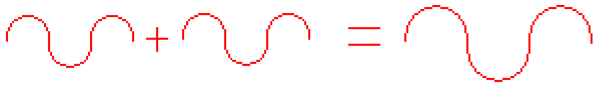
Molecular Orbital Theory

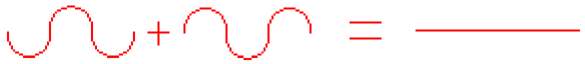
1. Orbitals are wave functions. One property of waves is that they can constructively or destructively interfere with each other.

2. What is constructive interference?



When two waves constructively interfere the resultant wave has an increased amplitude.

3. What is destructive interference?



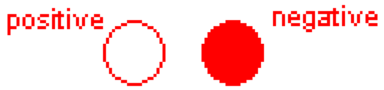
When two waves destructively interfere they basically cancel each other out.

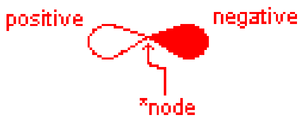
4. How does this relate to our understanding of orbital interactions?

Just as waves have a positive phase  and negative phase  - so do orbitals.

s orbital phases:

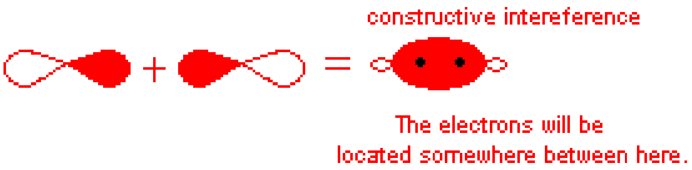
p orbitals phase



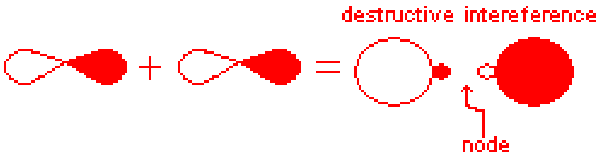


* a node is a location where there can be no electrons.

When orbitals of the same phase interact with each other a bond forms. The electrons are located, primarily, between the two nuclei of each atom.



When orbitals of different phases interact with each an “anti-bond” occurs. There is a node between the two nuclei of the atoms.



5. What is Molecular Orbital Theory?

In this theory the atomic orbitals of *different* atoms are combined to make new bonding orbitals called molecular orbitals.

6. Facts about molecular orbitals?

a. Molecular orbitals can hold up to $2e^-$ with opposite spin.

b. (Molecular Orbital)^2 = 90% probablility of finding e^- within orbital.

c. Only Molecular Orbitals exist after combining, no atomic orbitals.

d. Molecular orbitals can be used to electron configuration for molecules.

e. # of atomic orbitals used = # of molecular orbitals formed.

f. When atomic orbitals interact they can do so constructively and destructively.

g. Constructive interference produces bonding molecular orbitals that are lower in energy than the atomic orbitals contributors.

h. Destructive interference produces anti-bonding molecular that are higher in energy than the atomic orbital contributors.

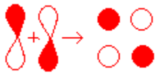
i. Generally sigma bonds are lower in energy than pi bonds.

7. Why do bonds occur?

The energy of the atoms combined is lower than the sum of all their energies independent from one another.

8. Fill in the following chart

Atomic Orbitals Molecular Orbitals

Orbital combination	**Visual Depiction**	**Resulting Bond Type**	**Energy Relative to AOs**
$s + s$		σ_s	Lower
$s - s$		σ^*_s	Higher
$s + p_z$		σ_{s+p}	Lower
$s - p_z$		σ^*_{s+p}	Higher
$p_z + p_z$		σ_p	Lower
$p_z - p_z$		σ^*_p	Higher
$p_x + p_x$		π_p	Lower
$p_x - p_x$		π^*_p	Higher
$p_y + p_y$		π_p	Lower
$p_y - p_y$		π^*_p	Higher

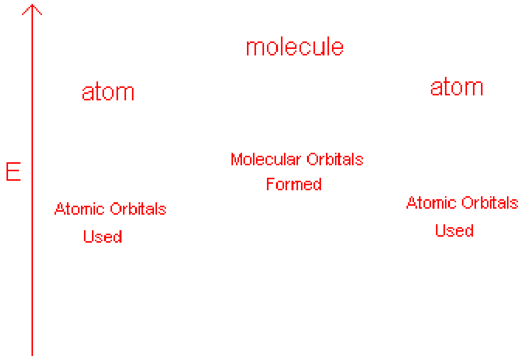
Degenerate

Degenerate

Remember that degeneracy is when orbitals are at the same energy level.

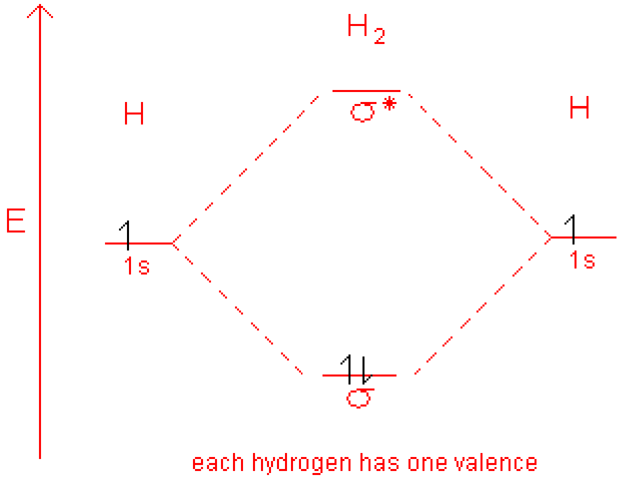
9. What is a Molecular Orbital Diagram?

A diagram that shows which atomic orbitals are being contributed to by the atoms and what molecular orbitals they will form. Additionally it indicates the relative energy level of all orbitals.



10. Draw the Molecular Orbital Diagram

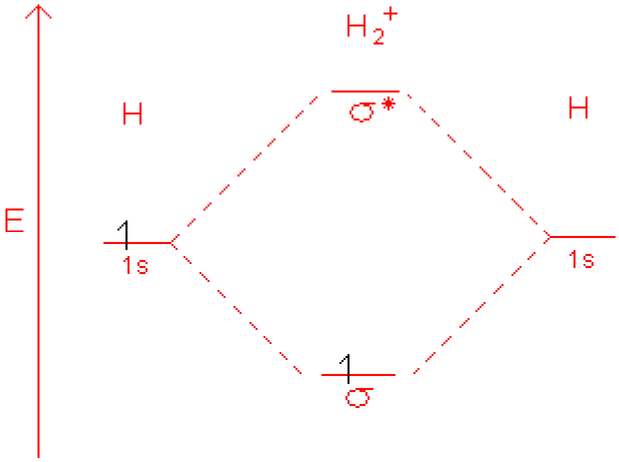
a. H_2



each hydrogen has one valence electron which is contributed to the new molecular orbital.

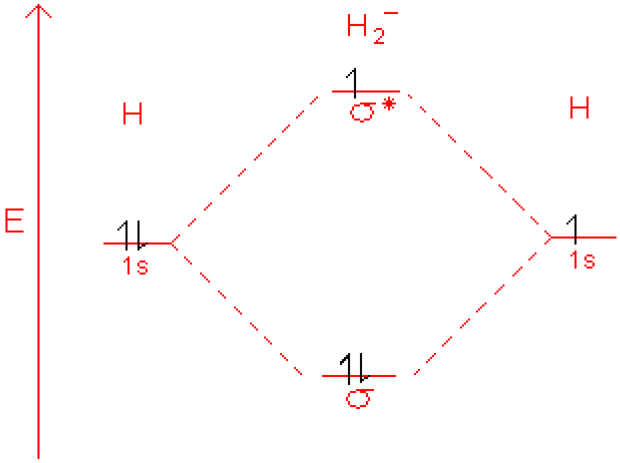
When filling in the diagram always fill in lowest available molecular orbital first.

b. H_2^+



In this case the molecule being formed is H_2^+. The positive charge indicates that one electron has been lost – thus only one electron will be contributed. It does not matter which hydrogen you leave as the electron contributor.

c. H_2^-



In this case the molecule being formed is H_2^-. The negative charge indicates that an extra electron has been gained – thus three electrons are being contributed. It doesn't matter which hydrogen you add the electron to.

11. What is bond order?

Bond order indicates the relative strength/stability of a bond.

$$\uparrow\text{Bond Order}, \quad \uparrow\text{Strength}, \quad \uparrow\text{Stability}$$

The formula for determining the bond order of a compound is:

$$\text{Bond Order} = \frac{(\text{\# of bonding } e^-) - (\text{\# of antibonding } e^-)}{2}$$

12. Some facts about bond order:

    a. A bond order of zero indicates that the compound does not exist.

    b. The bond order typically corresponds to the type of bond present.
    i.e.
    Bond order = 1 indicates a single bond
    Bond order = 2 indicates a double bond
    Bond order = 3 indicates a triple bond

13. What do the bond orders for #41 tell us about relative stabilities of H_2, H_2^+, H_2^-?

$H_2 = (2 - 0) / 2 = 1$ $H_2^+ = (1\text{-}0)/2 = ½$ $H_2^- = (2\text{-}1)/(2) = ½$

Based on these bond orders we can see that H_2 is the most stable compound.

14. Paramagnetic substances have unpaired electrons and are therefore attracted toward a magnetic field.
Diamagnetic substances have paired electrons and are therefore repelled by a magnetic field.

15. What is the order of molecular orbitals for B_2, C_2 and N_2?

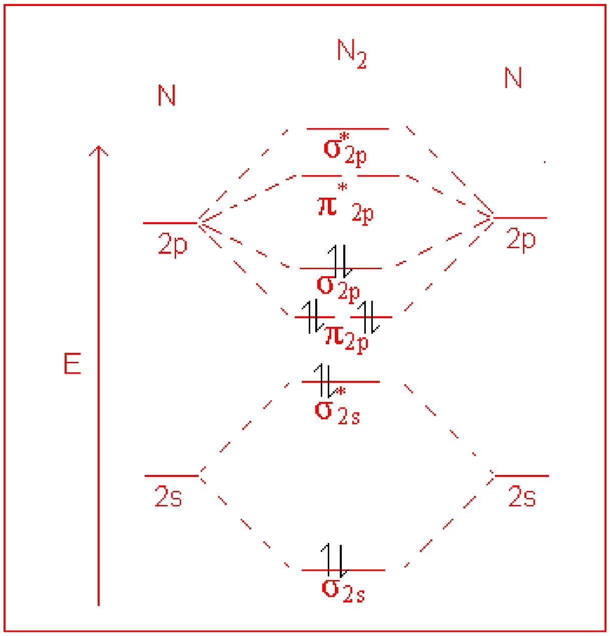
$$\sigma_{2s}\ \sigma^{*}_{2s}\ \pi_{2p}\ \sigma_{2p}\ \pi^{*}_{2p}$$

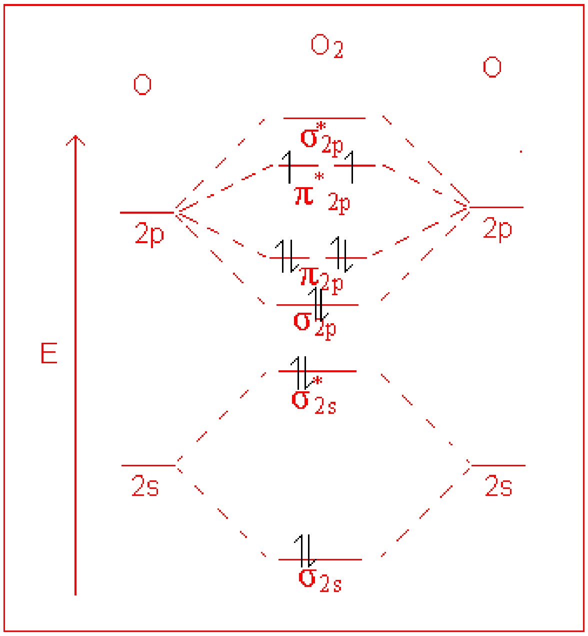
Remember that there are 2 degenerate orbitals in both the π and π^*. Thus there are a total of 4 electrons that are contained within the π orbitals.

16. What is the order of molecular orbitals for O_2 and F_2?

$$\sigma_{2s}\ \sigma^{*}_{2s}\ \sigma_{2p}\ \pi_{2p}\ \pi^{*}_{2p}$$

17. Draw the Molecular orbital diagrams for N_2 and O_2.





18. Why do B_2, C_2 and N_2 have a different MO order compared to O_2 and F_2?

π_{2p} is lower in energy for B_2, C_2 and N_2 because of e^- repulsion σ_{2p} has with σ_{2s}. Additionally there is some s/p orbital mixing that changes energies.

σ_{2p} is lower in energy because as protons are added the 2s orbital diminishes in size such that the e^- repulsion is minimalized.

19. Write out the MO electron configuration for each.

N_2^{2-}, O_2^{2-}, F_2^{2-}

N_2^{2-}:

$$\underbrace{(\sigma_{1s}^{2})(\sigma^{*}_{1s}{}^{2})}_{\text{core}}\ \underbrace{\sigma_{2s}^{2}\ \sigma^{*}_{2s}{}^{2}\ \pi_{2p}^{4}\ \sigma_{2p}^{2}\ \pi^{*}_{2p}{}^{2}}_{\text{valence}}$$

O_2^{2-}:

$$\underbrace{(\sigma_{1s}^{2})(\sigma^{*}_{1s}{}^{2})}_{\text{core}}\ \underbrace{\sigma_{2s}^{2}\ \sigma^{*}_{2s}{}^{2}\ \sigma_{2p}^{2}\ \pi_{2p}^{4}\ \pi^{*}_{2p}{}^{4}}_{\text{valence}}$$

F_2^{2-}:

$$\underbrace{(\sigma_{1s}^{2})(\sigma^{*}_{1s}{}^{2})}_{\text{core}}\ \underbrace{\sigma_{2s}^{2}\ \sigma^{*}_{2s}{}^{2}\ \sigma_{2p}^{2}\ \pi_{2p}^{4}\ \pi^{*}_{2p}{}^{4}\ \sigma^{*}_{2p}{}^{2}}_{\text{valence}}$$

* it is not necessary to include the core electrons as they don't particpate in the bond. Now and then you may run a cross cases where they have been included. Just follow whatever guidelines have been set out.

a. Which of the following is predicted to be the most stable diatomic species?

In order to determine this we will have to look at the bond orders of each molecule. You can look at all the electrons or just the valence electrons to determine the bond order – you will get the same answer using either method.

N_2^{2-}: using all electrons (10-6)/2 = 2 , gives the same answer as looking only at the valence electrons (8-4)/2 = 2.

O_2^{2-}: (8-6)/2 = 1

F_2^{2-}: (8-8)/2 = 0

Based on these bond order values we can determine that N_2^{2-} is the most stable of all the species. We can also determine that F_2^{2-} doesn't exist as it has a bond order equal to zero.

b. Indicate whether each is paramagnetic or diamagnetic.

In order to determine this, you will need to determine if the electrons in the last molecular orbital are paired up or not. If they are paired up, it is diamagnetic; if not, paramagnetic.

N_2^{2-} - paramagnetic
O_2^{2-}: diamagnetic
F_2^{2-}: paramagnetic

20. Use the MO model to predict the bond order and magnetism for Ne_2 and P_2.

Ne₂:

Because Ne comes after O and F on the periodic table, we will use their molecular orbital configuration.

$\sigma_{2s}^{2}\,\sigma_{2s}^{*\,2}\,\sigma_{2p}^{2}\,\pi_{2p}^{4}\,\pi_{2p}^{*\,4}\,\sigma_{2p}^{*\,2}$

Bond Order = (8-8)/2 = 0
This compound does not exist.

P_2:

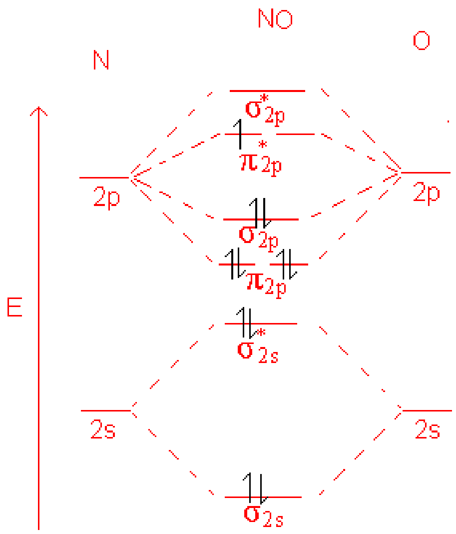
Because P is in the same family as N, we will use the B_2, C_2, N_2 configuration.

$\sigma_{3s}^{2}\ \sigma^{*}_{3s}{}^{2}\ \pi_{3p}^{4}\ \sigma_{3p}^{2}$

Bond Order = (8-2)/2 = 3

Diamagnetic

21. Complete the MO diagram for NO.

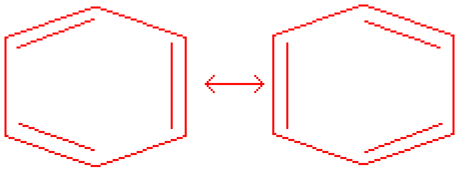


When creating the MO diagram for a molecule that has elements has B, C or N and O or F – default to the B, C, and N MO order. Notice that when using molecular orbital theory, there is absolutely no issue with an odd number of electrons, unlike Lewis.

22. How do we reconcile these two theories (i.e. LE and MO models)?

For simplicities sake we will view σ bonds as being localized (hybrid orbitals) and we will view π bonds through molecular orbital theory, in which the electrons are delocalized.

To better understand this, we will consider benzene, C_6H_6, a resonance structure.



In the combined view of localized σ bonds and delocalized π, the new depiction looks like: