MO Diagrams for First Row Diatomic Molecules

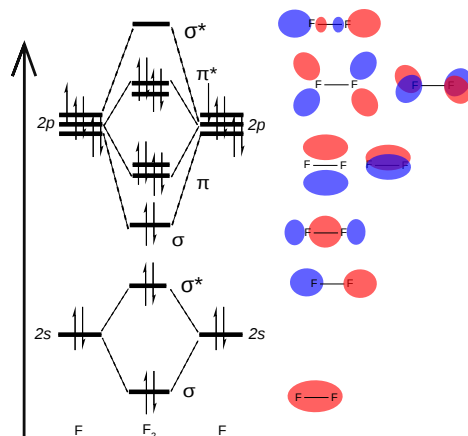- Construct MO diagrams for simple diatomic molecules

Overview

In this section, we will compare MO diagrams for diatomic molecules X-X, from Li_2 to Ne_2. We will predict their bond order and see how the energies of the different orbitals change. We will also compare our predictions to experimental evidence. First, though, we need to talk about a new effect, s-p mixing.
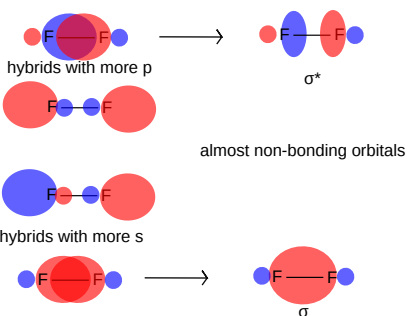
s-p Mixing

Let's think about the orbitals we use to make MO diagrams for the first row elements, Li-Ne. We don't have to worry about 1s orbitals, because their interactions don't have much effect on the properties of the molecule. The core orbitals are completely full, so there can't be any net bonding between them. They are also smaller, so they have worse overlap with core orbitals on other atoms, and lower energy, so they have bad energy match with valence orbitals on other atoms.

We will use 2s and 2p orbitals. The 2p orbitals that make π combinations don't do anything new. But we have to think more about the σ orbitals. Both 2s and $2p_z$ can make σ bonds. Do they do this separately? It turns out that sometimes they do and sometimes they don't. In molecules like F_2, they mostly interact separately, because the energy match between them is very bad. F 2s is much lower energy than F 2p. So you get an MO diagram as shown in the figure. You can see that including the 2s orbitals does not change the bond order, because both the bonding and anti-bonding combination are filled.

Full valence MO diagram for F_2, showing all valence orbitals and electrons.

However, in elements with less difference between the 2s and 2p energies, like carbon, the 2s and $2p_z$ orbitals can mix. This means that we can add some p-character to the bonding s combination, so the overlap is better. And we can add some p-character to the s anti-bonding combination so that the overlap is worse, and it is less anti-bonding. (Basically they form sp hybrids, like you have seen before. However, they are unequal hybrids, with more s in one and more p in the other.) We can picture sp hybrids making 4 combinations. We get a strongly bonding combination, a weakly bonding combination, a weakly anti-bonding combination, and a strongly anti-bonding combination. Or you can think of it as making a bonding, 2 non-bonding, and an anti-bonding combination. The combinations are shown in the figure.
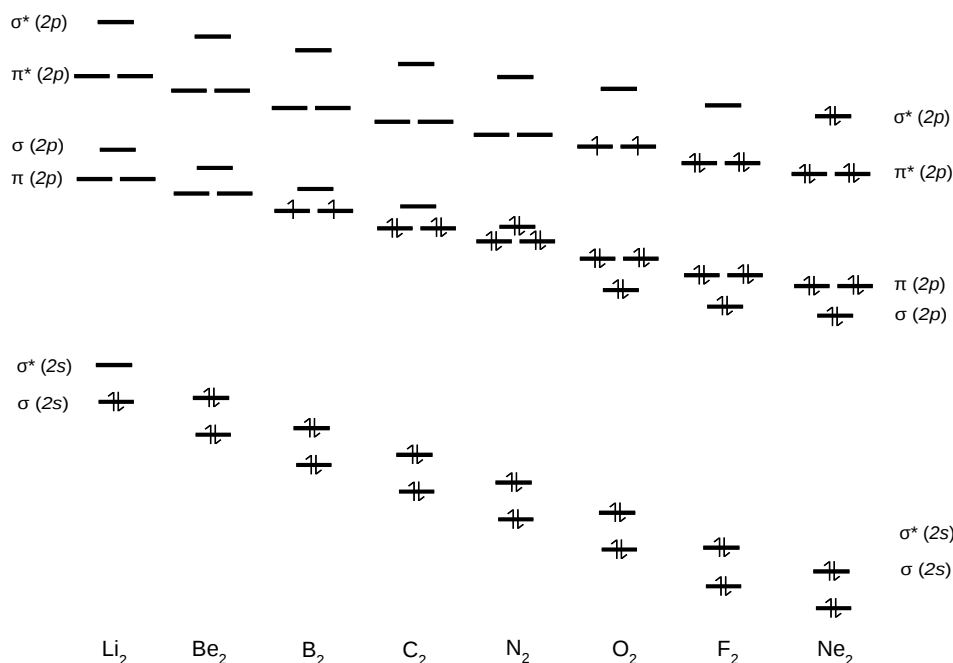
MOs made from sp hybrid orbitals. The slightly anti-bonding orbital is lower than the slightly bonding orbital, because it is still mostly made of s orbitals.

What effect does sp-mixing have on the MO diagram? The 2s bonding orbital becomes more bonding, and gets lower in energy. The 2p anti-bonding orbital becomes even more anti-bonding, and gets higher in energy. The two in the middle might be harder to predict (especially because the molecule will use whatever ratios of s and p in the hybrids is best for lowering the total energy) but probably the lower one gets lower and the higher one gets higher. We would have to use complicated computer calculations to know exactly, but we can make pretty useful predictions just by thinking about it.

MO Diagrams

Now we're ready to look at MO diagrams for the first row series. Note that the molecules that aren't common and stable might still be more stable in the gas phase than single atoms. For instance, in a gas of Li metal, diatomic molecules will form.

The figure shows a summary of the energy levels, so we can see how they change. The number of electrons increases as we move from right to left. You can also see that the gap between the s and p-based orbitals gets bigger from left to right. (Also see that here.) The result is that sp-mixing decreases from left to right, because orbitals only mix well if they have similar energies. Between N and O the σ(2p) crosses below the π MOs. We can match up the MO diagrams with the experimental data, such as bond length and bond strength, which suggests the bond order, and the magnetic properties, which tell us how many unpaired electrons the molecule has.

Energy levels for homonuclear diatomic molecules.

Let's go through the list. Also, you can check the table below for some data.

- Li_2: Using Lewis structures, we predict 1 bond. MO theory also predicts 1 bond. This is a longer and weaker bond than in H_2 because we are using 2s orbitals instead of 1s orbitals. The Coulomb attractions between the nuclei and bonding electrons are

weaker because they are farther apart, and there is electron-electron repulsion. However, in the gas phase the molecule is stable.

- Be_2: Using Lewis structures, we predict 2 bonds. MO theory predicts <1 bond, however, because 2 electrons are in a bonding orbital and 2 are in a weakly anti-bonding orbital. The molecule is not normally stable, but has been detected at very low temperatures in the gas phase.
- B_2: Using Lewis structures, we predict 3 bonds and no unpaired electrons. Experimentally, B_2 is paramagnetic, with 2 unpaired electrons. MO theory can explain this once we include sp-mixing, which makes the 2p σ bonding orbital mostly non-bonding, moving it above the π bonding orbitals. Following Hund's Rule, we put electrons in the π orbitals unpaired. What is the bond order? It depends how much sp-mixing there is, which we can't know without computer calculations, but it should be between 1 and 2 bonds. This is a shorter and stronger bond than in Li_2 so probably it is close to a double bond.
- C_2: Using Lewis structures, we probably aren't sure how to draw it. MO theory suggests that it has 2 π bonds, and a partial σ bond (we don't know how anti-bonding the 2s σ* orbital is because we aren't sure about sp-mixing). The bond length and strength match a bond order of 2-3.
- N_2: Using Lewis structures, we predict a triple bond. MO theory also predicts 3 bonds, which match the experimental very short strong bond. Notice that in MO theory, the "lone pairs" (the 2 mostly non-bonding σ MOs) are shared over both atoms, and have different energies.
- O_2: Using Lewis structures, we predict 2 bonds and no unpaired electrons. MO theory also predicts 2 bonds, but correctly predicts 2 unpaired electrons. This is a longer and weaker bond than in F_2 as we would expect. If we reduce O_2 by adding electrons, they go into the π* orbitals, and make the bond weaker; this matches experimentsm showing that peroxide has a longer, weaker bond.
- F_2: Using Lewis structures, we predict 1 bond. MO theory also predicts 1 bond. This matches experiments showing a long, weak bond.
- Ne_2: Using Lewis structures, we predict no bond. MO theory also predicts no bond. Ne_2 has never been detected experimentally.

Bond Enthalpies (kcal/mol) and Bond Lengths (Å) for the Homonuclear Diatomic Molecules

Molecule	D (kcal/mol)	r (Å)
H_2	103	0.74
Li_2	26	2.67
B_2	66	1.59
C_2	144	1.24
N_2	225	1.10
O_2	118	1.21
F_2	37	1.42

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