Reading and Writing MO Diagrams

Skills to Develop

- Construct MO diagrams for simple diatomic molecules and/or compounds

We saw two simple MO diagrams in the section on H_2. Now let's think about how to make some slightly more complicated MO diagrams. First, we need to know a little about how big the energy **splitting** between the bonding and anti-bonding MOs is. Splitting is the energy difference between the bonding and anti-bonding orbitals. Usually the bonding orbital goes down almost as much as the anti-bonding orbital goes up, so the average energy stays almost the same. The size of the splitting depends on the **energy match** and the **overlap**.

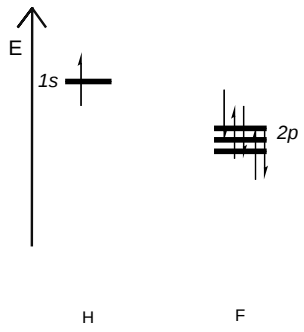
Energy match means how close the orbital energies are. The reason we can consider only valence orbitals is that the core orbitals have much lower energy, and the higher empty orbitals have much higher energy, than the valence electrons. Interactions between completely completely empty orbitals don't matter because there are no electrons. Interactions between completely filled orbitals are usually repulsive, which is why the noble gases don't usually make bonds. Interactions between partially-filled valence orbitals and either core orbitals or higher shell orbitals aren't important because the energy match is bad, so the splitting is almost zero.

We talked about overlap a little in the previous section. Overlap means how much the orbitals touch. For example, usually σ combinations have bigger overlap than π combinations, because the orbitals are pointed right toward each other. You can see this in the pictures on the previous page. For this reason, usually σ MOs have bigger splitting than π MOs.

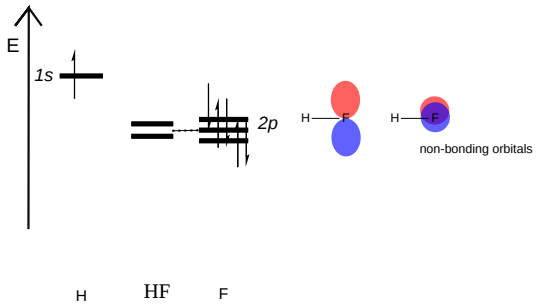
MO Diagram for HF

In the last section, we talked about the bonding, non-bonding, and anti-bonding MOs in HF. Now let's put these ideas together to make an MO diagram for HF.

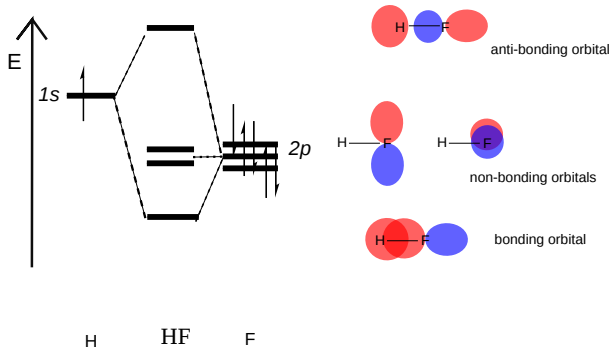
1. We need to know what orbitals we are using. We are only going to consider valence orbitals. H has a 1s orbital. F has a 2s orbital and 3 2p orbitals (x,y,z).
2. We want to know the energies of the orbitals. We can use photoelectron spectroscopy data, which tells us the energy of the different orbitals. Here is some data you can use. We see that H 1s orbital has energy -13.6 eV, F 2s has energy -40 eV and F 2p has energy -18.7 eV. Because there is a big energy difference, more than 12eV, between H 1s and F 2s (bad energy match), we can put just H 1s and F 2p in our diagram.
3. We draw the AOs on the outside of the diagram and include the right number of electrons. H has 1 valence electron, and F has 7 valence electrons. We are only including the F 2p orbitals, which have 5 electrons; the F 2s orbital holds 2 electrons and isn't in the diagram (it's like a lone pair).



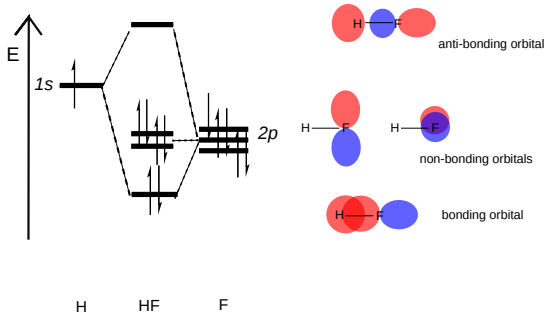
4. We remember which orbitals interact. Before, we saw that bonding and anti-bonding combinations only form between H 1s and the F 2p orbital that points straight toward it. The other 2p orbitals are non-bonding, so we can draw them in the middle at the same starting energy.



5. The H 1s and F $2p_z$ make a bonding and anti-bonding combination, so we draw these new MO energy levels. We don't know exactly how big the splitting is, but that's ok, don't worry about it.



6. We put the same number of valence electrons we had in the AOs on the outside into the MOs at the center, starting at the bottom. In this case, we have 6 electrons. They will go into the bonding MO and the 2 non-bonding MOs. The anti-bonding MO is empty because it is too high in energy. We're done!

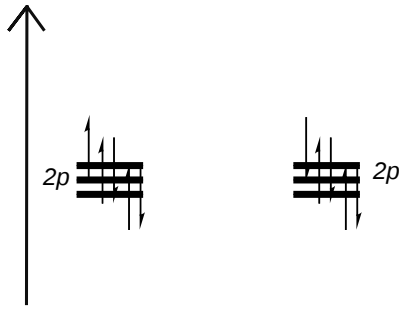


MO diagram for HF. Notice that the bond order is 1, as we expect from the Lewis structure (2 electron in bonding MO, 4 electrons in non-bonding MOs).

MO Diagram for F_2

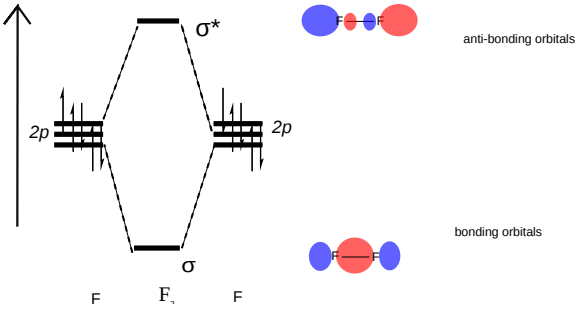
Let's do another example. This time we'll do F_2, which is a little more complicated. This time we'll use σ and π bonds.

1. What orbitals we are using? F has a 2s orbital and 3 2p orbitals (x,y,z). For now, let's just consider the 2p orbitals. We'll see what happens with 2s orbital in the next section.
2. We don't need to worry about the energies this time, because they all start the same.
3. We draw the AOs on the outside of the diagram and include the right number of electrons. F has 7 valence electrons. We are only including the F 2p orbitals, which have 5 electrons; the F 2s orbital holds 2 electrons and isn't in the diagram yet.

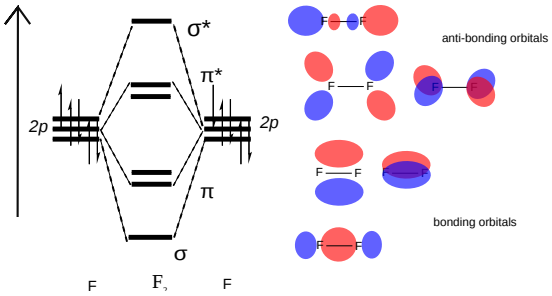


F F, F

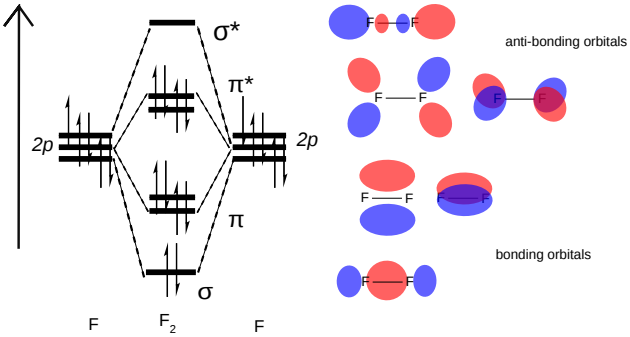
4. We remember which orbitals interact. Before, we saw that we make σ bond and anti-bonding combinations using the 2p orbitals that point toward each other. Let's draw those in.



5. We also make π bonding and anti-bonding combinations using the other 2p orbitals. Because these have less overlap than the σ combinations, the splitting will be smaller, so we'll draw these in between the σ bonding and anti-bonding orbitals. There are 2 of each (π bonding and anti-bonding), so we draw 2 lines for each. They are the same energy because the are the same except rotated 90°.



6. We put the same number of valence electrons we had in the AOs on the outside into the MOs at the center. In this case, we have 10 electrons. They will go into the σ bonding MO and all 4 π MOs. Only the σ* MO is left empty. We're done!



MO diagram for F_2. Notice that the bond order is 1, as we expect from the Lewis structure (6 electrons in bonding MOs, 4 electrons in anti-bonding MOs).

Reading MO Diagrams

When you look at an MO diagram, you can see what AOs are included by checking the outside of the diagram. The middle shows you how they combine and approximately what the energies of the combinations are. You can tell which orbitals are bonding because they have lower energy than the AOs. Non-bonding orbitals have about the same energy as the AOs, and anti-bonding orbitals have higher energy than the AOs. You can use the number of electrons in each type of MO to find the bond order. You can also tell how many unpaired electrons there are, which tells you about the magnetic properties. You can make some guesses about colors, because these usually come from having a small gap between full and empty orbitals. Finally, you can tell which parts of the molecule are most reactive: they will have a low energy empty MO or a high energy full MO. We'll see some more examples of this later.

Contributors and Attributions

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