5.111 Lecture Summary #13 Monday, October 6, 2014

Readings for today: Section 3.8 – 3.11 Molecular Orbital Theory (Same in 5th and 4th ed.)
Read for Lecture #14: Sections 3.4, 3.5, 3.6 and 3.7 – Valence Bond Theory (Same in 5th and 4th ed).

Topics: **I. Molecular orbital theory**
A. Homonuclear molecules with MOs originating from s orbitals
B. Homonuclear molecules with MOs originating from s and p orbitals
C. Heteronuclear diatomic molecules

I. 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.

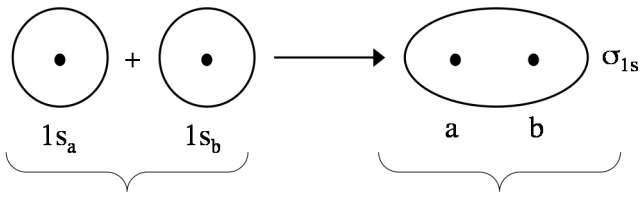
Molecular orbitals (_____) of diatomic molecules arise from adding together (**superimposing**) atomic orbitals.

A Linear Combination of Atomic Orbitals (LCAO) creates molecular orbitals (bonding orbitals and antibonding orbitals)

N molecular orbitals can be constructed by *N* atomic orbitals.

A. Homonuclear molecules with MOs originating from s orbitals

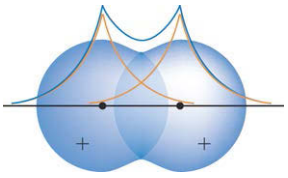
Bonding orbitals arise from LCAO under conditions of **constructive** interference



_____ orbitals _____ orbital

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

_____ + _____ = σ_{1s} ≡ bonding molecular orbital (MO) and also a **wavefunction**.

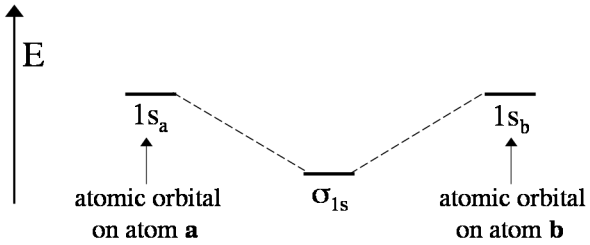


When waves interfere constructively, the amplitude **increases** where they overlap.

Increased amplitude in the internuclear region translates to an **enhanced** probability density (ψ^2) between the nuclei.

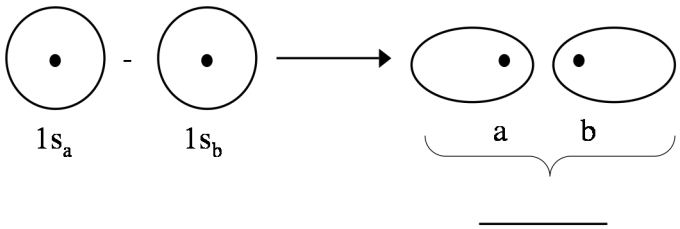
Any electron that occupies a bonding MO will be attracted to BOTH nuclei, and therefore will be _____ compared to an atomic orbital associated with a single nucleus.

Energy of interaction. The energy of a **bonding orbital** is_____ compared to the atomic orbitals!

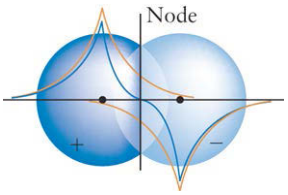


For H_2, when its two electrons both occupy the bonding orbital, the molecule is _____ stable.

Antibonding orbitals (result of **destructive** interference of two atomic orbitals)



_____ - _____ = σ_{1s}^* ≡ antibonding molecular orbital.

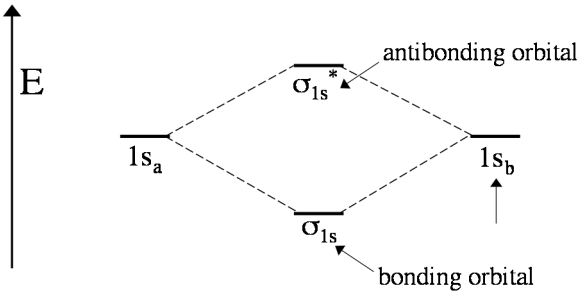


When wavefunctions interfere **destructively**, the amplitude **decreases** where they overlap.

Decreased amplitude in the internuclear region translates to a **diminished** probability density (ψ^2) between the nuclei and a **node** between the two nuclei.

An electron in this **antibonding orbital** would be essentially excluded from the internuclear region, and thus have a _____ energy than if in an atomic orbital.

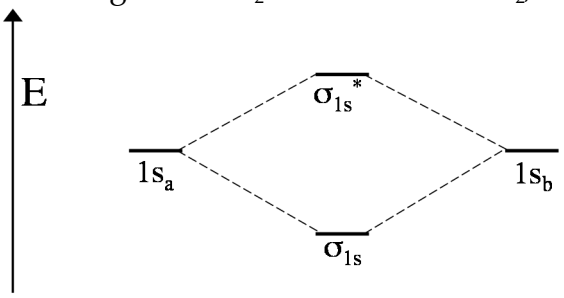
Energy of interaction. The energy of an **antibonding orbital** is_____ compared to the atomic orbitals!



An antibonding orbital is raised in energy by approximately the same amount that the bonding orbital is lowered in energy.

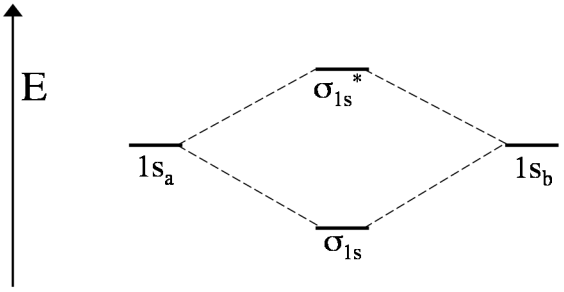
N molecular orbitals can be constructed by *N* atomic orbitals. Thus, 2 atomic orbitals generate 2 molecular orbitals (one bonding and one antibonding, one lower in energy and one higher in energy).

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



Electron configuration of H_2: _____

MO diagram of He_2:



Electron configuration of He_2: _____

There is_____in energy for He_2 compared to 2 He.

MO theory predicts He_2 **does not** exist because no net gain in E.

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

He_2: $(\sigma_{1s})^2(\sigma_{1s}^*)^2$

bond order = _____ _____ bond

H_2: $(\sigma_{1s})^2$

bond order =_____ _____ bond

Reality: He_2 does exist. 'Discovered' in 1993. Weakest chemical bond known.
ΔE_d = 0.01 kJ/mol for He_2
ΔE_d = 432 kJ/mol for H_2

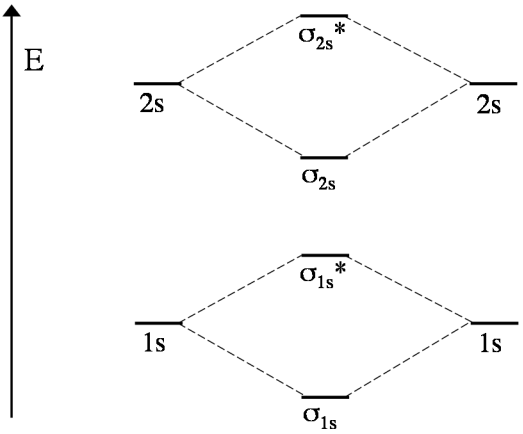
The MOs formed by LCAO for 2s orbitals are analogous to those formed by 1s.

Li_2

Electron configuration: $(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2$

Bond order: ½ ( ) =

ΔE_d =_____ kJ/mol



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

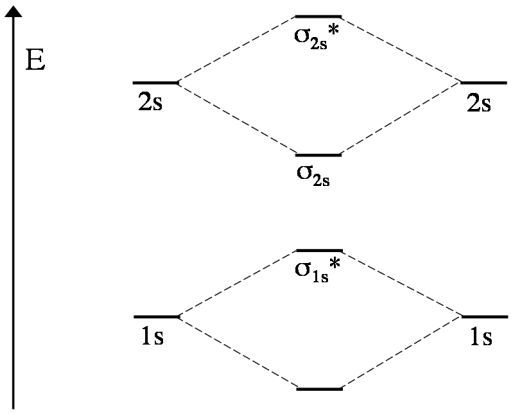
Be_2

e^- configuration: $(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2$

Bond order (counting all electrons):
½ ( ) =

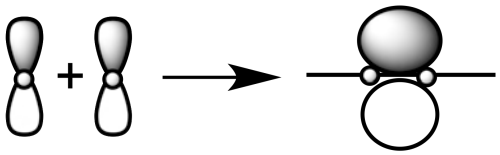
Bond order (counting only valence e^-s):
½ ( ) =

ΔE_d = _____ kJ/mol - very weak



B. Homonuclear molecules with MOs originating from s and p orbitals

Bonding MOs formed by LCAO of $2p_x$ and $2p_y$ as a result of **constructive** interference



Bond axis and nodal plane

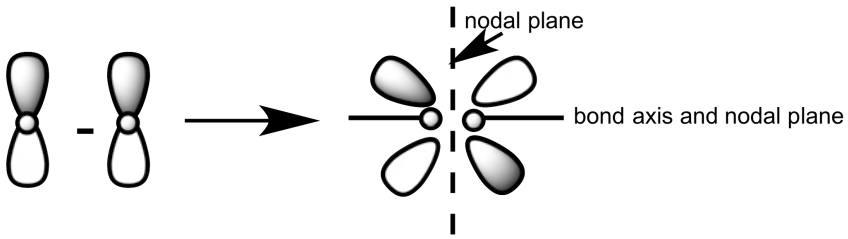
$2p_{xa}$ + $2p_{xb}$ = π_{2px}

or or

$2p_{ya}$ + $2p_{yb}$ = _____

π-orbital: Molecular wavefunction (molecular orbital) with a nodal plane through the _____ axis.

Antibonding MOs formed by LCAO of $2p_x$ and $2p_y$ as a result of **destructive** interference



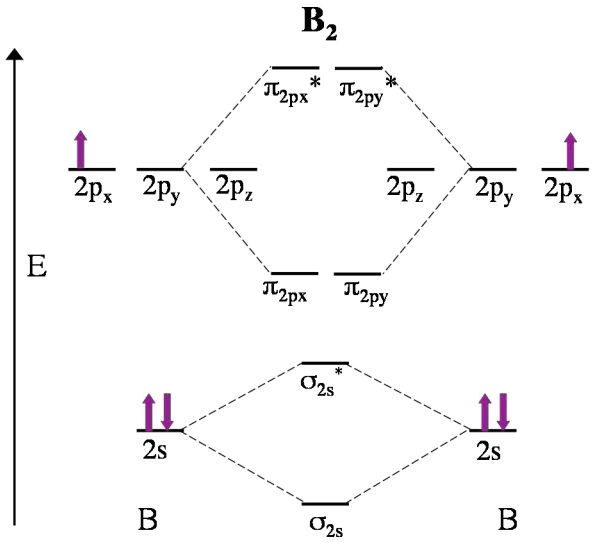
$2p_{xa}$ - $2p_{xb}$ = _____

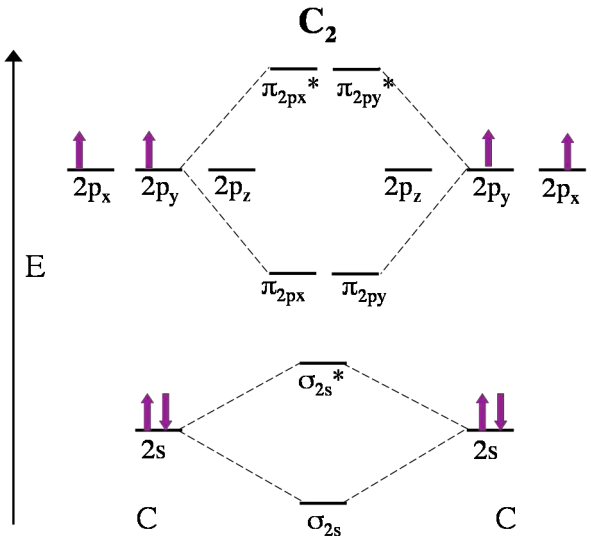
or or

$2p_{ya}$ - $2p_{yb}$ = _____

π*-orbitals: Molecular wavefunction (molecular orbital) with TWO nodal planes. One nodal plane is through the bonding axis and the other is between nuclei.

Please note that MO diagrams for B_2 and C_2 below are incomplete since they do not include the $2p_Z$ molecular orbitals!





Valence electron configuration:

_____

Bond order = ½ (4 - 2) = _____

Valence electron configuration:

_____

Bond order = _____ = _____

Just considering 2s, $2p_x$, and $2p_y$ for the moment, let's sum it up:
Two 2s AOs generate **two** σ_{2s} MOs (lower energy σ_{2s} & higher energy σ_{2s}*).
Two $2p_x$ AOs generate **two** π_{2px} MOs (lower energy π_{2px} & higher energy π_{2px}*).
Two $2p_y$ AOs generate **two** π_{2py} MOs (lower energy π_{2py} & higher energy π_{2py}*)

The stability of the resulting molecule depends on the # electrons that occupy lower energy orbitals compared to the # that occupy higher energy orbitals.

If the net result of molecule formation is that more electrons have a lower energy, then the molecule is _____.

If the energy differential is small, then the molecule is not as stable.

For B_2: $(\sigma_{2s})^2(\sigma_{2s}^*)^2 \pi_{2px} \pi_{2py}^*$
___e^- in lower energy (bonding orbital)
___e^- in higher E (antibonding orbital)

Bond order = ½(4-2) = 1

ΔE_d = _____

For C_2: $(\sigma_{2s})^2(\sigma_{2s}^*)^2 (\pi_{2px})^2 (\pi_{2py}^*)^2$
___ e^- in lower energy (bonding orbital)
___ e^- in higher E (antibonding orbital)

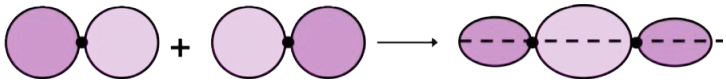
Bond order = ½(6-2) = 2

ΔE_d = _____

Please note that complete MO diagrams for B_2 and C_2 must include the $2p_Z$ molecular orbitals even if no electrons are in those orbitals.

Bonding MOs formed by LCAO of $2p_z$

σ: cylindrically symmetric with no nodal plane about the bond axis



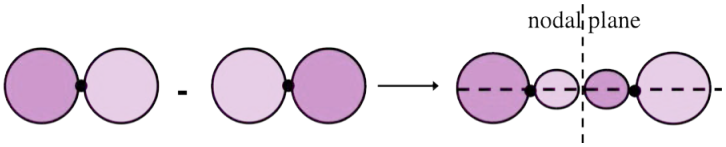
$2p_{za}$ + $2p_{zb}$ = _____

Nodes pass **through** nuclei, but no nodes along the bond axis.

Constructive interference results in a region of **increased** amplitude between nuclei, and thus an **increased** probability density between nuclei (therefore **lower** energy MO)

Antibonding MOs formed by LCAO of $2p_z$

σ: cylindrically symmetric with no nodal plane about the bond axis



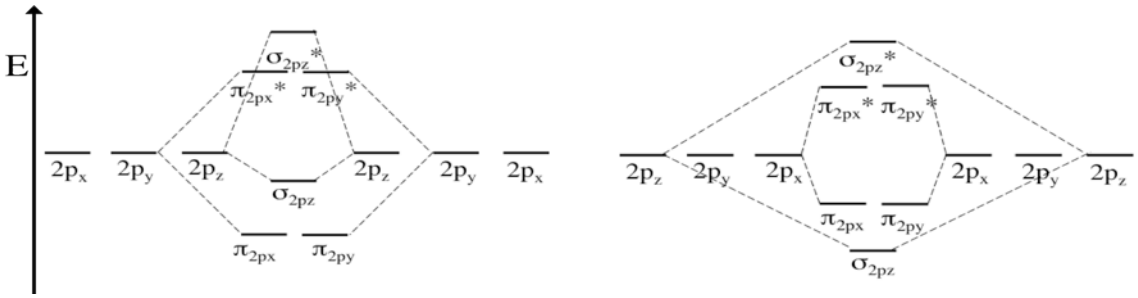
$2p_{za}$ - $2p_{zb}$ = σ_{2pz}^*

Nodes pass **through** and **between the nuclei**, but no nodes along the bond axis.

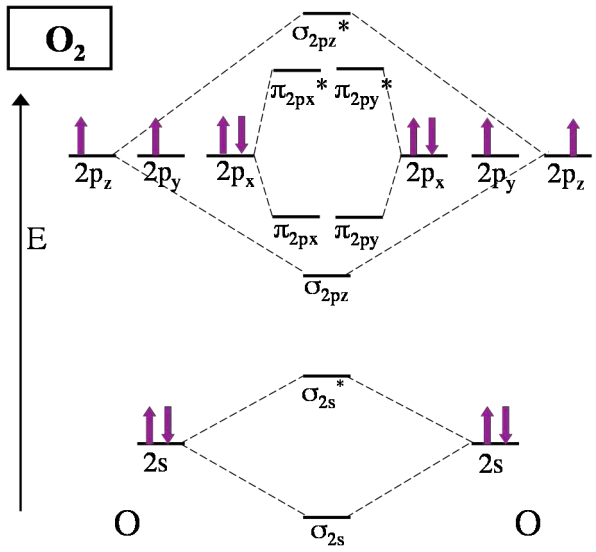
Destructive interference results in **a nodal plane between the nuclei**, and **decreased** probability density between nuclei (therefore **higher** energy MO)

The relative energies of the σ_{2pz} orbital compared to the π_{2px} and π_{2py} orbitals depend on the_____ value of the atoms.

For simple **homonuclear** diatomic molecules:

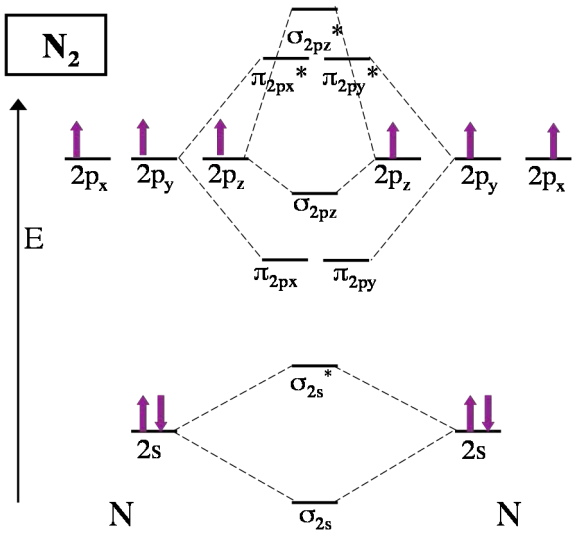


- The relative E ordering is (π_{2px}) and (π_{2py}) < (**σ_{2pz}**) if **Z <** ____.
- The relative E ordering is (**σ_{2pz}**) < (π_{2px}) and (π_{2py}) if **Z = or >** ____.
- The relative E ordering of antibonding orbitals doesn't change with Z.



$(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2pz})^2(\pi_{2px})^2(\pi_{2py})^2$
$(\pi_{2px}^*)^1(\pi_{2py}^*)^1$

B.O. = ΔE_d = 494 kJ/mol
O_2 is a _____! Two unpaired electrons (paramagnetic)



$(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2px})^2(\pi_{2py})^2(\sigma_{2pz})^2$

B.O. = ΔE_d = 941 kJ/mol
No unpaired electrons (diamagnetic)

MO theory does a better job describing the properties of O_2 than Lewis Structures do. Both MO theory and Lewis Structures do a good job with N_2.

Note: Molecules possessing **unpaired** electrons are paramagnetic (attracted by magnetic field); those in which the electrons are paired are diamagnetic (repelled by magnetic field).

C. For **HETERONUCLEAR** diatomic molecules:

- The relative E ordering is (π_{2px}) and $(\pi_{2py}) < (\boldsymbol{\sigma_{2pz}})$ if Z < 8 for both atoms.
- You are NOT responsible for predicting the energy level ordering if either one of the atoms has Z = or > 8.

For full credit on MO diagrams,

- label increasing energy with an arrow next to the diagram.
- pay attention to whether the question asks for *valence* electrons or *all* electrons.
- for any bonding orbital drawn, include the corresponding anti-bonding orbital, even if it is not filled with any electrons.
- label each atomic orbital (1s, 2s, $2p_x$, $2p_y$, etc.) and each molecular orbital (∫2s, $\pi 2p_x$, $\pi 2p_y$, etc.) that you draw.
- fill in the electrons for both the atomic and molecular orbitals.

5.111 Principles of Chemical Science
Fall 2014