

Thoughts for the Day
CH301 Fall 2010
10/21/10

More Molecular Orbitals.

We are going to look at the orbitals for homonuclear diatomics. The situation is similar to what we had for multi-electron atoms. We have a set of orbitals for which the energy ordering is the same. If we know the order we are going to put electrons in starting at the lowest energy and filling up. We will put electrons in separate degenerate orbitals before pairing them.

So what is the order?

Last time we found the two lowest energy MO's for homonuclear diatomics.

σ_{g1s} and σ_{u1s}^*

Let's look at how we got these and their names.

They both have 1s in the name as they are combinations of 1s AO. This is a common theme with MO. What orbitals will we combine? One with the same (or similar energy). How many combinations are there? As many as there are AO.

Thus if we have 2 AO (1s and 1s) there are two combinations. For these the AO either have the same sign (1s + 1s) or different signs (1s - 1s).

We looked in class at what happened when we brought these two together. I will not attempt to draw this here. There are many drawing in the book. The key idea is the following? Do the two wavefunctions interfere constructively (add up) or destructively (subtract). If the parts of the wavefunction that overlap have the same sign, then they interfere constructively and this leads to bonding MOs. If they have opposite sign then they interfere destructively and this leads to a node and thus they are anti-bonding. In addition to this we need to name them based on their shape. The depends on where they are sigma (electron density along the bond axis) or pi (no electron density along the bond axis). In addition we looked at whether they are even (g) or odd (u).

For this we found the following combinations

$$1s + 1s = \sigma_{g1s}$$

$$1s - 1s = \sigma_{u1s}^*$$

$$2s + 2s = \sigma_{g2s}$$

$$2s - 2s = \sigma_{u2s}^*$$

The next highest energy levels are the 2ps. Each AO has three 2p orbitals. Thus we expect 6 MOs. They are all oriented differently. The convention is to choose the z-axis as the “special” axis. In this case it is the bond axis. Thus x and y are the same and both perpendicular to z.

We found that the

$$2p_x + 2p_x = \pi_{u2px}$$

$$2p_x - 2p_x = \pi_{g2px}^*$$

We found two more pi orbitals that were the same but combinations of the 2 py.

The 2pz were different as they made sigma orbitals.

$$2p_z - 2p_z = \sigma_{g2pz}$$

$$2p_z + 2p_z = \sigma_{u2pz}^*$$

Note: we have p orbitals combining to make a sigma. We also have AO of opposite sign combining to make the bonding orbital.

Now the order in energy is essentially always the same.

$\sigma_{g1s}, \sigma_{u1s}^*, \sigma_{g2s}, \sigma_{u2s}^*, \pi_{upx}, \pi_{upy}, \sigma_{g2pz}, \pi_{gpx}^*, \pi_{gpy}^*, \sigma_{u2pz}^*$ (note: the 2px and 2py pi's are degenerate)

Now we just fill in the electrons.

Quiz for you.

What is the bond order of F_2^+ ?

Is F_2^{2+} paramagnetic?

Which has a longer bond length N_2 or N_2^+ ?

Of the elements in row 2, which would you predict would not form stable diatomic molecules?