Theories of Bonding Tutorial

1. Hybrid Orbitals

If we use atomic orbitals to make molecules, the problem is that not all atomic orbitals are equivalent (they exist as s, p, d and f, for instance). However, when we make a molecule of CH_4, for instance, we know that all four bonds from C to H are in fact equivalent. To explain this, we use hybrid orbitals.

In the case of carbon, the electronic configuration is $1s^2\ 2s^2\ 2p^2$. The valence electrons are the only ones of interest. Hence, $2s^2\ 2p^2$. We imagine promoting an electron from the 2s to the 2p orbital so that each orbital now has one electron ($2s^1\ 2p^3$ - remember three are three p-orbitals). We then "make" four equivalent "hybrid" orbitals from these four atomic orbitals, and call them "sp^3" orbitals (i.e. made from one s and three p orbitals).

Making CH_4 then consists only of overlapping these four sp^3 hybrid orbitals of C with the 1s orbitals of each H atom. Each resulting orbital in the molecule will consist of two electrons. Each of these bonds is a sigma (s) bond, since it results from the end-on overlap of the sp^3 hybrid with the H 1s orbital.

In the case of ethylene (C_2H_2), we again promote the 2s electron of C to a 2p orbital. However, only two of the p-orbitals plus the s orbital are used to make three equivalent sp^2 orbitals. These make sigma bonds with other atoms. The remaining p-orbital makes pi (π) bonds with the other C.

What you really need to know about hybrid orbitals is what kind are used in by each "central" atom in a molecule. This boils down to figuring out the number of charge clouds about the central atom, then using the following table:

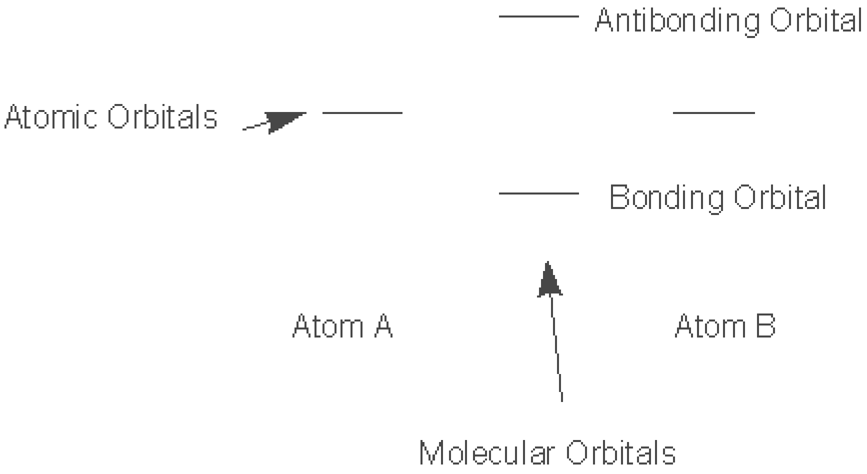
Charge Clouds	Hybridization of Central Atom	Shape of Charge Clouds Around Central Atom
2	sp	linear
3	sp^2	trigonal planar
4	sp^3	tetrahedral
5	sp^3d	trigonal bipyramidal

6	sp^3d^2	octahedral

2. Molecular Orbitals

Recall that orbitals are wave functions, implying that they can be treated as wave-like objects. Thus, when two atoms bind with each other, their atomic orbitals overlap, forming molecular orbitals, which are also wave-like. Thus, these molecular orbitals can have the properties of waves, namely that nodes can exist (places of zero electron density). The ramification is that molecular orbitals can be bonding orbitals (electron density between the atoms) or anti-bonding (nodes between the atoms).

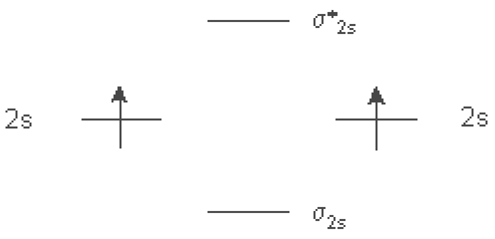
For s-type atomic orbitals, the molecular orbital diagram looks like:



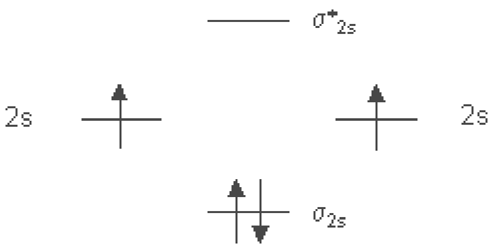
Note that the bonding orbital is lower in energy than the antibonding orbital.

For instance, let’s look at the bonding between two Li atoms. Li has the electronic configuration $1s^2\ 2s^1$. Only the valence electrons are of interest here. First, draw the atomic orbitals of the two Li atoms at the same energy level:

Recognize that if we start out with two (atomic) orbitals, we must have two molecular orbitals (MO’s) formed. These are a bonding (so-called σ_{2s}) MO and an antibonding (so-called σ^*_{2s}) MO. Note that the antibonding orbital is at a higher energy.

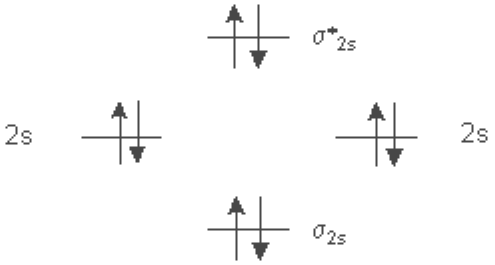


Then, all you need to do is to place the available electrons in the MO's, starting from the bottom up. Place two in each MO, and use Hund's rule where necessary:



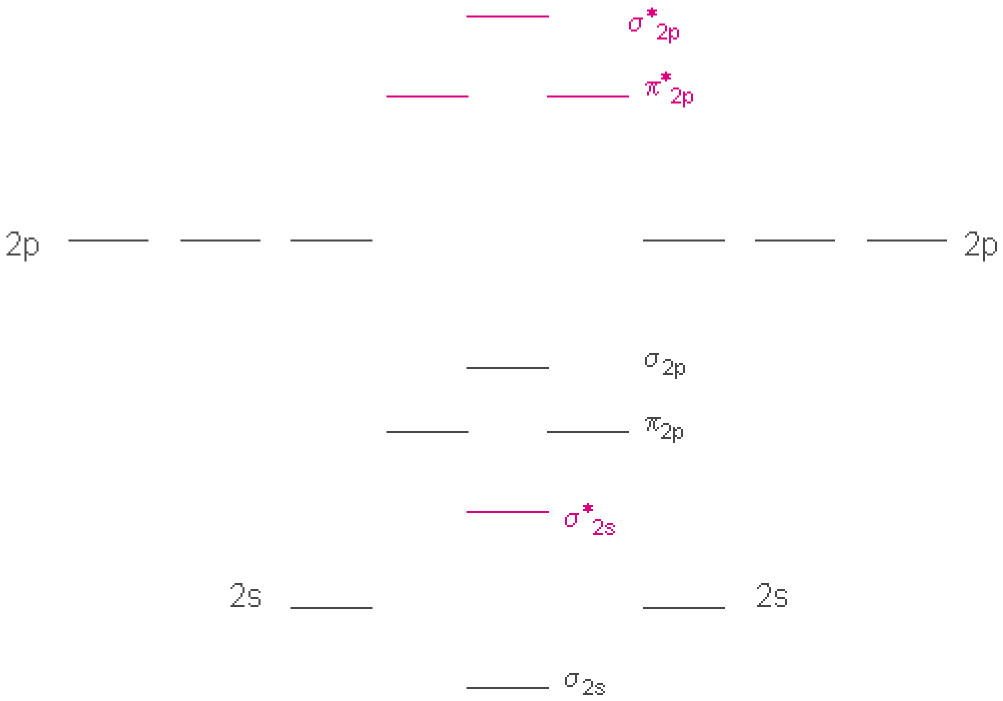
Note that we do not have four electrons now, but that the two are left in the atomic orbitals as reminders of where the electrons in the MO came from. For Li_2, the bond order is (2-0)/2 = 1. Since the bond order is greater than 1, we predict that the molecule should be stable.

Following the same procedure, we can draw the MO diagram for Be_2. Note that Be has two valence electrons:

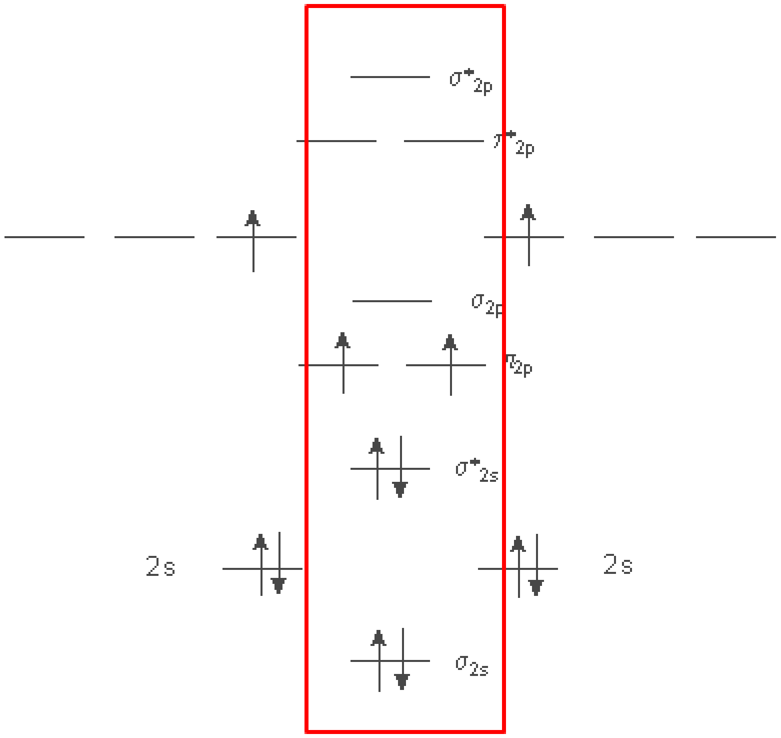


Here, the bond order is (2-2)/2 = 0, and we predict that Be_2 should not exist.

For overlap of p-orbitals, the situation is the same, except that if we start with 6 p-orbitals (3 from each atom), we must also end up with 6 molecular orbitals. Some will be sigma orbitals (end-on overlap of the p-orbitals), but most will be pi-orbitals (sideways overlap). Both bonding and antibonding are possible. The result is a molecular orbital diagram that looks like the following (note that s orbitals are also shown for completeness and that the antibonding orbitals are in red):

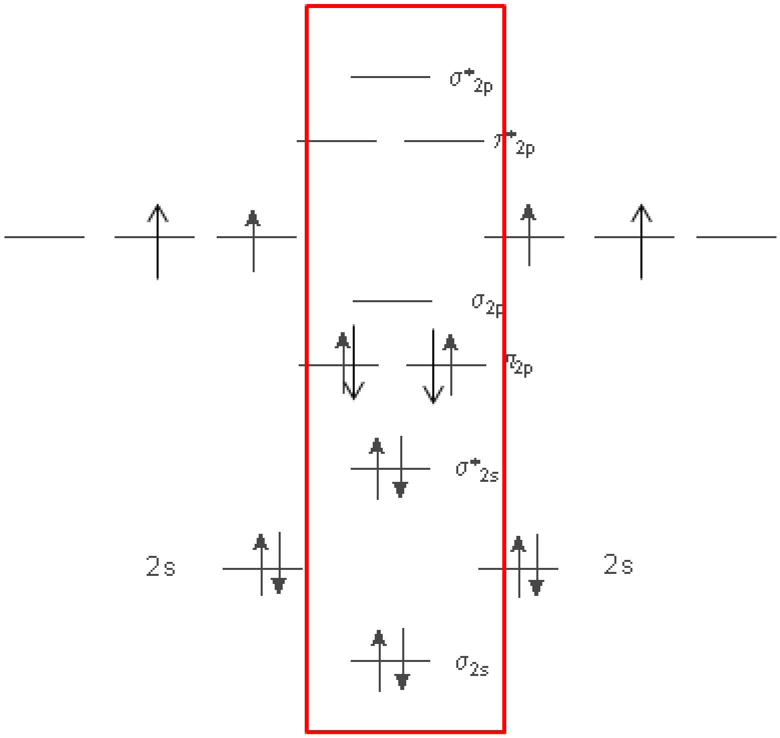


For instance, for B_2, we now have three valence electrons from each atom. The σ_{2s} and σ^*_{2s} orbitals are the same as for the smaller molecules shown above. However, p-orbitals can overlap in two ways. End-on overlap results in a σ_{2p} MO, while sideways overlap of the other p-orbitals results in two π_{2p} orbitals. Both bonding and antibonding orbitals are possible. The overall MO diagram looks like the diagram below. NOTE that the electrons actually move from the atomic into the molecular orbitals (i.e. inside the red box).

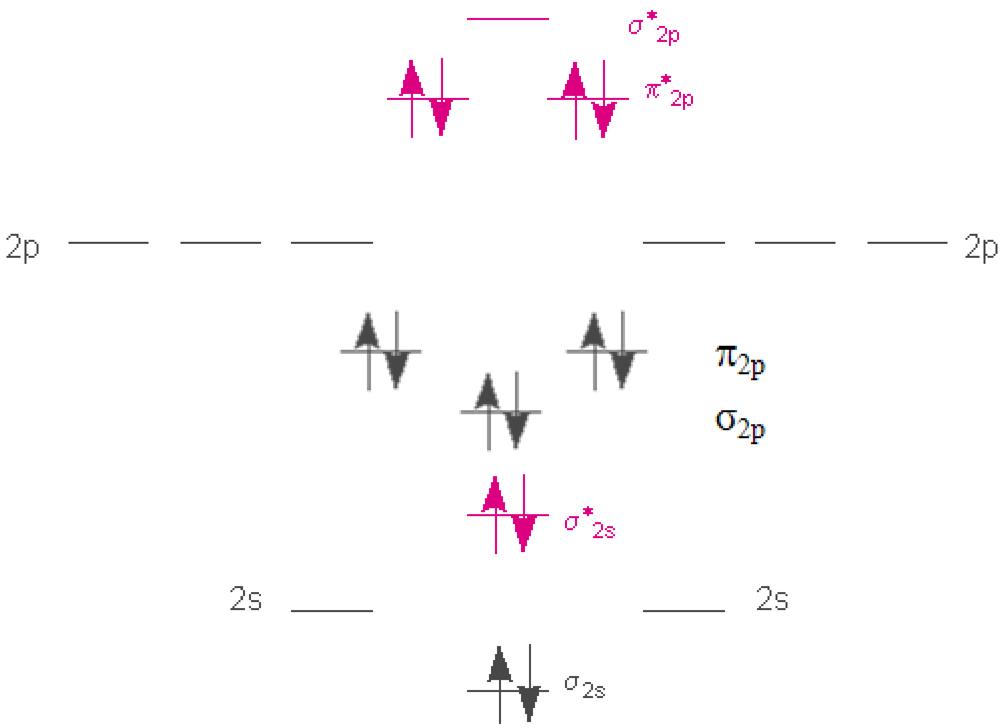


The bond order in this case is (4-2)/2 = 1, indicating a single bond between the two atoms, so we predict that the molecule is stable. Second, using Hund's rule, we had to put two electrons in separate π_{2p} orbitals. These unpaired electrons make the compound paramagnetic.

In C_2, we must add another two electrons, one from each C atom. These go into the π_{2p} bonding MOs, causing the bond order to increase to 2. The molecule is diamagnetic:

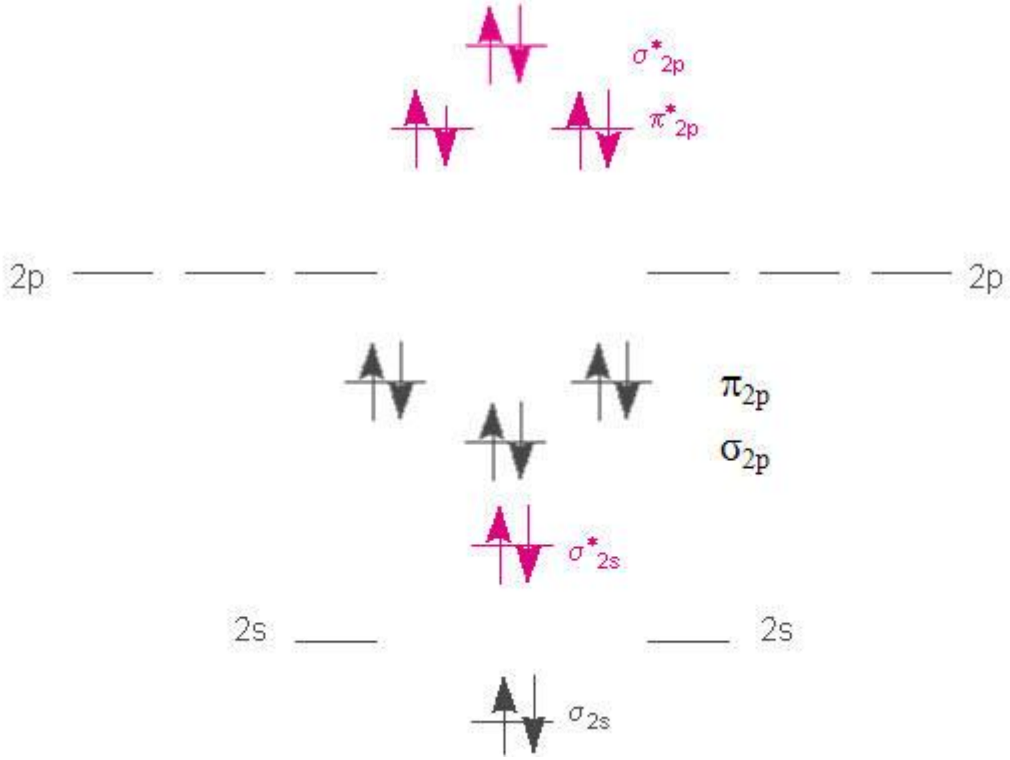


The F_2 molecule, for example, has a total of 14 valence electrons ($2s^2\ 2p^5$ from each F atom). These are placed in the MO's starting from the bottom up. Note that the π_{2p} and σ_{2p} orbitals have changed place (happens between N_2 and O_2):



The bond order is again 1, and we predict that F_2 is diamagnetic, since there are no un-paired electrons.

The third example is Ne_2. We expect that this will not exist, since we refer to Neon as being a Noble or Inert gas. The MO diagram looks like:



We see that the bond order = (8-8)/2 = 0, and so the molecule Ne_2 does not exist.

Relationship to Bond Length and Energy

In general, as the bond order increases, the bond gets shorter and stronger because the number of bonding electrons is increasing, or the number of antibonding electrons in decreasing.

For instance, compare B_2 and B_2^+ in terms of bond length, energy, and magnetic properties

B_2 (as shown above) has a bond order of 1, and the HOMO is the π_{2p} MO, i.e. a bonding MO. If we positively ionize B_2, we must remove an electron from the HOMO. This will cause the bond order to decrease. B_2^+ will therefore have a longer and weaker bond than B_2. Both are paramagnetic becauser both contain at least one unpaired electron

Do the same for Ne_2 and Ne_2^+.

Ne_2 has a bond order of zero and does not exist. However, Ne_2^+ would have a bond order of 0.5 because the electron removed would have been in the σ^*_{2p} MO, increasing the bond order. Furthermore, Ne_2^+ would be paramagnetic.