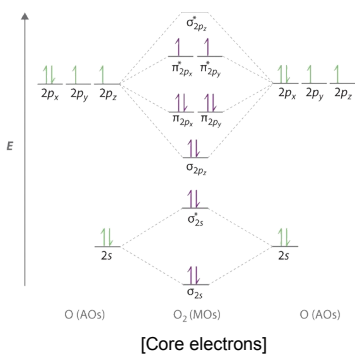


# Bonding and Molecular Structure: Orbital Hybridization and Molecular Orbitals

Chapter 8

Chemistry 222  
Professor Michael Russell

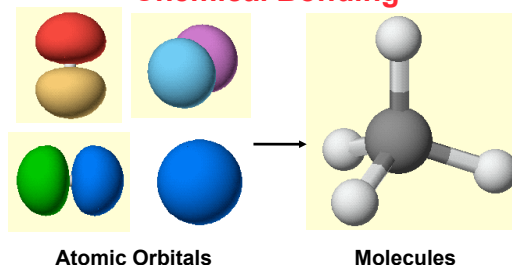
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Last update: 4/28/24

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## Advanced Theories of Chemical Bonding



Atomic Orbitals

Molecules

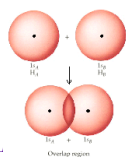
## Two Theories of Bonding

### VALENCE BOND (VB) THEORY - Linus Pauling

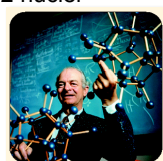
valence electrons are **localized** between atoms (or are lone pairs)

half-filled atomic orbitals overlap to form bonds.

electrons stabilized by 2 nuclei

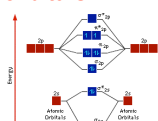


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### MOLECULAR ORBITAL (MO) THEORY - Robert Mulliken

valence electrons are **delocalized** over entire molecule in **molecular orbitals**



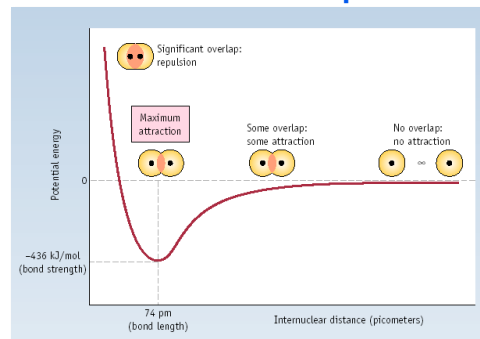
Robert Mulliken



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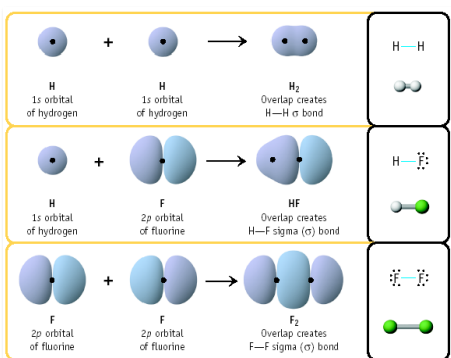
## Sigma Bond Formation by Orbital Overlap

Two s orbitals overlap



## Sigma Bond Formation by Orbital Overlap

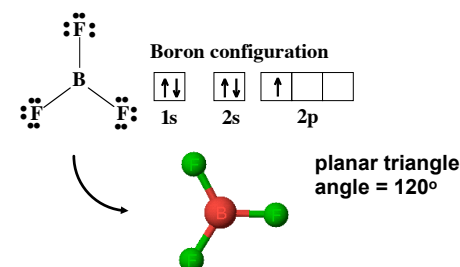
Two s orbitals overlap



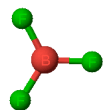
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## Using Valence Bond Theory

Bonding in  $BF_3$



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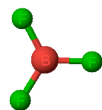
### Bonding in BF<sub>3</sub>

How to account for 3 bonds 120° apart using a spherical s orbital and p orbitals that are 90° apart?

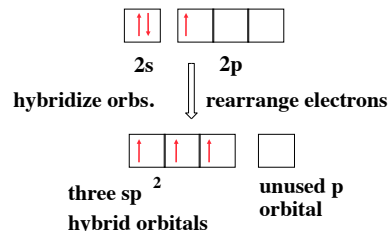
Pauling said to modify VB approach with **ORBITAL HYBRIDIZATION**

- mix available orbitals to form a new set of orbitals - **HYBRID ORBITALS** - that will give the maximum overlap in the correct geometry.

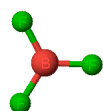
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### Bonding in BF<sub>3</sub>

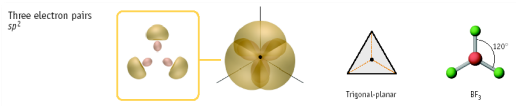


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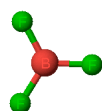
### Bonding in BF<sub>3</sub>

The three hybrid orbitals are made from 1 s orbital and 2 p orbitals create 3 sp<sup>2</sup> hybrids.

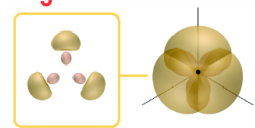
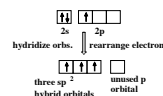


Now we have 3, half-filled HYBRID orbitals that can be used to form *planar* B-F sigma bonds.

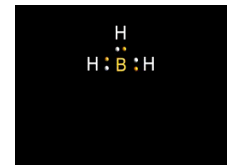
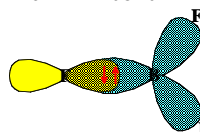
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### Bonding in BF<sub>3</sub>



An orbital from each F overlaps one of the sp<sup>2</sup> hybrids to form a B-F σ bond.

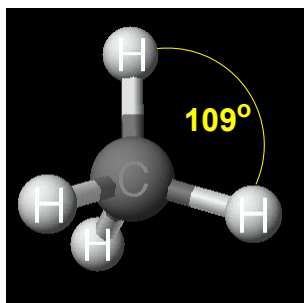


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### Bonding in CH<sub>4</sub>

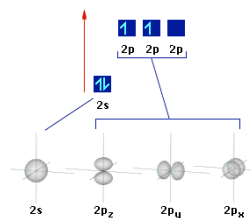
How do we account for 4 C-H sigma bonds 109° apart?

Need to use 4 atomic orbitals - s, p<sub>x</sub>, p<sub>y</sub>, and p<sub>z</sub> - to form 4 new hybrid orbitals pointing in the correct direction.



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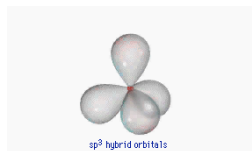
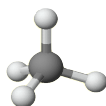
### Bonding in a Tetrahedron - Formation of Hybrid Atomic Orbitals



4 C atom orbitals hybridize to form four equivalent sp<sup>3</sup> hybrid atomic orbitals.

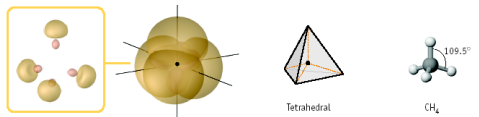
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## Bonding in a Tetrahedron - Formation of Hybrid Atomic Orbitals



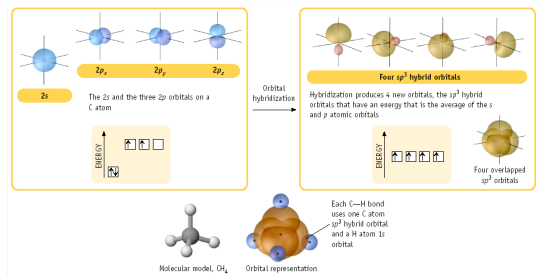
4 C atom orbitals hybridize to form four equivalent  $sp^3$  hybrid atomic orbitals.

Four electron pairs  $sp^3$



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## Bonding in $CH_4$



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## Orbital Hybridization

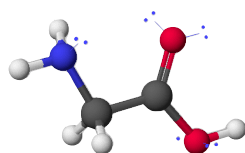
Bonds	EPG	Hybrid	REMAINING p orbs?
2	linear	$sp$	2 p
3	trigonal planar	$sp^2$	1 p
4	tetrahedral	$sp^3$	none
5	trigonal bipyramid	$sp^3d$	---
6	octahedral	$sp^3d^2$	---

see: VSEPR Guide

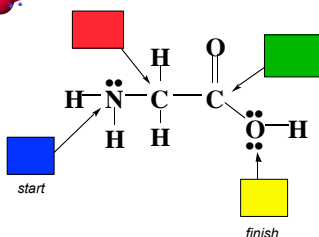
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	Arrangement of Hybrid Orbitals	Geometric figure	Example
Two electron pairs $sp$		Linear	$180^\circ$ $BeCl_2$
Three electron pairs $sp^2$		Trigonal-planar	$120^\circ$ $BF_3$
Four electron pairs $sp^3$		Tetrahedral	$109.5^\circ$ $CH_4$

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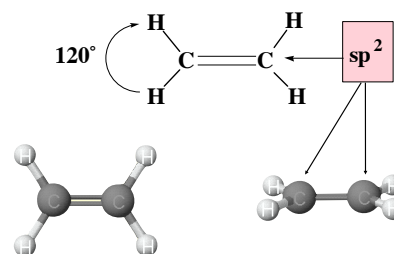
## Bonding in Glycine



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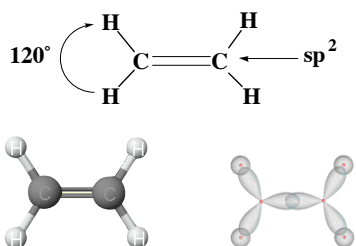
## Multiple Bonds

Consider ethylene,  $C_2H_4$



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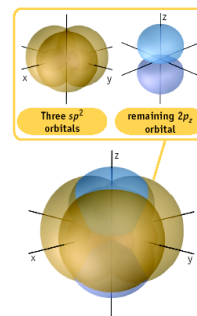
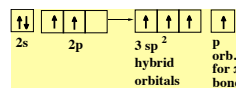
### Sigma Bonds in C<sub>2</sub>H<sub>4</sub>



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### π Bonding in C<sub>2</sub>H<sub>4</sub>

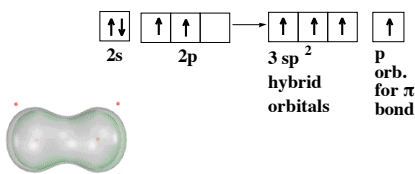
The unused p orbital on each C atom contains an electron and this p orbital overlaps the p orbital on the neighboring atom to form the π bond.



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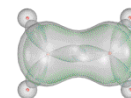
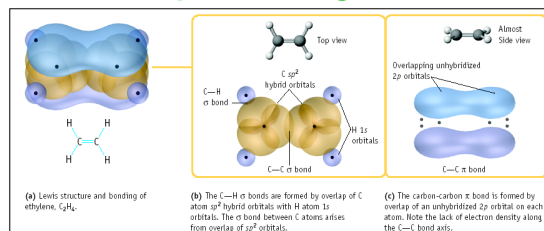
### π Bonding in C<sub>2</sub>H<sub>4</sub>

The unused p orbital on each C atom contains an electron, and this p orbital overlaps the p orbital on the neighboring atom to form the π bond.



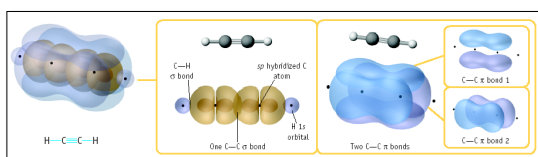
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### Multiple Bonding in C<sub>2</sub>H<sub>4</sub>



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### σ and π Bonding in C<sub>2</sub>H<sub>2</sub>

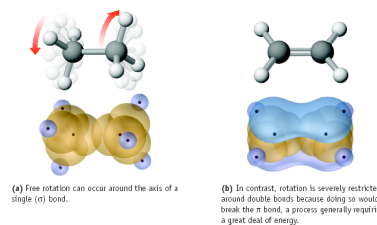


C<sub>2</sub>H<sub>2</sub> has a *triple bond*

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### Consequences of Multiple Bonding

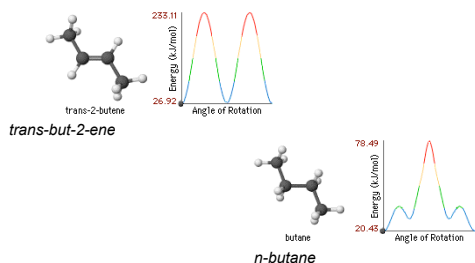
There is restricted rotation around C=C bond.



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## Consequences of Multiple Bonding

Restricted rotation around C=C bond.

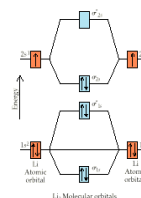


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## Molecular Orbital Theory

- Accounts for paramagnetism, color, bonding
- Atomic orbitals delocalize into **molecular orbitals**
- Bonding, Antibonding and Nonbonding orbitals**
- Quite complicated, need computers; we will only look at **diatomics (2 atom systems)** from the **first and second periods only**



## Advantages of MO Theory



Dioxygen should be electron paired (**diamagnetic**) by VB Theory, but dioxygen is actually **paramagnetic**. MO Theory accounts for paramagnetism of O<sub>2</sub>

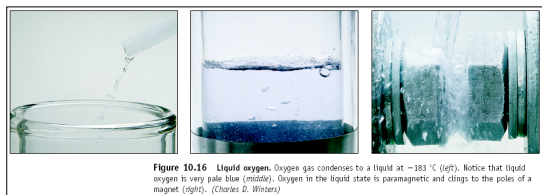


Figure 10.16 Liquid oxygen. Oxygen gas condenses to a liquid at  $-183^{\circ}\text{C}$  (left), notice that liquid oxygen is very pale blue (middle). Oxygen in the liquid state is paramagnetic and clings to the poles of a magnet (right). (Charles D. Winters)

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## Four Principles of MO Theory

**Principle #1:**

Number of Molecular Orbitals =  
Number of Atomic Orbitals

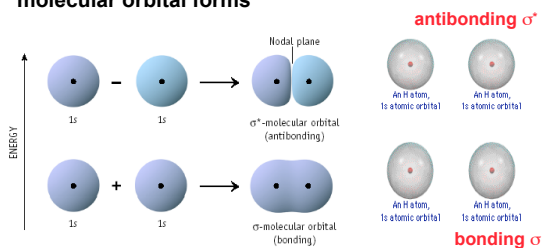
Two 1s orbitals from two hydrogen atoms create two molecular orbitals in H<sub>2</sub>

Two 1s orbitals and two 2s orbitals from two lithium atoms create four molecular orbitals in Li<sub>2</sub>

See Four Principles of MO Handout

## Molecular Orbital Type

When two atomic 1s H orbitals combine, a bonding ( $\sigma$ ) and antibonding ( $\sigma^*$ ) molecular orbital forms



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## Four Principles of MO Theory

**Principle #2:**

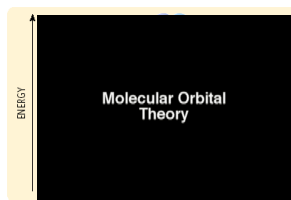
Bonding MO lower in energy than the parent orbital  
Antibonding MO higher in energy than the parent orbital

**Principle #3:**

Electrons of molecule assigned to successively higher MOs

Use **Pauli Exclusion Principle** and **Hund's Rule** when assigning electrons

## MO Diagram for H<sub>2</sub>



Antibonding MO

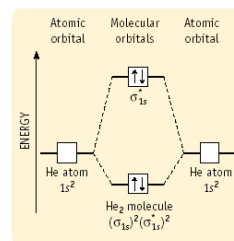
Atomic Orbitals

Bonding MO

Two 1s electrons from two H atoms occupy the  $\sigma$  orbital in H<sub>2</sub>

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## MO Diagram for He<sub>2</sub>



Antibonding MO

Atomic Orbitals

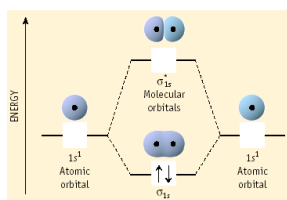
Bonding MO

Two 1s electrons in  $\sigma$ ,  
Two 1s electrons in  $\sigma^*$

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## Bond Order in MO Theory

$$\text{Bond Order} = \frac{1}{2} (\# \text{ bonding } e^- - \# \text{ antibonding } e^-)$$



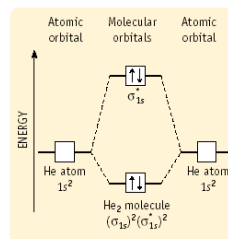
Bond Order > 0,  
**stable molecule**  
Bond Order = 0 or < 0,  
**unstable molecule**

In H<sub>2</sub>,  
Bond Order =  
 $\frac{1}{2} (2 - 0) = 1$ ;  
**stable**

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## Bond Order in MO Theory

$$\text{Bond Order} = \frac{1}{2} (\# \text{ bonding } e^- - \# \text{ antibonding } e^-)$$



Bond Order > 0,  
**stable molecule**  
Bond Order = 0 or < 0,  
**unstable molecule**

In He<sub>2</sub>,  
Bond Order =  
 $\frac{1}{2} (2 - 2) = 0$ ;  
**unstable**

**∴ He<sub>2</sub> does not exist**

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## Four Principles of MO Theory

### Principle #4:

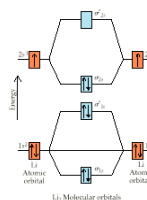
Atomic orbitals combine to give molecular orbitals **only** when the atomic orbitals are of **similar energy**

Similar energy = better overlap

- 1s + 1s = good MO
- 1s + 2s = poor MO
- 2s + 2s = good MO
- 2s + 2p = poor MO
- 3s + 2s = poor MO
- ... etc. ...

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## Example: Dilithium, Li<sub>2</sub>



Note: no overlap between 1s and 2s

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

Stable molecule

Would you expect Be<sub>2</sub> to exist? Why?



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### p orbitals and $\pi$ bonds

Three possible p orbitals on each atom - *six total* p MO orbitals

Two p orbitals create **2  $\sigma$  MO bonds**

Four remaining p orbitals create **4  $\pi$  MO bonds**

Four p atomic orbitals create four  $\pi$  molecular orbitals,  
 $\pi$  = bonding (2)  
 $\pi^*$  = antibonding (2)

... but there's a catch!

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### p orbitals and $\pi$ bonds

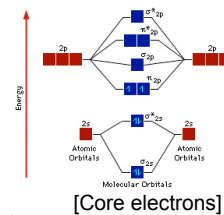
For **B, C and N**,

$\pi$  orbitals lower energy than  $\sigma$  orbital

$\pi^*$  orbitals lower energy than  $\sigma^*$  orbital

Example:  $B_2$

Bond Order = 1



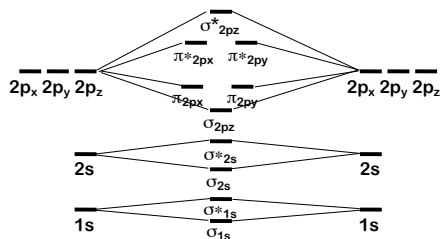
MAR See MO Diagram ( $B_2 - N_2$ ) Handout

### p orbitals and $\pi$ bonds

For **O, F and Ne**,

$\sigma$  orbital lower energy than  $\pi$  orbitals

$\pi^*$  orbitals lower energy than  $\sigma^*$  orbital



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### p orbitals and $\pi$ bonds

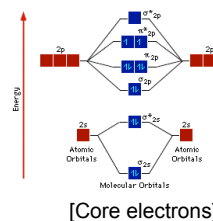
For **O, F and Ne**,

$\sigma$  orbital lower energy than  $\pi$  orbitals

$\pi^*$  orbitals lower energy than  $\sigma^*$  orbital

Example:  $O_2$

Bond Order = 2

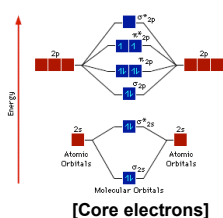


MAR See MO Diagram ( $B_2 - N_2$ ) Handout

### Paramagnetism

Paramagnetism exists when unpaired electrons in MO diagram

$O_2$  is paramagnetic; unpaired electrons in two  $\pi^*$  orbitals

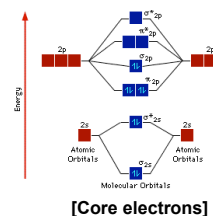


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### Paramagnetism

Paramagnetism exists when unpaired electrons in MO diagram

$N_2$  is diamagnetic; all electrons paired

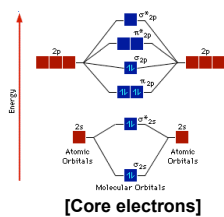


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## Molecular Orbital Notation

Used to abbreviate the MO diagrams

- Ignore core electrons
- Write in order of increasing energy



For N<sub>2</sub>:

$$[\text{core electrons}](\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^4(\sigma_{2p})^2$$

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## Sigma and Pi Bonds

Determine sigma and pi bonds using:

$$\# \sigma \text{ bonds} = \frac{1}{2} (\# \sigma \text{ bonding e}^- - \# \sigma \text{ antibonding e}^-)$$

$$\# \pi \text{ bonds} = \frac{1}{2} (\# \pi \text{ bonding e}^- - \# \pi \text{ antibonding e}^-)$$

and

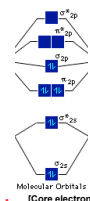
$$\# \sigma \text{ bonds} + \# \pi \text{ bonds} = \text{bond order}$$

For N<sub>2</sub>: [core electrons](σ<sub>2s</sub>)<sup>2</sup>(σ\*<sub>2s</sub>)<sup>2</sup>(π<sub>2p</sub>)<sup>4</sup>(σ<sub>2p</sub>)<sup>2</sup>

$$\# \sigma \text{ bonds} = \frac{1}{2}(4 - 2) = 1 \sigma \text{ bond}$$

$$\# \pi \text{ bonds} = \frac{1}{2}(4 - 0) = 2 \pi \text{ bonds}$$

$$\text{bond order} = \frac{1}{2}(8 - 2) = 3 = 1 \sigma + 2 \pi \text{ bonds}$$



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## MO Diagram for Diatomics

	Large 2s-2p interaction			Small 2s-2p interaction		
	B <sub>2</sub>	C <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>	F <sub>2</sub>	Ne <sub>2</sub>
σ <sub>2p</sub>	□	□	□	□	□	□
π <sub>2p</sub>	□	□	□	□	□	□
σ <sub>2p</sub>	□	□	□	□	□	□
π <sub>2p</sub>	□	□	□	□	□	□
σ <sub>2s</sub>	□	□	□	□	□	□
σ* <sub>2s</sub>	□	□	□	□	□	□
Bond order	1	2	3	2	1	0
Bond enthalpy (kJ/mol)	298	620	941	495	155	—
Bond length (Å)	1.59	1.31	1.10	1.21	1.43	—
Magnetic behavior	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic	—

Note: all should have [core electrons]

Changes in MO diagrams due to s-p mixing and/or electron repulsion

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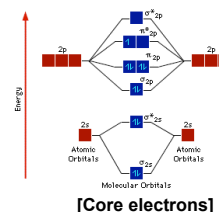
## Ionic Diatomic Molecules

Predicting Ionic Diatomic MO diagrams simple  
Use Hund and Pauli

Example: O<sub>2</sub><sup>+</sup>

Remove electron from π\*<sub>2p</sub> orbital

Check bond order, paramagnetism



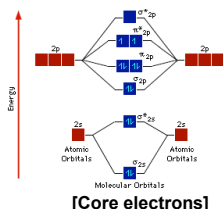
[Core electrons]

## Ionic Diatomic Molecules

Predicting Ionic Diatomic MO diagrams simple  
Use Hund and Pauli

Example: O<sub>2</sub><sup>-</sup>

Using the O<sub>2</sub> diagram on the right, where would you place the extra electron? Is O<sub>2</sub><sup>-</sup> more or less stable than O<sub>2</sub>? Why?



[Core electrons]

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## Application: Vision

Molecular Orbital Theory helps to describe the process of vision - photochemistry





## Application: Band Theory

In **metallic** bonding, electrons delocalized over metallic lattice - a **sea of electrons**

MO energies identical, excellent overlap

Helps explain conductivity, malleability, more



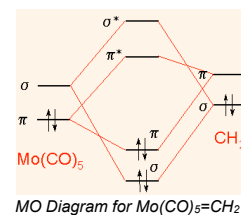
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## End of Chapter 8

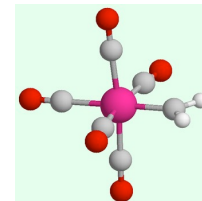
See:

- [Chapter Eight Study Guide](#)
- [Chapter Eight Concept Guide](#)
- [Important Equations \(following this slide\)](#)
- [End of Chapter Problems \(following this slide\)](#)

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MO Diagram for  $\text{Mo}(\text{CO})_5=\text{CH}_2$



### Important Equations, Constants, and Handouts from this Chapter:

- the bond order, bond energy and bond length relationships still apply to both theories
- know the advantages and disadvantages of the Valence Bond and Molecular Orbital theories
- see the [Geometry and Polarity Guide](#) and the two [Molecular Orbital Theory diagrams \(NBC and FONE\)](#) (handouts)

**Valence Bond / Hybridization Theory:** types of hybridization (sp, sp<sup>2</sup>, etc.), sigma and pi bonds

**Molecular Orbital Theory:** bonding and antibonding orbitals, sigma bonds and pi bonds, paramagnetic and diamagnetic, the “NBC” vs. “FONE” diagrams

$$\text{bond order (MO theory)} = \frac{1}{2}(\# \text{ bonding } e^- - \# \text{ antibonding } e^-)$$

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### End of Chapter Problems: Test Yourself

Be sure to view practice problem set #2 and self quizzes for **MO theory and Valence Bond theory examples and practice**

1. Specify the electron-pair and molecular geometry for each of the following. Describe the hybrid orbital set used by the central atom in each molecule or ion.  
a. BBr<sub>3</sub> b. CO<sub>2</sub> c. CH<sub>2</sub>Cl<sub>2</sub> d. XeF<sub>4</sub>
2. Use MO theory to tell which has the largest bond order: C<sub>2</sub> or F<sub>2</sub>. Are either species paramagnetic?
3. Use MO theory to speculate on the existence of dilithium.
4. Which compound is stronger by MO theory: Be<sub>2</sub> or B<sub>2</sub><sup>+</sup>.
5. Describe the hybridization change on carbon as methane (CH<sub>4</sub>) is burned to create carbon dioxide.

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### End of Chapter Problems: Answers

1. a. trigonal planar, trigonal planar, sp<sup>2</sup>. b. linear, linear, sp. c. tetrahedral, tetrahedral, sp<sup>3</sup>. d. octahedral, square planar, sp<sup>3</sup>d<sup>2</sup>
2. BO(C<sub>2</sub>) = 2, diamagnetic. BO(F<sub>2</sub>) = 1, diamagnetic.
3. By MO theory, dilithium (Li<sub>2</sub>) should exist (BO = 1, diamagnetic.)
4. MO theory would predict that B<sub>2</sub><sup>+</sup> (bond order = 0.5, paramagnetic) is stronger than Be<sub>2</sub> (bond order = 0, this should not exist at all.)
5. sp<sup>3</sup> to sp

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