LECTURE 13. MOLECULAR ORBITAL THEORY

We use molecular orbital (MO) theory to actually explain chemical bonding. MO theory is superior to VSEPR and VB which focus only on the central atom; they cannot explain resonance and they do not actually explain what a molecular orbit *is*.

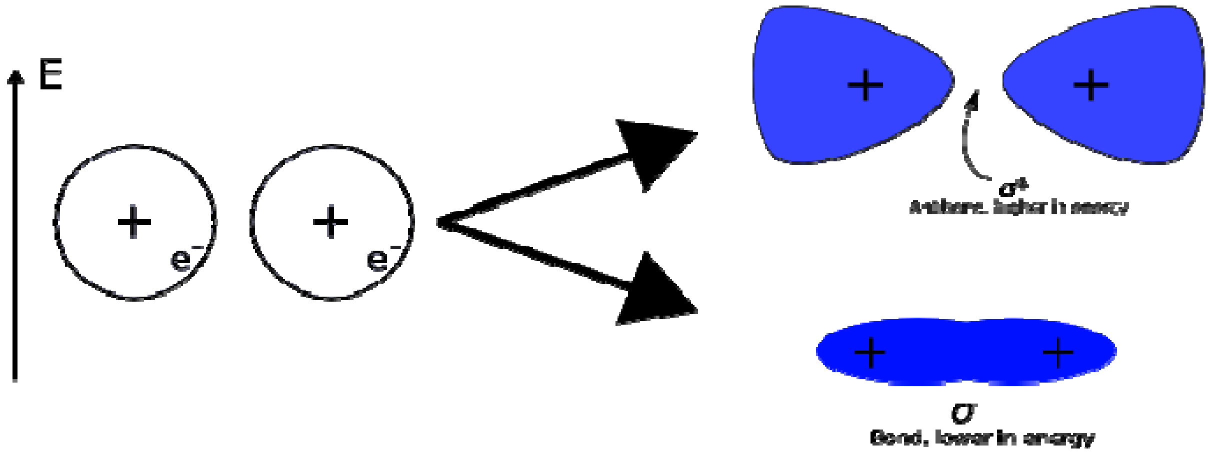
MO theory will allow us to do the following:

- Predict the existence of bonds.
- Rank energy and bond length.
- Predict paramagnetism.
- Explain resonance.

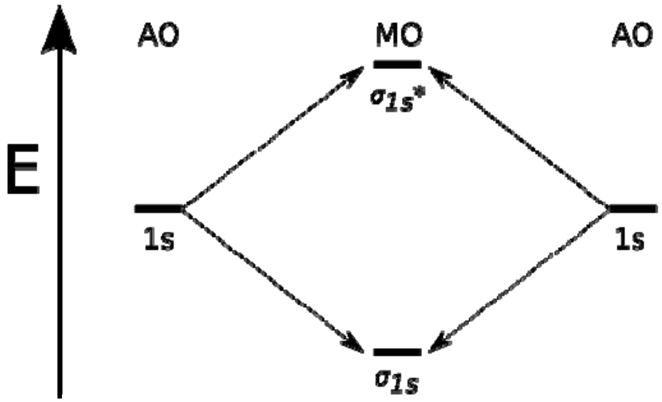
MO theory is complex, so we will look only at the simple case of diatomic molecules such as H_2, O_2, N_2, CO, and HF.

Recall that bonds are formed from overlap of electron cloud density from two atomic orbitals. The bond that is formed is a molecular orbital and to this point, we have simply called them σ and π bonds using VB theory.

In contrast, according to MO theory, we can view bonding in a more sophisticated manner by assuming atomic orbits overlap to form either an antibond or a bond, which look like the following:

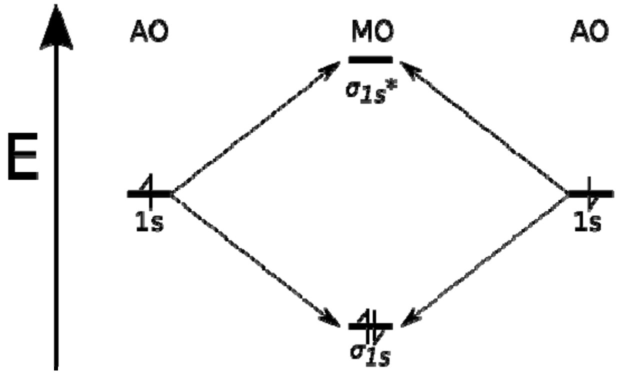


Redrawing this in the form of electronic orbits as seen in early lectures on atomic orbits.

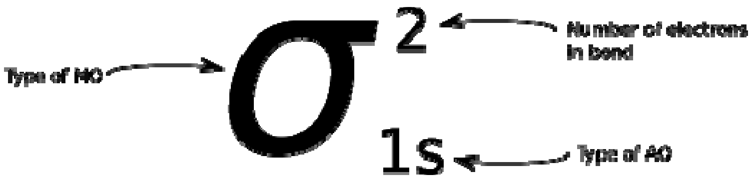


MO Theory gives us H_2

Now as applied to the formation of a bond between two Hs, they combine to make H_2:

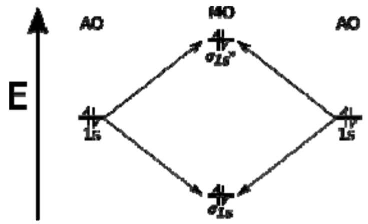


We describe the above bond using the symbol



MO Theory gives us He_2

Now for another example, let's see what happens with two He atoms:



However, the bond and antibond cancel each other, and so He_2 is not formed.

Bond Order

A simple way to determine from MO theory whether or not a bond forms is by using bond order (b.o.) Simply put,

If b.o. = 0, no bond forms;
If b.o. > 0, there is a bond.

where we define the bond order as

$$b.o. = \frac{\left(\sum \left(bonding\ electrons\right) - \sum \left(antibonding\ electrons\right)\right)}{2}$$

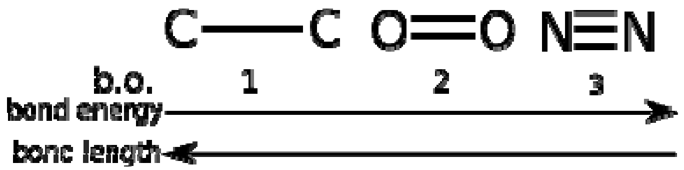
If b.o. = 1, there is a single bond; if b.o. = 2, there is a double bond; and if b.o. = 3, then there is a triple bond.

We see then, that for H_2, b.o. = (2 – 0)/2 = 1, implying that H_2 is single bonded.

For He_2, b.o. = (2 – 2)/2 = 0, meaning that He_2 does not exist.

The Length and Energy of Bonds from MO Theory

Bond order can also tell us about bond length and bond energy ranking. The larger the bond order, the stronger the bond and the shorter the bond length. This is illustrated schematically below:



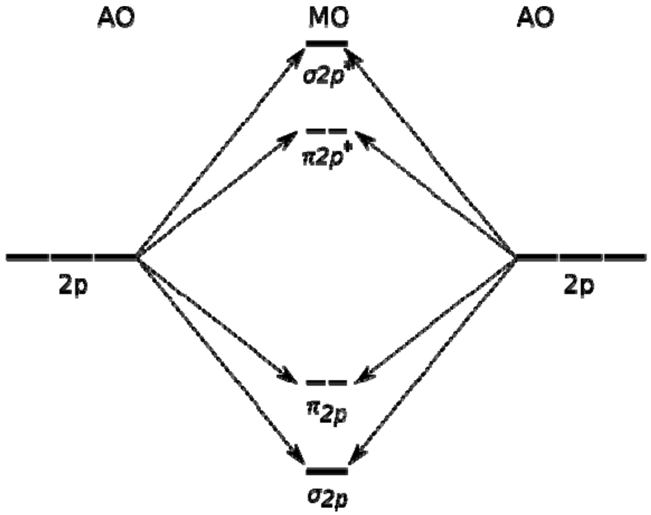
In the case above, N_2 is has both the highest energy bond and the shortest bond length because the bond order is the largest.

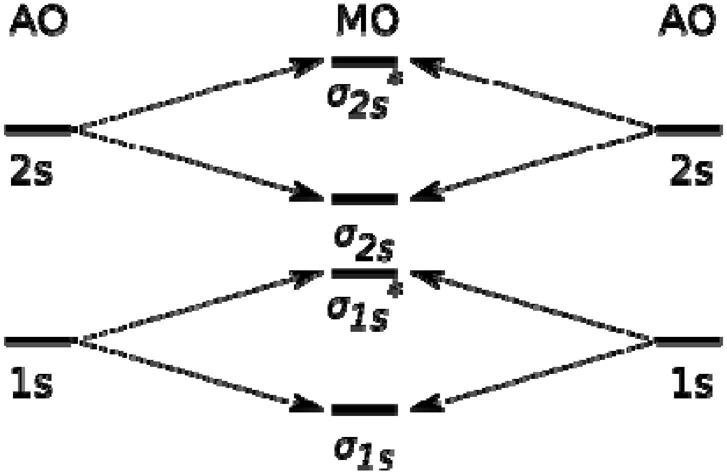
Paramagnetism

It turns out the magnets form from unpaired electrons. This means that any time we draw an atomic or molecular orbit, if we see a single unpaired electron, we are looking at a magnet. You will see then, that something like B_2, in which the electrons do not pair up in the π MOs, is paramagnetic. O_2, which has unpaired electrons in the antibonding π MOs, is also observed experimentally to be a magnet.

Creating MOs for all homonuclear diatomics.

Beyond He_2, we can continue to fill the bonding and antibonding orbits of all the n=2 row elements that form diatomic compounds.



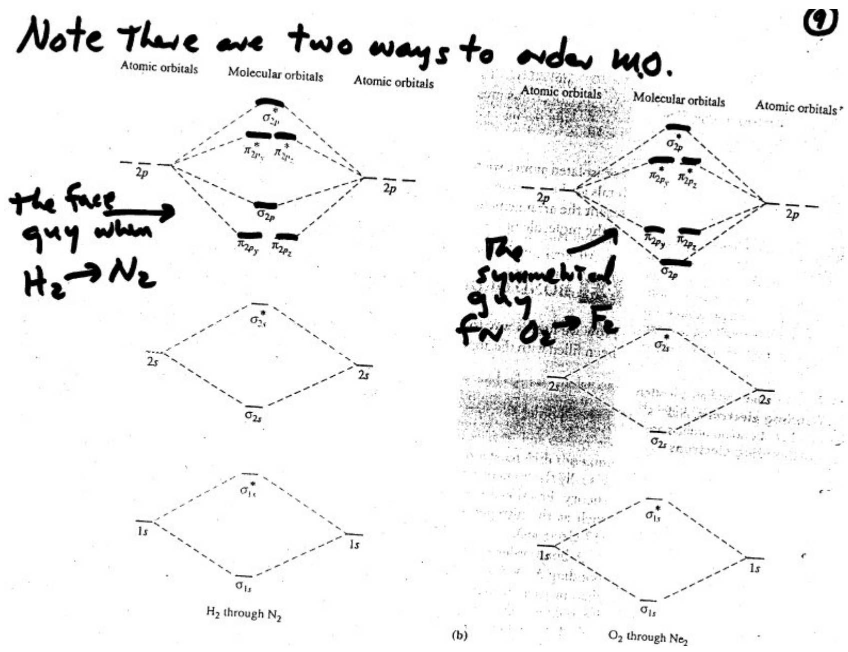


Some things to notice from the MO energy level charts above:

1. For every AO, there is a MO.
2. For every bonding MO, there is an antibonding MO.

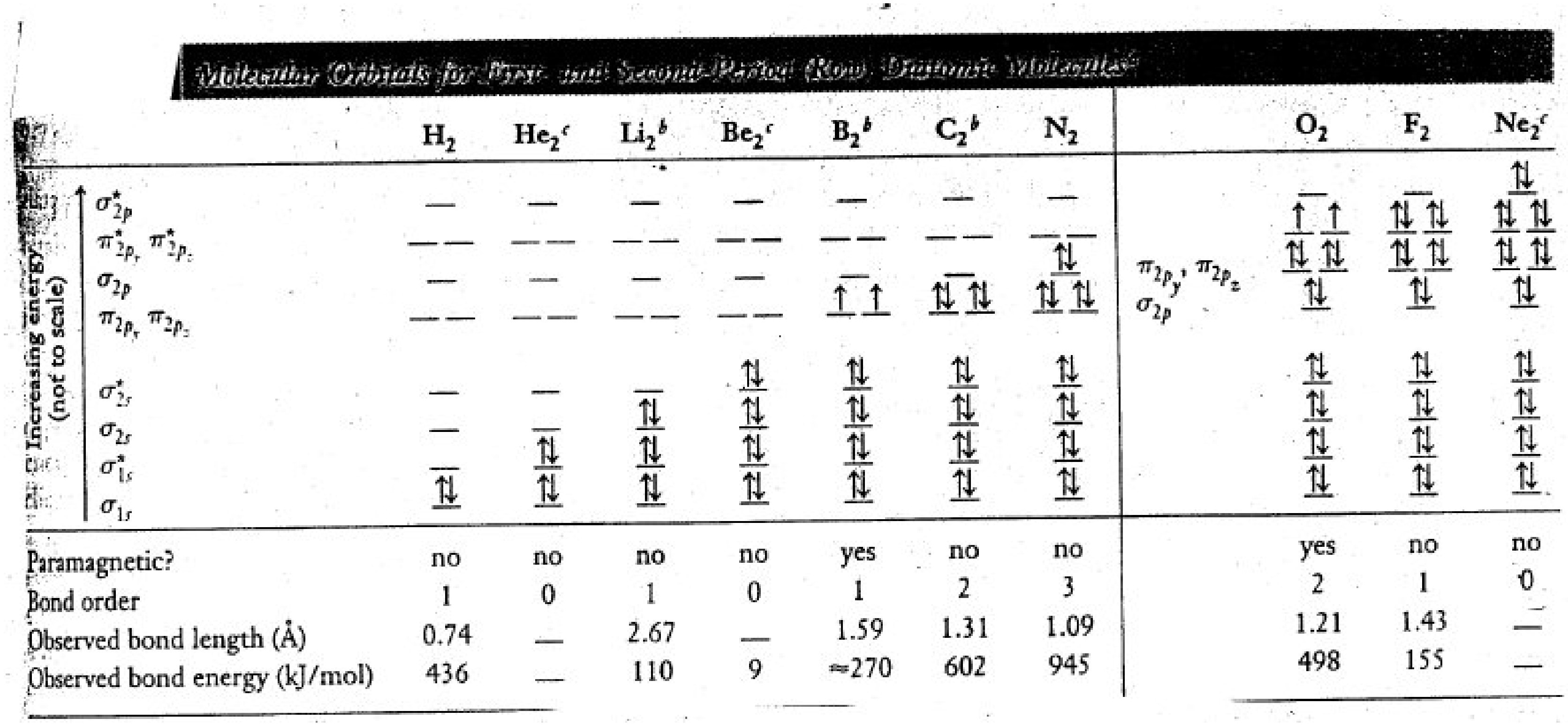
3. The 6 2p AO make 6 MO: Two sigmas (bonding and antibonding), and 4 pis (one bonding and one antibonding on the *x* axis, and one bonding and one antibonding on the *y* axis).
4. The reason for one sigma for every two pi bonds is the same as the reason discussed with VB theory. That is, it is because there are two axes for the pi bonds to occur on.

There is one other complication for the diatomic atoms in the second row. The energy levels of the molecular orbits that form change for the larger diatomic compounds. Note the for $H_2 \rightarrow N_2$ the order on the left is used. For the $O_2 \rightarrow Ne_2$, the MO order on the right is used.



The greatest table ever:

Presented below is a table of MO data for all the homonuclear diatomic molecules. Note that the table presents the order in which the MOs fill and also provides experimental data that confirms how the bond order for each compound corresponds to concepts like magnetism, bond length and bond energy. The table also shows the reordering of the MOs for the larger diatomic compounds. Learn this table cold and you will be able to handle 90% of MO theory in this class.



Molecular Orbitals for First- and Second-Period (Row) Diatomic Molecules[a]

Increasing energy (not to scale)	H_2	He_2[c]	Li_2[b]	Be_2[c]	B_2[b]	C_2[b]	N_2		O_2	F_2	Ne_2[c]
σ^*_{2p}	—	—	—	—	—	—	—		—	—	⇅
$\pi^*_{2p_y}, \pi^*_{2p_z}$	— —	— —	— —	— —	— —	— —	— —		↑ ↑	⇅ ⇅	⇅ ⇅
σ_{2p}	—	—	—	—	—	—	⇅	π_{2p_y}, π_{2p_z}	⇅ ⇅	⇅ ⇅	⇅ ⇅
π_{2p_y}, π_{2p_z}	— —	— —	— —	— —	↑ ↑	⇅ ⇅	⇅ ⇅	σ_{2p}	⇅	⇅	⇅
σ^*_{2s}	—	—	—	⇅	⇅	⇅	⇅		⇅	⇅	⇅
σ_{2s}	—	—	⇅	⇅	⇅	⇅	⇅		⇅	⇅	⇅
σ^*_{1s}	—	⇅	⇅	⇅	⇅	⇅	⇅		⇅	⇅	⇅
σ_{1s}	⇅	⇅	⇅	⇅	⇅	⇅	⇅		⇅	⇅	⇅
Paramagnetic?	no	no	no	no	yes	no	no		yes	no	no
Bond order	1	0	1	0	1	2	3		2	1	0
Observed bond length (Å)	0.74	—	2.67	—	1.59	1.31	1.09		1.21	1.43	—
Observed bond energy (kJ/mol)	436	—	110	9	≈270	602	945		498	155	—

Heteronuclear diatoms.

The text spends considerable time developing more complicated cases for MOs. One example is the heteronuclear diatomic compound. Without going into too much depth, there is something to be learned from these cases simply by following the rules for homonuclear cases and simply adding the total number of atomic orbital electrons, and then filling the MOs. For example, HF has 10 electrons and CO with 14 electrons can have MOs formed simply by following Aufbau, Pauli and Hund and filling MOs as above. The energy levels with not be correct, but concepts like bond order and paramagnetism are still applicable.