

## CHEMISTRY 109 – Help Sheet #10

### Chemical Bonding (Part I): Molecular Orbital Theory

Do the topics appropriate for your lecture

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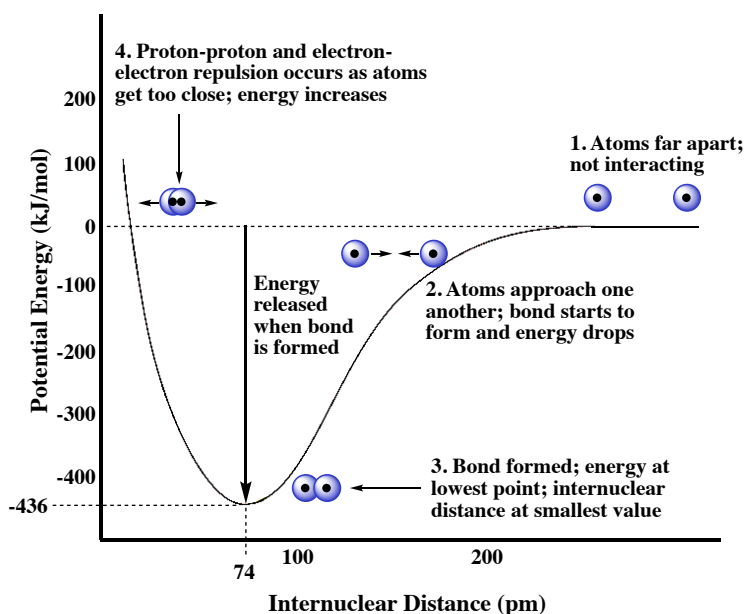
<https://clc.chem.wisc.edu> (Resources page)

**Nuggets:** Forming a Covalent Bond; Molecular Orbital Theory: MO Shapes; MO Diagram; Bond Order; MO  $e^-$  Configuration; Stability

**Form a Bond:** Shown below is the energy change as  $H_2$  forms a covalent bond. A covalent bond occurs when two orbitals overlap with two shared electrons of opposite spin in the overlap region. When the covalent bond is formed the overall energy of the system decreases as shown in the graph below. A covalent bond can also be expressed as:

$$\Psi_{\text{molecule } H_2} = \Psi_{\text{atom } H_A} + \Psi_{\text{atom } H_B}$$

where  $\Psi_{\text{atom } H_A}$  (an atomic wave function) is combined with  $\Psi_{\text{atom } H_B}$  (the wave function of the other atom) to yield  $\Psi_{\text{molecule } H_2}$  (the molecular wave function)

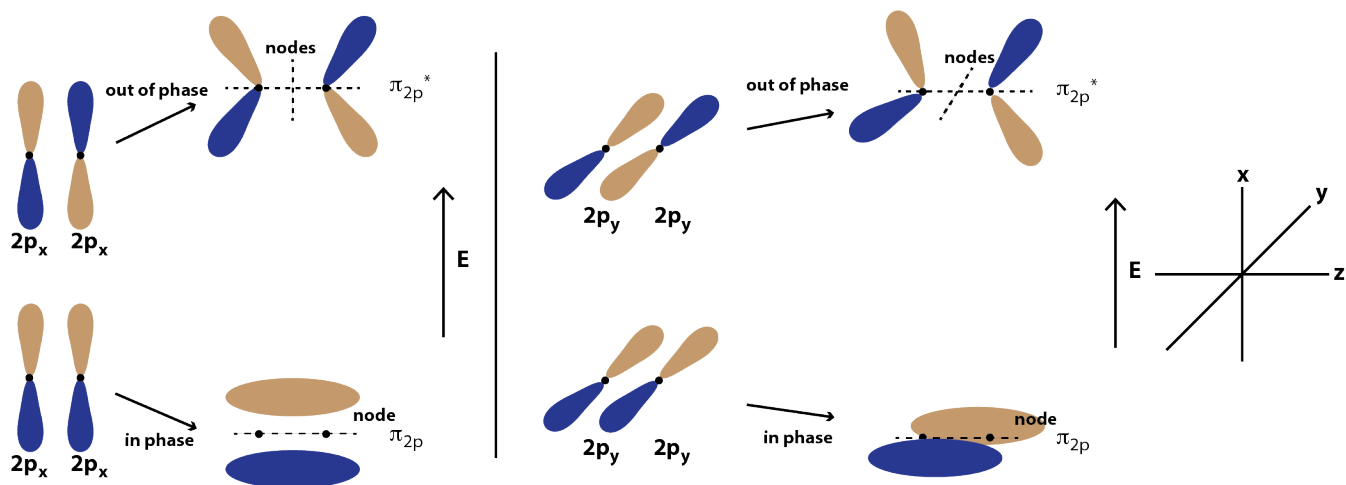
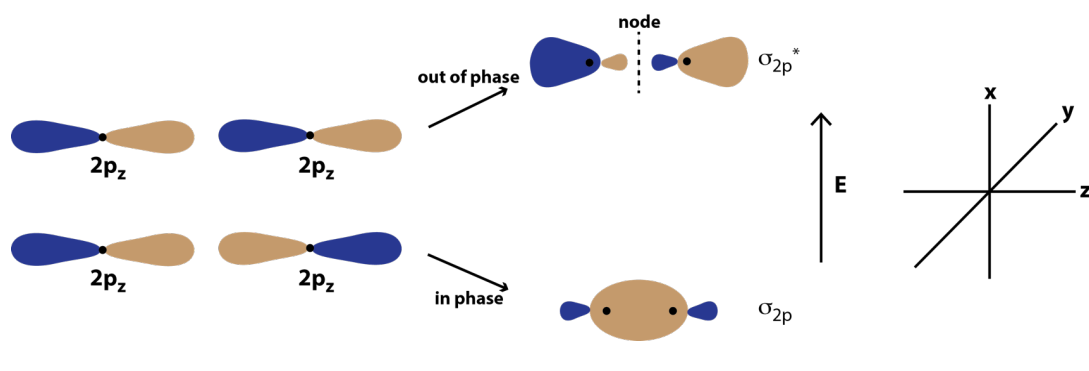
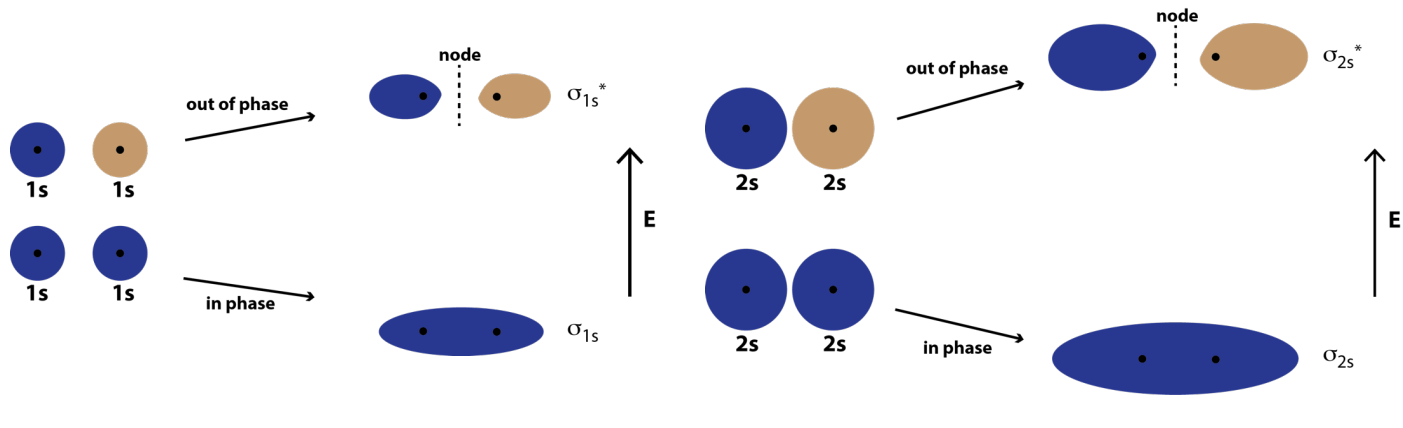


**MOLECULAR ORBITAL (MO) THEORY:** bonding model in molecules

- #MOs = #AOs (MO = molecular orbitals; AO = atomic orbitals).
- Each MO can hold 2 electrons with opposite spins.
- MOs can be localized on one atom, between atoms, or over multiple atoms.
- Lower energy MOs fill first and MOs follow Hund's rule when adding electrons.
- AOs overlap more effectively with other AOs that are close in energy.
- The energy of a MO increases with an increased number of nodes.

The MOs are generated by combining the AO wave functions in-phase or out-of-phase. *In-phase* combination creates lower energy orbitals called **bonding orbitals**, while *out-of-phase* combinations create higher energy orbitals called **anti-bonding orbitals**. The next diagram represents combining AOs with the two colors representing the two phases: If the *colors are the same*, the orbitals are *in-phase* and create a lower-energy molecular orbital; if the *colors are different* the orbitals are *out-of-phase* and create a higher-energy molecular orbital. When 2 AOs are combined they will generate 2 MOs: one bonding and one anti-bonding.

## MOLECULAR ORBITAL SHAPES - z-axis is internuclear axis



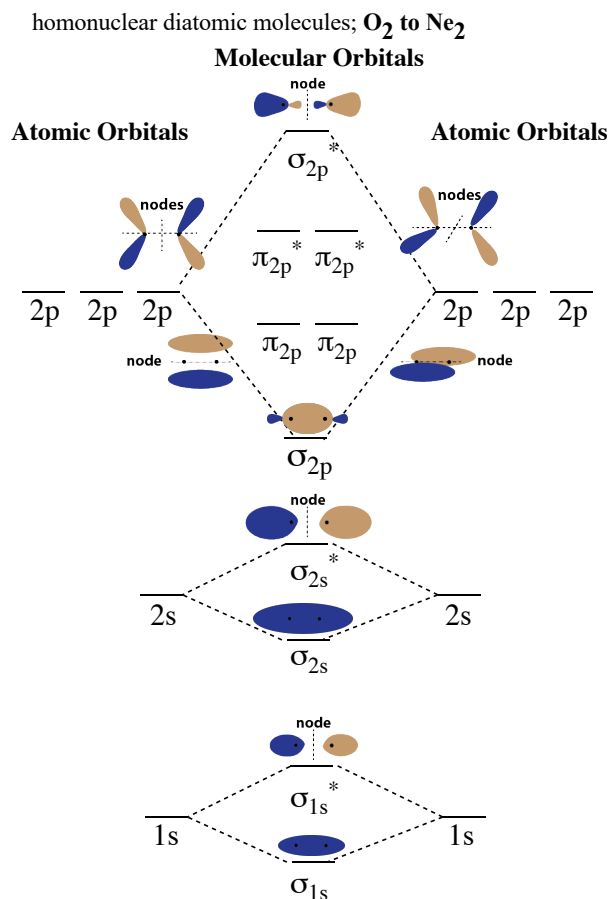
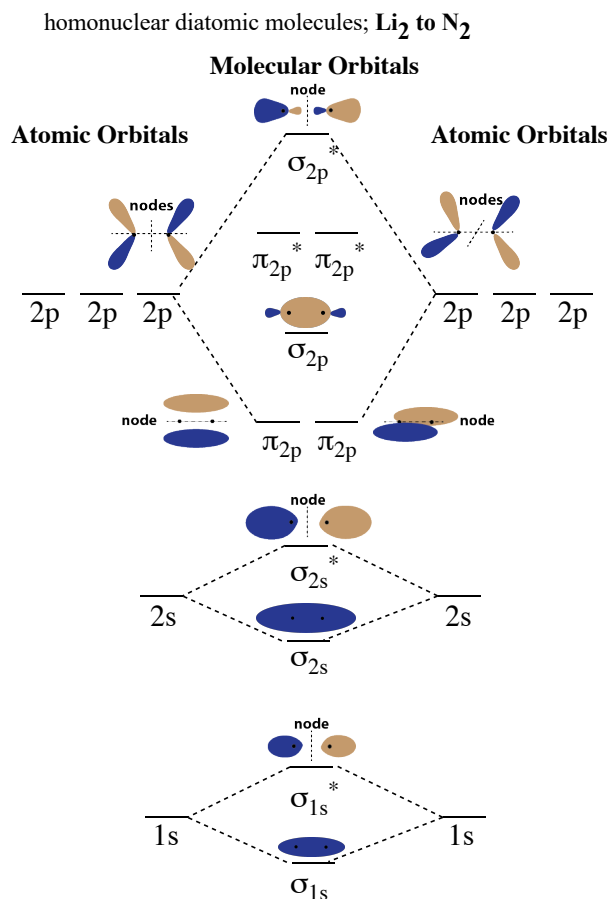
**Sigma ( $\sigma$ ) Bonds:** The bonds/electrons *lie* on the internuclear axis directly *between* the nuclei of the two atoms. Sigma bonds can rotate.

**Pi ( $\pi$ ) Bonds:** Bonds/electrons *do not lie* on the internuclear axis and instead lie *above* and *below* the internuclear axis. Pi ( $\pi$ ) bonds *occur with double or triple bonds*. One p-orbital from each atom is used to make the pi ( $\pi$ ) bond and are made from the *side-to-side* overlap of two p-atomic orbitals. Pi bonds *cannot rotate* as this would require the  $\pi$  bond to break.

From the MOs generated on the prior page, the following two Molecular Orbital Diagrams are created:

### MO DIAGRAMS

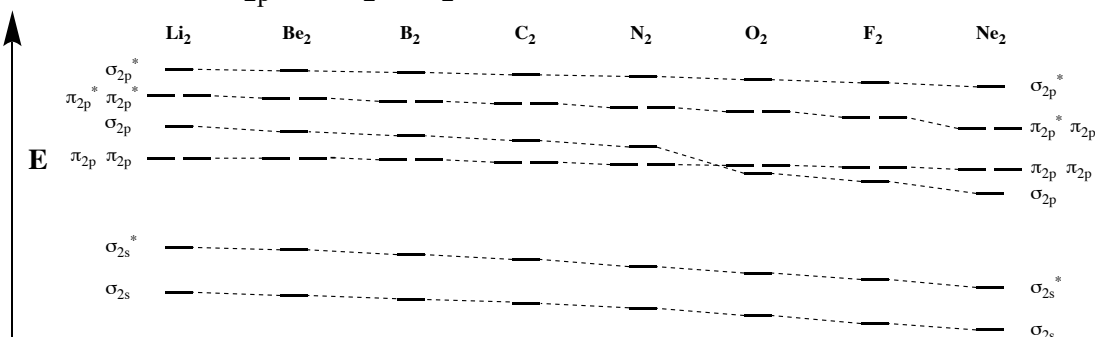
(often only valence electrons are included in a MO diagram; your course will clarify if all or just valence electrons should be included)



(note how the  $\sigma_{2p}$  and  $\pi_{2p}$  molecular orbitals are switched compared to the other MO diagram)

(Skip this paragraph and diagram if not covered!) Shown below are the MO diagrams of the homonuclear diatomic elements in the 2nd period,  $\text{Li}_2$  to  $\text{Ne}_2$  (no AOs are shown).

- First note how the **overall energy of the MO decrease** from  $\text{Li}_2$  to  $\text{Ne}_2$ . This gradual decrease in energy is primarily the result of the increasing  $Z_{\text{eff}}$  as you proceed left-to-right across the period.
- Second note how the  $\text{Li}_2$  to  $\text{N}_2$  MO diagrams differ from the  $\text{O}_2$  to  $\text{Ne}_2$  MO diagrams; the  $\sigma_{2p}$  is above the  $\pi_{2p}$  MO in the  $\text{Li}_2$  to  $\text{N}_2$  MO diagrams and below the  $\pi_{2p}$  in the  $\text{O}_2$  to  $\text{Ne}_2$  MO diagrams. See below for more information.



This switch of the  $\pi_{2p}$  and  $\sigma_{2p}$  MOs relative to one another is due to *s-p mixing* which occurs when the s-orbital and p-orbitals are similar in energy. The p-orbitals for Li to N are lower and similar in energy to the s-orbitals; this allows the  $\sigma_{2s}$  and  $\sigma_{2p}$  wave functions to interact and raise the relative energy of the  $\sigma_{2p}$  MO above the  $\pi_{2p}$  MO. For O to Ne, the energy of the p-orbitals are higher because of the energy needed to pair p-electrons, and therefore the p-orbitals are not similar in energy to the s-orbital and no  $\sigma_{2s}$  and  $\sigma_{2p}$  wave function interactions occur.

## MO ELECTRON CONFIGURATION - Ordering of filling of the molecular orbitals

The 1st energy level is filled as  $(\sigma_{1s})^2(\sigma_{1s}^*)^2$  while the

2nd energy level is filled as  $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2(\pi_{2p}^*)^4(\sigma_{2p}^*)^2$  (for elements from  $\text{Li}_2$  to  $\text{N}_2$ )

2nd energy level is filled as  $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^4(\sigma_{2p}^*)^2$  (for elements from  $\text{O}_2$  to  $\text{Ne}_2$ )

The superscripts represent the maximum number of  $e^-$  that can reside in the MO; the \* designates an *antibonding orbital*; those *without* an \* are *bonding orbitals*; the subscript describes the AOs used to generate the MO with the  $\sigma$  or  $\pi$  describing the type of MO formed.

**BOND ORDER (BO):** strength of a bond; range: 0 to 3; if  $\text{BO} > 0 \rightarrow$  molecule stable and theoretically exists

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

#total $e^-$	20	19	18	17	16	15	14	13	12	11	10	9	8	7	6	5	4	3	2	1
BO	0	1/2	1	1 1/2	2	2 1/2	3	2 1/2	2	1 1/2	1	1/2	0	1/2	1	1 1/2	2	2 1/2	3	4

total  $\#e^-$  = valence + core  $e^-$ ; total  $\#e^- = 4e^-$ ,  $8e^-$ , and  $20e^- \rightarrow \text{BO} = 0$  and molecule doesn't exist!  $14e^- \rightarrow \text{BO} = 3$  (maximum);

**Paramagnetic:** At least one unpaired  $e^-$ . This molecule will show magnetic properties.

**Diamagnetic:** All  $e^-$  are paired. This molecule shows no magnetic properties.

**Example 1:** a. Draw a MO Diagram for  $\text{C}_2^+$ ; include both core and valence  $e^-$ . (Note: Sometimes only valence electrons are drawn.)

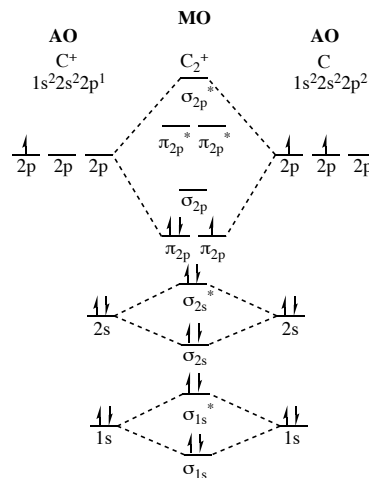
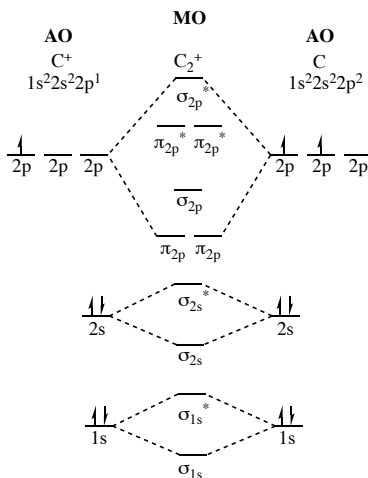
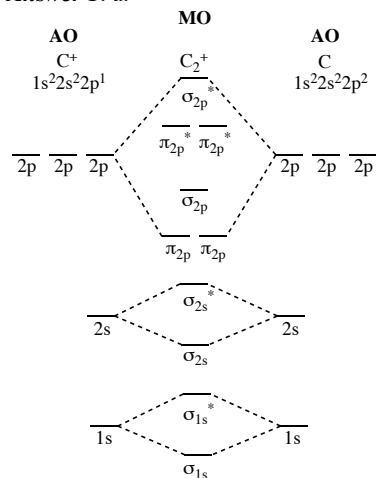
b. Write the MO electron configuration (use only valence  $e^-$ ).

c. Determine the bond order for  $\text{C}_2^+$ .

d. Is this molecule stable?

e. Is this molecule paramagnetic or diamagnetic?

**Answer 1:** a.



Draw an empty MO diagram showing MOs and AOs. Write the molecule and split the molecule into 2 parts (C and C); distribute the charge (+ for one, neutral for the other); write electron configuration (e.g.,  $1s^2 2s^2 2p^1$ ).

Fill in the electrons in the AOs; follow Hund's Rule.

**This diagram is the answer!**  
Using the electrons from the AOs fill in the electrons in the MOs; follow Hund's Rule.

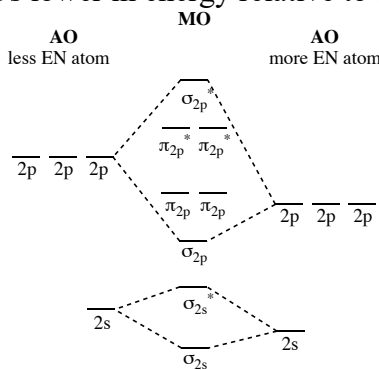
b. Write MO electron configuration right from the diagram:  $\sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p}^3$  [if all electrons (valence and core) were asked for in the MO electron configuration, it would then be:  $\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p}^3$ ]

c.  $\text{BO} = \frac{\# \text{bonding } e^- - \# \text{antibonding } e^-}{2}$ ;  $\text{BO} = \frac{5-2}{2} = 1.5$

d. since  $\text{BO} > 0 \rightarrow$  stable molecule

e. paramagnetic since there is an unpaired electron

**Heteronuclear Diatomic Molecules** (*skip if not covered*) – 2 different atoms with different electronegativities (EN); the more EN atom will have its AOs lower in energy relative to the AOs of the less EN atom



1. Write the MO  $e^-$  configuration for the following real and theoretical molecules (include only valence  $e^-$ ). Which are paramagnetic? What is the bond order for each of these molecules? Is the molecule stable?

a.  $H_2$    b.  $N_2$    c.  $F_2$    d.  $O_2$    e.  $C_2$    f.  $B_2$    g.  $O_2^-$    h.  $Li_2^+$

2. Which molecule has the greatest bond order?

a.  $N_2^{+2}$                       b.  $O_2^-$                       c.  $O_2^{+2}$                       d.  $N_2^{-2}$                       e.  $N_2^-$

3.  $He_2$  doesn't exist naturally. Using MO theory, explain why.

4. a. Draw the MO diagram for  $B_2^{-2}$ ; include the valence electrons in both the atomic and molecular orbitals.

b. From your diagram, predict the magnetic behavior of  $B_2^{-2}$  in a magnetic field.

c. Determine the bond order and predict whether this molecule would be stable.

d. Write the molecular electronic configuration for the molecule (use both core and valence electrons).

e. What occurs to the bond length relative to the original  $B_2^{-2}$  when 1  $e^-$  is removed from this molecule?

5. a. Draw the MO diagram for  $O_2$ ; include the valence electrons in both the atomic and molecular orbitals.

b. From your diagram, predict the magnetic behavior of  $O_2$  in a magnetic field.

c. Determine the bond order and predict whether this molecule would be stable.

d. Write the molecular electronic configuration for the molecule (use both core and valence electrons).

e. What occurs to the bond strength relative to the original  $O_2$  bond strength when 1 electron is added?

## ANSWERS

1. a.  $(\sigma_{1s})^2$ , diamagnetic,  $BO = \frac{\# \text{bonding } e^- - \# \text{antibonding } e^-}{2}$ ;  $BO = \frac{2-0}{2} = 1.0$ , stable

b.  $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2$ , diamagnetic,  $BO = \frac{8-2}{2} = 3.0$ , stable

c.  $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^4$ , diamagnetic,  $BO = \frac{8-6}{2} = 1.0$ , stable

d.  $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^2$ , paramagnetic,  $BO = \frac{8-4}{2} = 2.0$ , stable

e.  $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4$ , diamagnetic,  $BO = \frac{6-2}{2} = 2.0$ , stable

f.  $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^2$ , paramagnetic,  $BO = \frac{4-2}{2} = 1.0$ , stable

g.  $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^3$ , paramagnetic,  $BO = \frac{8-5}{2} = 1.5$ , stable

h.  $(\sigma_{2s})^2(\sigma_{2s}^*)^1$ , paramagnetic,  $BO = \frac{2-1}{2} = 0.5$ , stable

2. c {  $BO = \frac{\# \text{bonding } e^- - \# \text{antibonding } e^-}{2}$ ; "c":  $O_2^{+2}$  has  $14e^-$  total ( $O_2^{+2}$ :  $8 + 8 - 2 = 14e^-$ ); using the table on page 2 of this

HelpSheet:  $14e^-$  has  $BO = 3$ ;

"a":  $N_2^{+2}$  has  $12e^-$  total; using the table on page 2 of this HelpSheet:  $12e^-$  has  $BO = 2.0$ ;

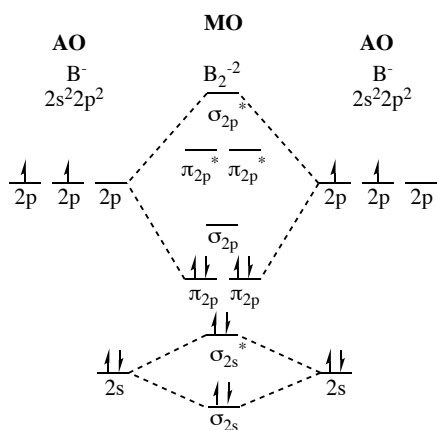
"b":  $O_2^-$  has  $17e^-$  total; using the table on page 2 of this HelpSheet:  $17e^-$  has  $BO = 1.5$ ;

"d":  $N_2^{-2}$  has  $16e^-$  total; using the table on page 2 of this HelpSheet:  $16e^-$  has  $BO = 2.0$ ;

"e":  $N_2^-$  has  $15e^-$  total; using the table on page 2 of this HelpSheet:  $15e^-$  has  $BO = 2.5$ }

3. The MO  $e^-$  configuration is  $(\sigma_{1s})^2(\sigma_{1s}^*)^2$ . The  $BO = (2 - 2)/2 = 0$ . Hence, it should not form.

4.



a.

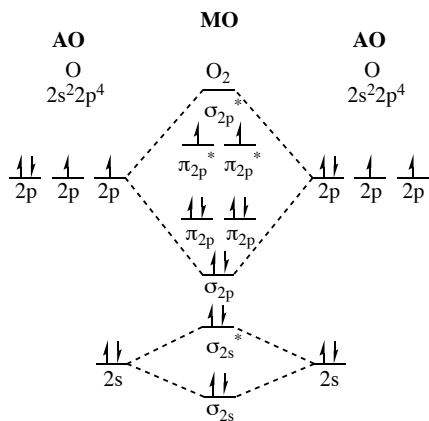
b. all  $e^-$  paired  $\rightarrow$  diamagnetic

c.  $BO = \frac{6-2}{2} = 2.0 \rightarrow BO > 0 \rightarrow$  molecule stable

d.  $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4$

e. the electron is being removed from a bonding orbital  $\rightarrow$   $BO \downarrow \rightarrow$  bond length increases

5.



a.

b. 2 unpaired  $e^- \rightarrow$  paramagnetic

c.  $BO = \frac{8 - 4}{2} = 2.0 \rightarrow BO > 0 \rightarrow$  molecule stable

d.  $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^2$

e. the electron added goes into an antibonding orbital  $\rightarrow$   $BO \downarrow \rightarrow$  the bond strength decreases