#### 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
	<b>A.</b> Molecules with MO's originating from s orbitals
	<b>B.</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**



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



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



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

$$P \propto (\_\_\_)^2 = (\_\_\_+\_\_)^2 = (1s_a)^2 + (1s_b)^2 + 2(1s_a)(1s_b)$$
  
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.



Probability density,  $P \propto (\_\_\_)^2 = (\_\_\_\_)^2 = (1s_a)^2 + (1s_b)^2 - 2(1s_a)(1s_b)$ 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!



σ<sub>1s</sub>\* is an \_\_\_\_\_ orbital.
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<sub>2</sub>: In the case of H<sub>2</sub>, both electrons are in the  $\sigma_{1s}$  orbital.



Electron configuration of H<sub>2</sub>:

MO diagram of He<sub>2</sub>:



Electron configuration of He<sub>2</sub>:

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.

 BOND ORDER = ½ (# of bonding electrons - # of antibonding electrons)

 He<sub>2</sub>:  $(\sigma_{1s})^2(\sigma_{1s}^*)^2$  

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

 H<sub>2</sub>:  $(\sigma_{1s})^2$  

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

 Problem Heredenergies (Directory Kin 1002)

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.



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

Be<sub>2</sub> e<sup>-</sup> configuration:  $(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s}^*)^2(\sigma_{2s}^*)^2$ Bond order (counting all electrons):  $\frac{1}{2}( ) =$ Bond order (counting only valence e<sup>-</sup>s):  $\frac{1}{2}( ) =$ 

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



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



Bonding MO's formed by LCAO of 2p<sub>x</sub> and 2p<sub>y</sub>

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



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.



Bond order =  $\frac{1}{2}$  (4 - 2) = \_\_\_\_\_

Bond order =  $\frac{1}{2}(6 - 2) =$ \_\_\_\_\_

 $\Delta E_{d} = 599 \text{ kJ/mol for } C_{2} \text{ where } B.O. = 2$ vs.  $\Delta E_{d} = 289 \text{ kJ/mol for } B_{2} \text{ where } B.O. = 1$ 

Bonding MO's formed by LCAO of 2p<sub>z</sub>



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

Antibonding MO's formed by LCAO of 2p<sub>z</sub>



destructive interference



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.

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