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5.111 Principles of Chemical Science  
Fall 2008

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## 5.111 Lecture Summary #14

**Readings for today:** Section 3.8 (3.9 in 3<sup>rd</sup> ed) – The Limitations of Lewis’s Theory, Section 3.9 (3.10 in 3<sup>rd</sup> ed) – Molecular Orbitals, Section 3.10 (3.11 in 3<sup>rd</sup> ed) – The Electron Configuration of Diatomic Molecules, Section 3.11 (3.12 in 3<sup>rd</sup> ed) – Bonding in Heteronuclear Diatomic Molecules.

**Read for Lecture #15:** Sections 3.4, 3.5, 3.6 and 3.7 (Sections 3.4, 3.5, 3.6, 3.7, and 3.8 in 3<sup>rd</sup> ed) – Valence Bond Theory.

- Topics:**      **Molecular orbital theory**
- I. Bonding and antibonding orbitals
  - II. Homonuclear diatomic molecules
    - A. Molecules with MO’s originating from s orbitals
    - B. Molecules with MO’s originating from s and p orbitals
  - III. Heteronuclear diatomic molecules

## MOLECULAR ORBITAL (MO) THEORY

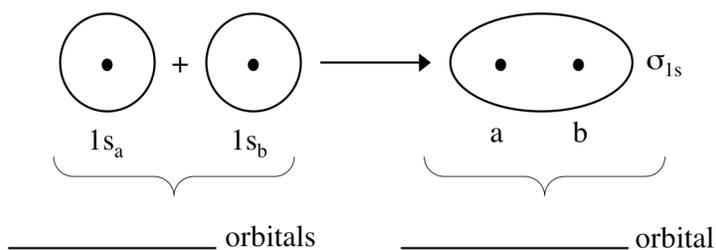
In MO theory, valence electrons are \_\_\_\_\_ over the entire molecule, not confined to individual atoms or bonds, as in Lewis and valence-bond models.

### I. BONDING AND ANTIBONDING ORBITALS

Molecular orbitals (\_\_\_\_\_) of diatomic molecules arise from adding together (**superimposing**) atomic orbitals:

linear combination of atomic orbitals (LCAO) to create a molecular orbital.

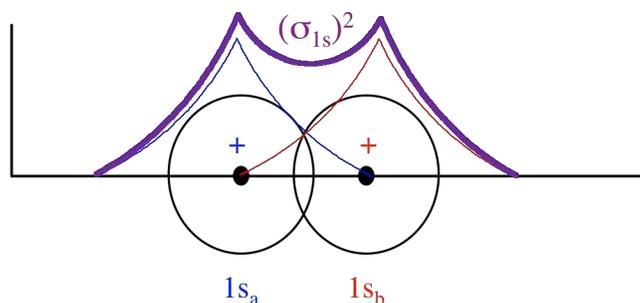
#### Bonding orbitals



$\sigma$ : designates a molecular orbital that is cylindrically symmetric about the bond axis (with no nodal plane along the bond axis).

\_\_\_\_\_ + \_\_\_\_\_ = \_\_\_\_\_  $\equiv$  bonding MO    P

$\sigma_{1s}$  is a wavefunction.



As with atomic wavefunctions, the physically significant quantity for molecular wavefunctions is probability density (P).

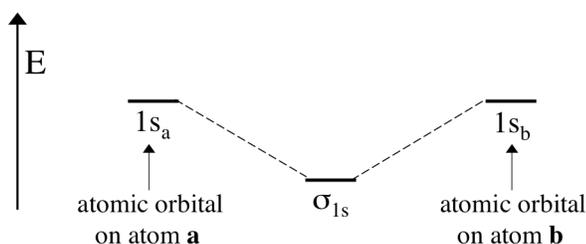
$$P \propto (\text{_____})^2 = (\text{_____} + \text{_____})^2 = (1s_a)^2 + (1s_b)^2 + \boxed{2(1s_a)(1s_b)}$$

interference term

The cross-term represents \_\_\_\_\_ interference between the two wavefunctions.

The result is a \_\_\_\_\_ orbital: higher probability density between the nuclei.

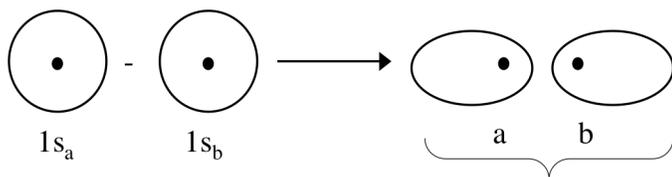
**Energy of interaction** for bonding orbitals. The energy \_\_\_\_\_ compared to the atomic orbitals!



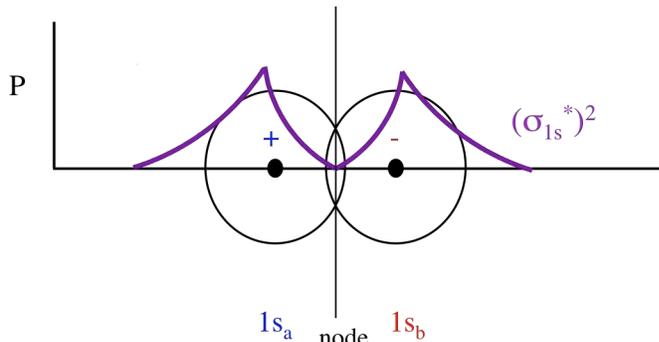
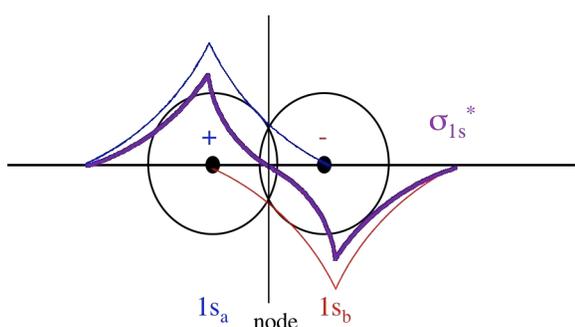
Molecule is more stable than the individual atoms.

### Antibonding orbitals

But since electrons are waves, they can also destructively interfere.



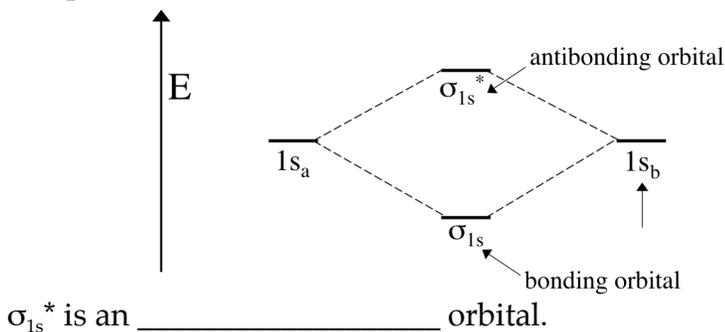
$$\text{_____} - \text{_____} = \text{_____} \equiv \text{antibonding molecular orbital.}$$



Probability density,  $P \propto (\text{_____})^2 = (\text{_____} \text{ _____})^2 = (1s_a)^2 + (1s_b)^2 - \boxed{2(1s_a)(1s_b)}$   
interference term

The cross-term represents \_\_\_\_\_ interference between the two wavefunctions. The result is lower probability density between the nuclei, an **antibonding** orbital.

**Energy of interaction** for antibonding orbitals. The energy \_\_\_\_\_ compared to the atomic orbitals!

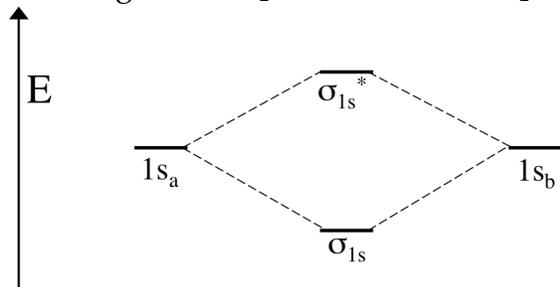


- Less electron density accumulates between nuclei, exposing nuclei to greater repulsions.
- Creates an effect exactly opposite to a bond. Antibonding is \_\_\_\_\_ nonbonding.
- An antibonding orbital is raised in energy by approximately the same amount that the bonding orbital is lowered in energy.

## II. HOMONUCLEAR DIATOMIC MOLECULES

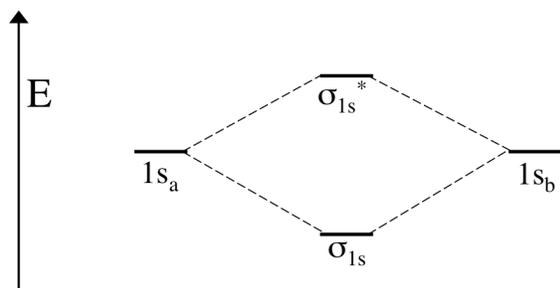
### A. Molecules with MO's originating from s orbitals

MO diagram of  $H_2$ : In the case of  $H_2$ , both electrons are in the  $\sigma_{1s}$  orbital.



Electron configuration of  $H_2$ :

MO diagram of  $He_2$ :

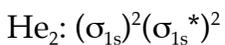


Electron configuration of  $He_2$ :

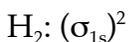
Because 2  $e^-$ s went into a bonding orbital and 2  $e^-$ s went into an antibonding orbital, no net gain or lowering in energy.

MO theory predicts He<sub>2</sub> \_\_\_\_\_ exist because no net gain in E.

$$\text{BOND ORDER} = \frac{1}{2} (\# \text{ of bonding electrons} - \# \text{ of antibonding electrons})$$



bond order = \_\_\_\_\_ bond



bond order = \_\_\_\_\_ bond

Reality: He<sub>2</sub> does exist. 'Discovered' in 1993. Weakest chemical bond known.

$$\Delta E_d = 0.01 \text{ kJ/mol for He}_2$$

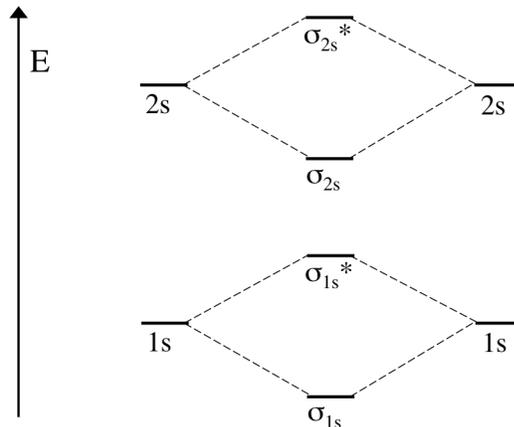
$$\Delta E_d = 432 \text{ kJ/mol for H}_2$$

The MO's formed by LCAO for 2s orbitals are analogous to those formed by 1s.

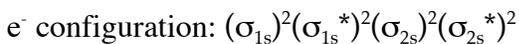


Bond order:  $\frac{1}{2} ( \quad ) =$

$\Delta E_d =$  \_\_\_\_\_ kJ/mol



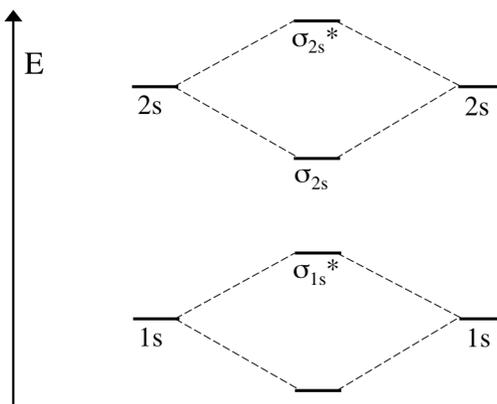
Note: Bond order can be calculated by considering all electrons or only valence electrons.



Bond order (counting all electrons):  
 $\frac{1}{2} ( \quad ) =$

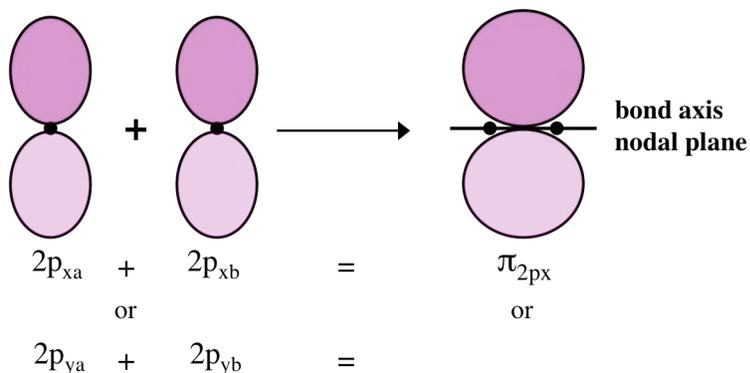
Bond order (counting only valence e<sup>-</sup>s):  
 $\frac{1}{2} ( \quad ) =$

$\Delta E_d =$  \_\_\_\_\_ kJ/mol - very weak



## B. Molecules with MO's originating from s and p orbitals

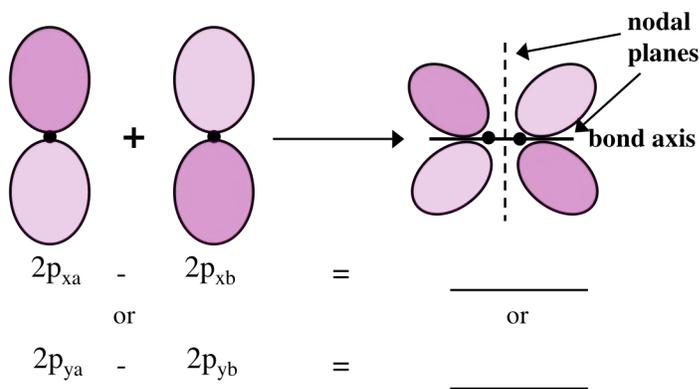
### Bonding MO's formed by LCAO of $2p_x$ and $2p_y$



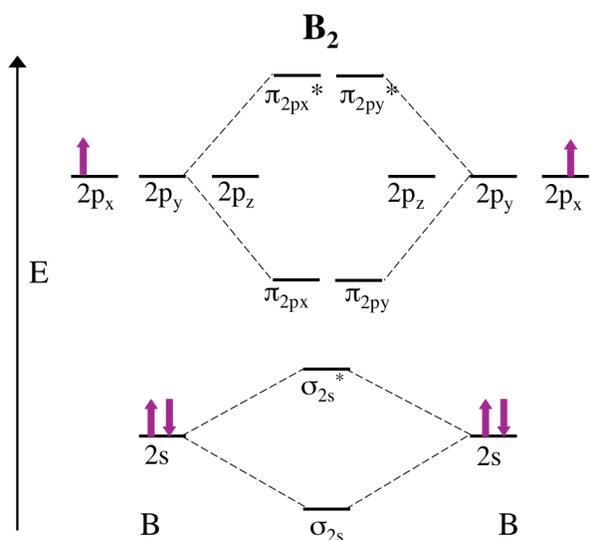
$\pi$ -orbital: Molecular wave function (molecular orbital) with a nodal plane through the \_\_\_\_\_ axis.

Probability density,  $P \propto (\underline{\hspace{2cm}})^2 = (\underline{\hspace{1cm}} + \underline{\hspace{1cm}})^2 = (2p_{xa})^2 + (2p_{xb})^2 + \boxed{2(2p_{xa})(2p_{xb})}$   
↑  
interference term

### Antibonding MO's formed by LCAO of $2p_x$ and $2p_y$



$\pi^*$ -orbitals result from the destructive interference of 2  $p_x$  or  $p_y$  orbitals.

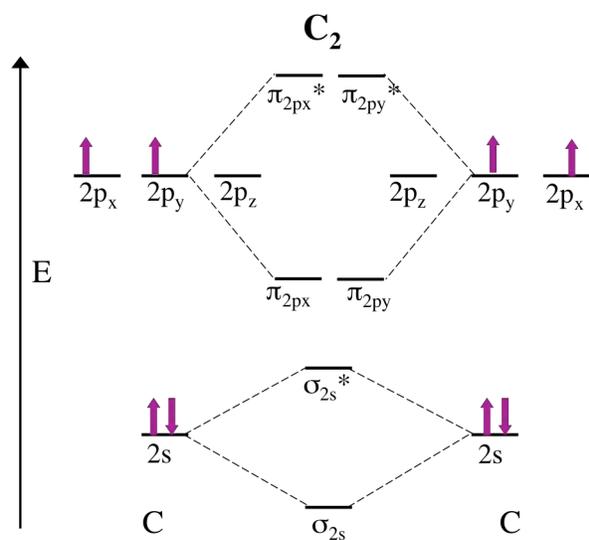


valence electron configuration:

\_\_\_\_\_

$$\text{Bond order} = \frac{1}{2} (4 - 2) = \underline{\hspace{2cm}}$$

$\Delta E_d = 599 \text{ kJ/mol}$  for  $\text{C}_2$  where B.O. = 2  
 vs.  $\Delta E_d = 289 \text{ kJ/mol}$  for  $\text{B}_2$  where B.O. = 1

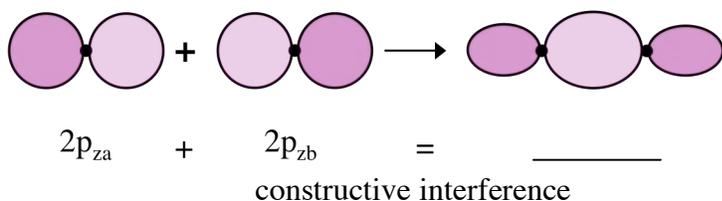


valence electron configuration:

\_\_\_\_\_

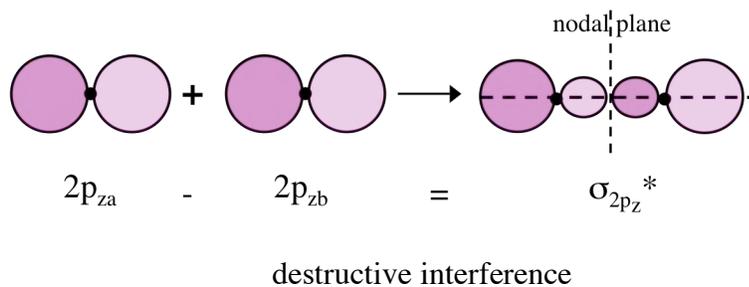
$$\text{Bond order} = \frac{1}{2} (6 - 2) = \underline{\hspace{2cm}}$$

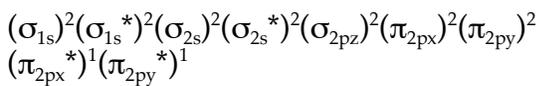
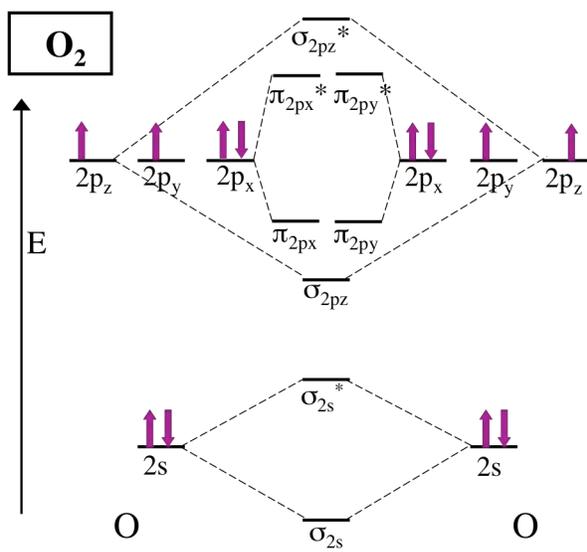
**Bonding MO's formed by LCAO of  $2p_z$**



$\sigma$ : MO with no nodal plane along the bond axis.

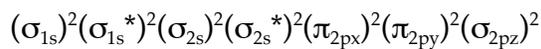
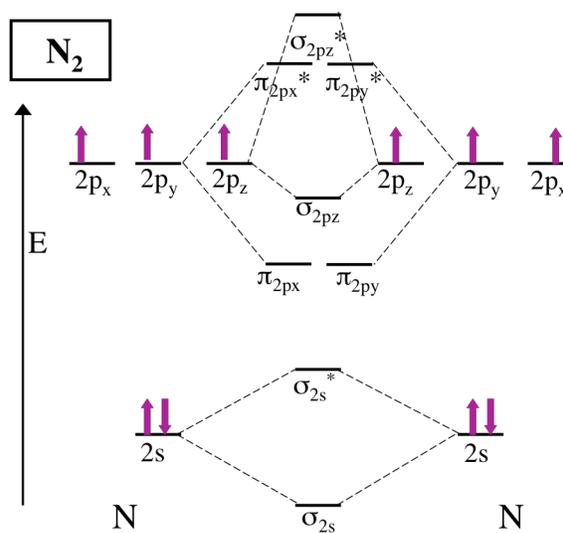
**Antibonding MO's formed by LCAO of  $2p_z$**





B.O. =  $\Delta E_d = 494 \text{ kJ/mol}$

O<sub>2</sub> is a \_\_\_\_\_! Two unpaired electrons.



B.O. =  $\Delta E_d = 941 \text{ kJ/mol}$

Note: The relative energies of the  $\sigma_{2pz}$  orbital compared to the  $\pi_{2p}$  orbitals depends on the Z value of the atoms. If Z is = or > 8, the  $\sigma_{2pz}$  orbital is lower in energy.