive interference (forming antibonding MO). Now we got 6 atomic orbitals so it is not so straightforward. The details of how they combine together is wayyyy to complex to explain so I will tell you the results of all these combining action. You get this energy level diagram here.

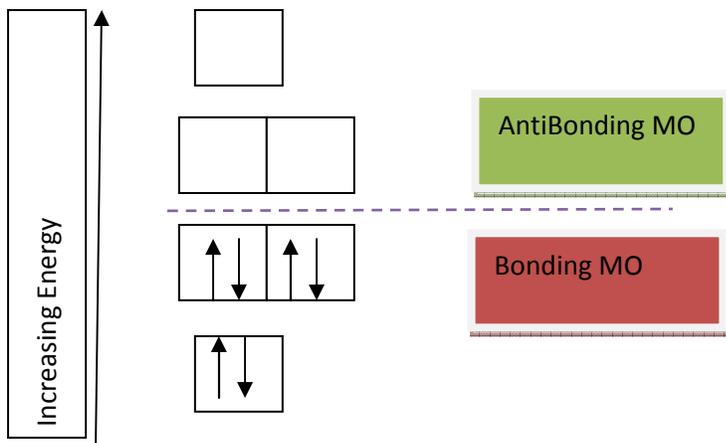


Hmm, I am not even going to label these molecular orbitals because the labelling wouldn't make much sense anyways. See that dotted line there? It means that you are going to have 3 π bonding MOs below that line (lower in energy) and 3 π antibonding MOs above that line (higher in energy)

The lowest MO (box) there is formed due to mostly constructive interference of atomic orbitals. Thus, it has the lowest energy. As we go up, the destructive interference increases and so we get into antibonding MOs until we reach the topmost box. The topmost MO (box) is formed by mostly destructive interference so it has the highest energy.

Ok.

Each carbon is going contribute 1 electron (if you are not sure why, look at the diagrams on page 2) so there are 6 valence electrons in total. We are going to fill these electrons into these MOs we have just created.



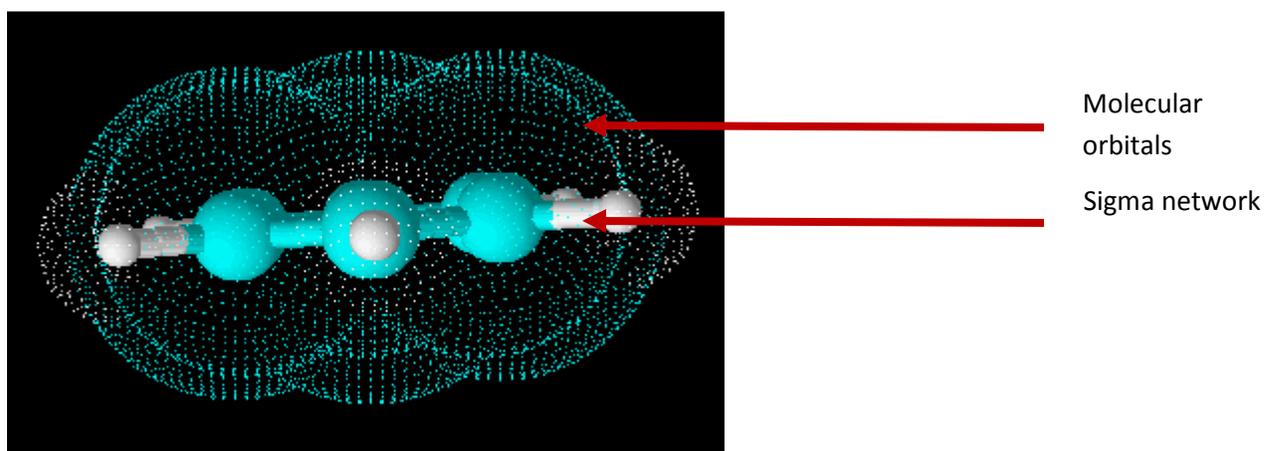
Hey look! We can put all these electrons into the bonding MOs without going into the antibonding MOs. That's great! Yeah so what's our bond order then? It is $\frac{1}{2}(6 - 0) = 3$. Wow! Not so fast though. Remember, this is something formed by all 6 carbons. Thus, for each pair of carbon, the bond order is $3/6 = 0.5$

If we add this 0.5 to the σ bonds that were already formed between C atoms using the VB theory (which has bond order of 1 per pair of carbon) we get a bond order of 1.5. (Yeah I know, we are adding MO bond order to VB bond order, two entirely different things. But since we are mixing the two theories here anyways, we are going to assume that we can mix the bond orders as well!)

Bond order of 1.5 is good because in the VB theory, it is halfway between a single bond and a double bond, which is really what resonance in benzene is all about!

I am not sure if I have stressed this or not but **these molecular orbitals are delocalized and shared between all the carbon atoms** in the benzene molecule.

Thus, this is why Benzene looks like this..



Now, you ask, why does such things as resonance/1.5 bond order happen? Well you see, with molecular orbitals, your electrons are holding the entire molecule together by spreading all over the atoms in the molecule. Thus, there is no need to provide one pair of electron for each pair of atoms. Instead, you just need 1 electron from carbon to form molecular orbitals and this together with your sigma bond between carbon atoms will hold the entire molecule together. If you can accomplish it with less electrons, why go for double bonds?

Note that this idea of theory mixing applies to all resonance structures. We can explain all of them by using VB theory to explain the 1 in 1.5 bond order and MO theory to explain rest of the 0.5.