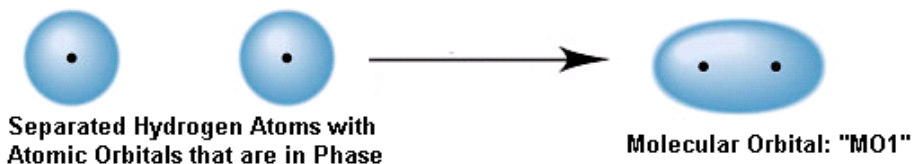


*ALE 16. Molecular Orbital Theory for Diatomic Molecules*(Reference: 11.3- *Silberberg 5<sup>th</sup> edition*)***Why is molecular O<sub>2</sub> paramagnetic when Valence Bond theory predicts O<sub>2</sub> to be diamagnetic ?*****The Model: Molecular Orbitals for Diatomic Molecules**

- a. Consider the bonding between two hydrogen atoms to form H<sub>2</sub>. The 1s *electron waves* of the two H atoms may have the same phase (e.g., both “crests” if waves coming together):

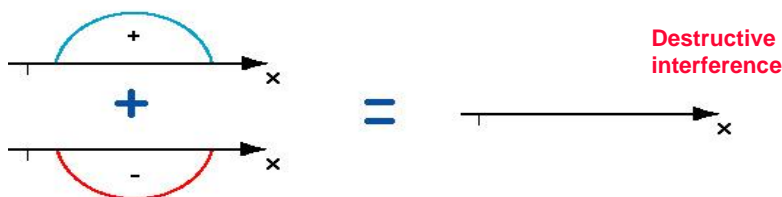


**Figure 1.** The combining of the electron waves of two hydrogen atoms that are in phase.

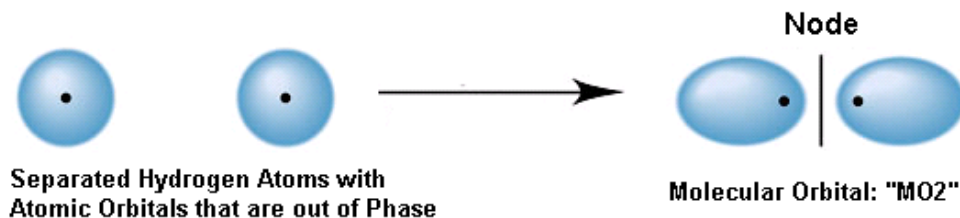


**Figure 2.** The combining atomic orbitals of two hydrogen atoms that each contains an electron wave *in phase* to form a *bonding molecular orbital*.

- b. Or the 1s *electron waves* of the two H atoms may have opposite phases (e.g., one is a “crest” while the other is a “trough”):



**Figure 3.** The combining of the electron waves of two hydrogen atoms that are out of phase.



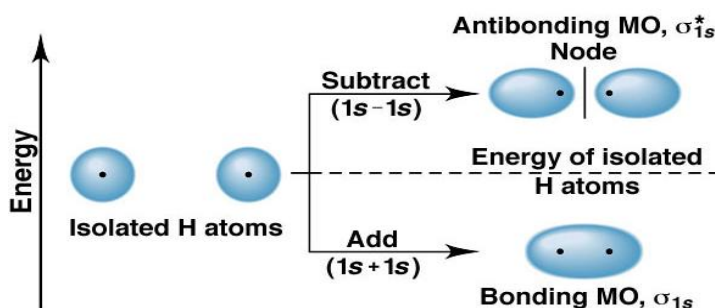
**Figure 4.** The combining atomic orbitals of two hydrogen atoms that each contains an electron wave *out of phase* to form an *antibonding molecular orbital*.

## Key Questions

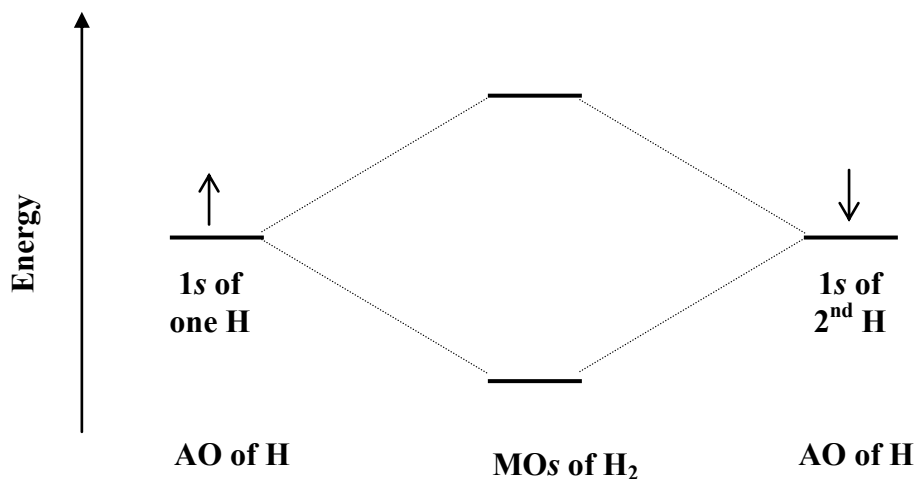
1. Suppose two waves interact such that crests of one wave overlap with crests of the second. Will the resultant wave exhibit constructive interference or destructive interference of the two waves that compose it? (Circle the correct choice.)
- 2a. Suppose two waves interact such that crests of one wave overlap with troughs of the second. Explain what will happen as the two waves interact to form a resultant wave.
- b. Why does MO2 (fig. 4) have two lobes of opposite phases and a node (*i.e.*, location where the probability of finding an electron is zero) between the H nuclei?
3. One of the molecular orbitals (MO1 or MO 2) in the Model is a **bonding MO** while the other is an **antibonding MO**. Which one is which, and how can you tell?

## Model: Bonding vs. Antibonding Molecular Orbitals

When two atomic orbitals of approximately the same energy interact, they form two molecular orbitals. However, one MO is stabilized—called the **Bonding MO**, while the other (the **Antibonding MO**) is destabilized relative to the energy of the atomic orbitals. When *s* orbitals come together to form a bonding MO, the MO is called a  $\sigma$  (“sigma”) **orbital**. When *s* orbitals come together to form an antibonding MO, the MO is called a  $\sigma^*$  (“sigma star”) **orbital**.



4. An MO energy level diagram for  $H_2$  is (the molecular orbitals are not yet labeled, nor are the arrows representing electrons drawn yet for  $H_2$ ):

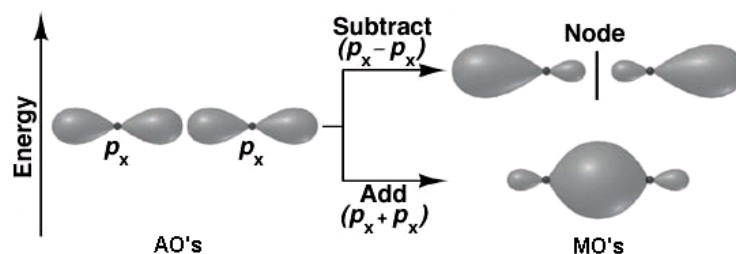


- a. Label the MOs (one with  $\sigma$ , the other with  $\sigma^*$ ) in the above energy level diagram. Which type of MO, bonding or antibonding, would be higher in energy? Why?
- b. Draw arrows ( $\uparrow$  and  $\downarrow$ ) above the lines representing the MOs in the central portion of the above energy level diagram in order to represent electrons occupying the MOs of  $H_2$  when the molecule is in its lowest-energy state. Are both electrons in the  $\sigma$  MO, or are both electrons in the  $\sigma^*$  MO, or will there be one electron in the  $\sigma$  MO and the other electron in the  $\sigma^*$  MO? Explain.
- c. According to MO Theory, a covalent bond consists of an electron pair in a \_\_\_\_\_ MO.

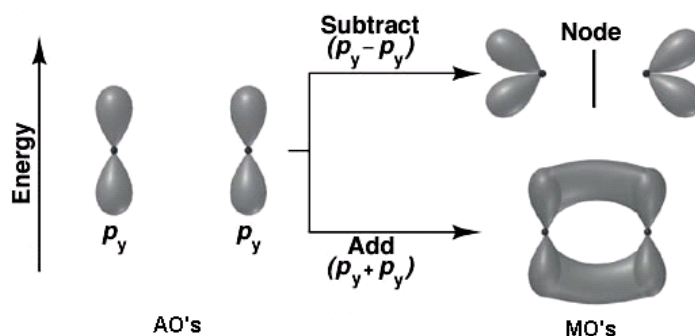
### The Model: Combining 2<sup>nd</sup> Shell Atomic Orbitals

The 2<sup>nd</sup> energy level of an atom is composed of one  $2s$  orbital, one  $2p_x$  orbital, one  $2p_y$  orbital, and one  $2p_z$  orbital. (The  $p$  orbitals are labeled with suffixes to let the reader know with which axis in Cartesian space that the orbital is aligned. If the orbitals of two atoms are interacting, the  $x$ -,  $y$ -, and  $z$ -axes of the two atoms are assumed to be consistently oriented, and the  $x$ -axis is often chosen to be the internuclear axis.) The simplest scenario encountered in Molecular Orbital Theory is when only atomic orbitals of approximately equal energy can combine to become MOs. So the  $2s$  orbital of one atom combines with the  $2s$  orbital of the neighboring atom to yield two MOs, a  $\sigma$  and a  $\sigma^*$  (just as when two  $1s$  orbitals combine to form MOs).

However, there is more than one way that a  $2p$  orbital of one atom can combine with a  $2p$  orbital of another atom.



**Case 1.** Head to head overlap of a  $p_x$  orbital of one atom with the  $p_x$  orbital of another atom.

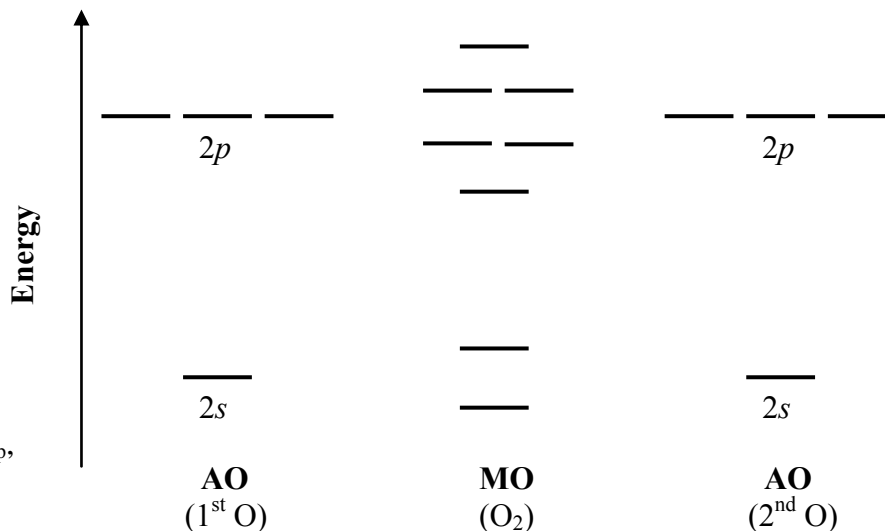


**Case 2.** Side to side overlap of a  $p_y$  orbital of one atom with a  $p_y$  orbital of another atom (or a  $p_z$  of one atom with the  $p_z$  of another atom)

### Key Questions

- Why do we not consider the case in which an  $s$  orbital combines with a  $p$  orbital? *Hint:* consider the relative energies of  $s$  and  $p$  orbitals.
- Why does the overlap of  $p_x$  and  $p_x$  orbitals of the same energy in case 1 (or the  $p_y$  orbitals in case 2), above, produce one MO of lower energy and another MO with higher energy?
- Label the bonding and antibonding MOs in cases 1 and 2, above, with the appropriate names and symbols: Bonding,  $\sigma$ ; Antibonding,  $\sigma^*$ ; Bonding,  $\pi$ ; Antibonding,  $\pi^*$ . How can you tell which are the bonding MOs and which are antibonding MOs in cases 1 and 2 above?

8. The energy level diagram for the orbitals of the valence electrons of molecular oxygen is shown to the right.



- a. Label each of the MOs with one of the of the following symbols:  $\sigma_{2s}$ ,  $\sigma^*_{2s}$ ,  $\pi_{2p}$ , or  $\pi^*_{2p}$ .

- b. How many *valence* electrons does an oxygen atom have? Draw that number of arrows ( $\uparrow$  and  $\downarrow$ ) above the lines that represent the atomic orbitals for the two separate oxygen atoms in order to represent the valence electrons in the atomic orbitals of the two oxygen atoms. (Recall the valence electron configuration of oxygen in the ground-state oxygen.)
- c. Draw the total number of arrows above the lines that represent the MOs for the diatomic oxygen molecule in order to represent the valence electrons in the molecular orbitals of  $O_2$ . (Recall Hund's Rule: Orbitals of the same energy (sublevel) half fill before electrons pair. Likewise, MOs of the same energy (sublevel) half fill before electrons pair.)
- d. Calculate the bond order of  $O_2$  according to MO Theory. According to MO Theory, the bond order of a diatomic molecule is obtained by subtracting the number of electrons in antibonding MOs from the number of electrons in bonding MOs and then dividing by 2:

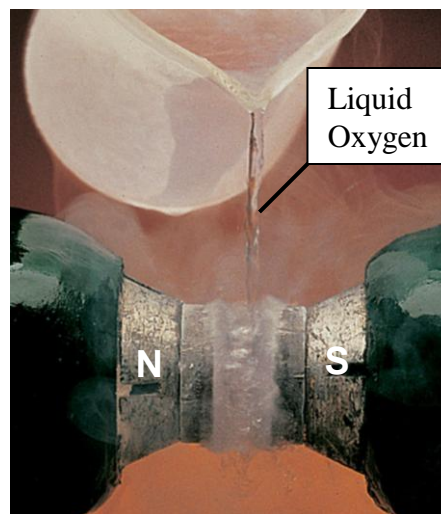
$$\text{Bond Order} = \frac{1}{2} [(\# \text{ e}^- \text{ in } \sigma \text{ and } \pi) - (\# \text{ e}^- \text{ in } \sigma^* \text{ and } \pi^*)]$$

- e. Draw the Lewis structure for molecular oxygen,  $O_2$ . What is the bond order of  $O_2$  predicted by the Lewis structure? BO = \_\_\_\_\_
- f. A **diamagnetic** substance is one with no unpaired electrons. A **paramagnetic** substance is one with at least one unpaired electron.
- According to Valence Bond (VB) Theory is  $O_2$  Paramagnetic or Diamagnetic? (Circle your choice.)
  - According to Molecular Orbital (MO) Theory is  $O_2$  Paramagnetic or Diamagnetic? (Circle your choice.)

- g. Liquid oxygen ( $O_2$ ) becomes trapped between the N and S poles of the electromagnet (as in the picture to the right), but flows unobstructed (not shown) between the poles when the electromagnet is turned off.

Is oxygen paramagnetic or diamagnetic? (Circle your choice.)

- h. Which theory, VB or MO, best explains both the bonding and magnetic properties of  $O_2$ . Justify your response fully indicating the shortcomings and merits of each theory.



### Model: Using MO Theory to Predict the B.O. and the Strength of a Covalent Bond

As stated before, MO Theory can be used to determine the bond order:

$$\text{B.O.} = \frac{1}{2} [\# \text{ of Bonding } e^- - \# \text{ of Antibonding } e^-]$$

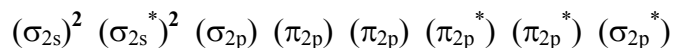
- If the B.O.  $> 0$ , then the molecule is more stable than the separate and unbonded atoms
- If the B.O. = 0, then there is zero probability of bond formation
- The greater the B.O., the stronger the bond

9. Complete the MO diagram, below, for the superoxide radical,  $O_2^-$ , and use it to answer the following questions.

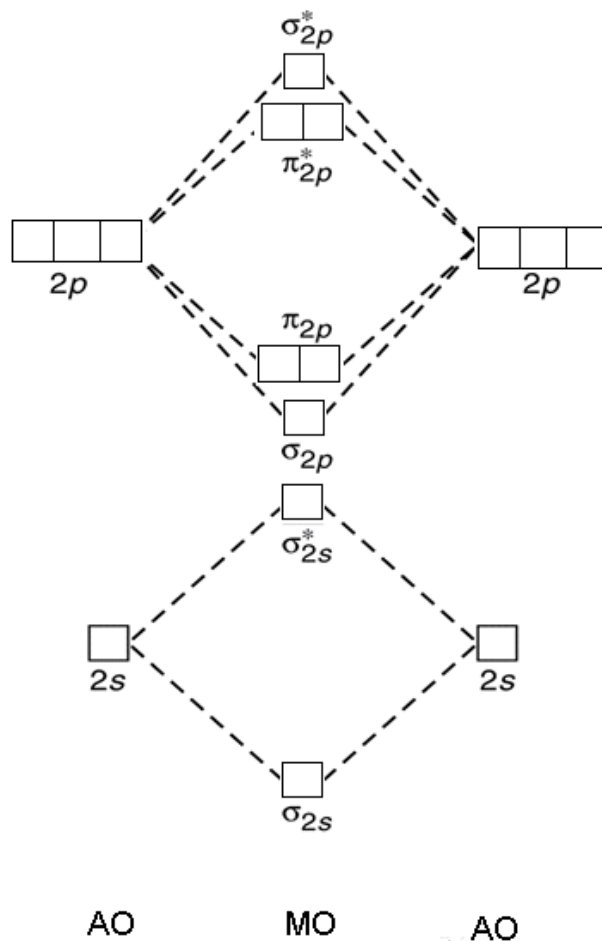
a.) Is the superoxide radical,  $O_2^-$ , stable? Briefly justify your response.

b.) Is  $O_2^-$  paramagnetic or diamagnetic? Briefly justify your response.

c.) What is the valence electron configuration of  $O_2^-$ ? Answer this question by filling in the appropriate superscripts next to the parentheses below—the first two MOs have been completed for you.



d. The superoxide radical is produced each day as a natural (but unwanted!) byproduct in the mitochondria in all human cells as they use oxygen during cellular respiration. Offer an explanation why the superoxide radical is very reactive and therefore damages cells, causes mutations (changes in DNA) and leads to the aging of our body.



MO Energy Levels for  
 $O_2$ ,  $F_2$  and  $Ne_2$   
(without 2s-2p mixing)

10. Use the MO diagram to the right the valence electron configurations for each of the following:

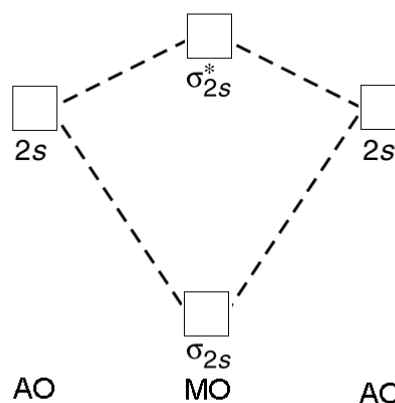
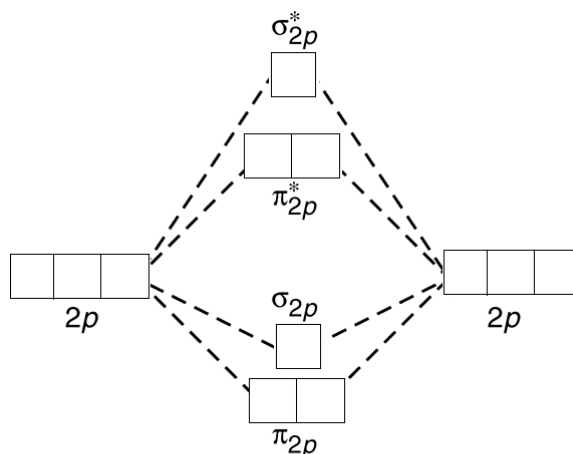
a.)  $B_2^+$

b.)  $B_2$

c.)  $B_2^-$

d.) Place  $B_2^+$ ,  $B_2$  and  $B_2^-$  in order of *decreasing* bond energy:

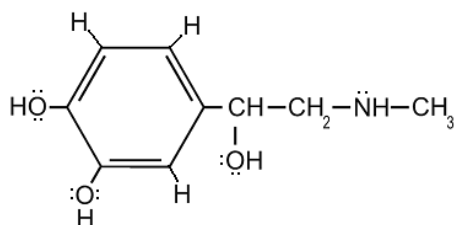
e.) Place  $B_2^+$ ,  $B_2$  and  $B_2^-$  in order of decreasing bond length:



MO Energy Levels for  
 $B_2$ ,  $C_2$  and  $N_2$   
(with 2s-2p mixing)

### Comprehensive Problems

11. Epinephrine (or adrenaline) is a naturally occurring hormone that is also manufactured commercially for use as a heart stimulant, a nasal decongestant, and a glaucoma treatment. A valid Lewis structure for epinephrine is below.



a.) Label in the figure above the hybridization of each C, O, and N atom in epinephrine.

b.) How many  $\sigma$  bonds are present in each molecule of epinephrine? \_\_\_\_\_

c.) How many  $\pi$  electrons are delocalized in the ring of epinephrine? \_\_\_\_\_



12. Complete the Table below.

<b>Ion</b>	<b>Lewis Structure</b>	<b>VSEPR Formula and Hybridization of Central Atom</b>	<b>Sketch of 3-D shape</b> (include ideal bond angles and any expected deviations from the ideal bond angle)	<b>Name of 3-D Shape</b>
$\text{BrO}_3^-$				
$\text{AsCl}_4^-$				
$\text{SeO}_4^{2-}$				