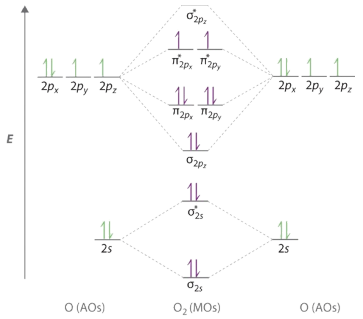
Chapter 5: Advanced Theories of Bonding

Chemistry 221
Professor Michael Russell
http://mhchem.org/221



[Core electrons]

Last update: 7/7/25

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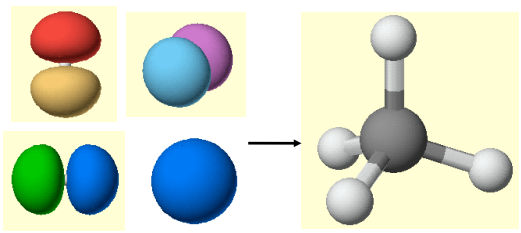
5.1 - Valence Bond Theory

How to go from atomic orbitals to the geometries described via VSEPR in molecules?



Atomic Orbitals → Molecules

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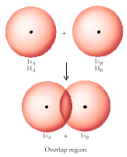
Two Theories of Bonding

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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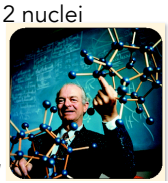
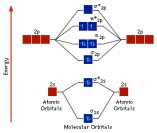


Linus Pauling

MOLECULAR ORBITAL (MO) THEORY - Robert Mulliken

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

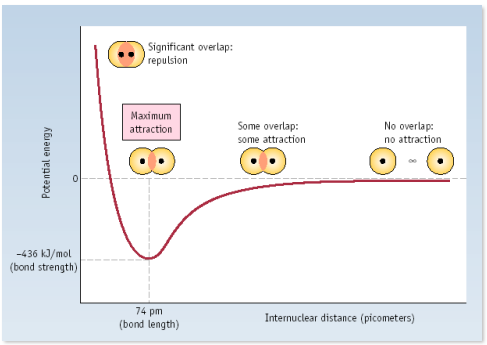


Robert Mulliken

Sigma Bonds

For both theories, consider the 'overlap' between orbitals to make a sigma (σ) bond

This diagram is for two 1s orbitals (H_2)



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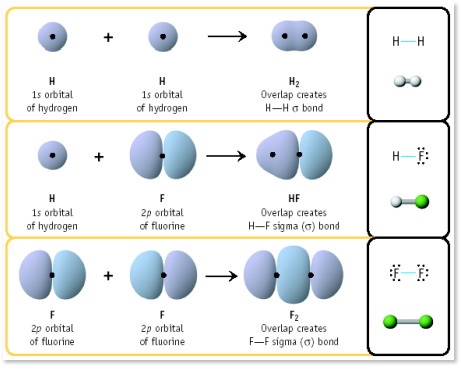
Other Types of Sigma Bonds

Two s orbitals overlap

One s & one p overlap

Two p orbitals overlap



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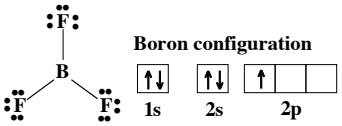
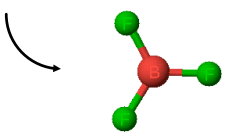
5.2 - Hybrid Atomic Orbitals

Bonding in BF_3





trigonal planar
angle = 120°

We can use BF_3 to discus Valence Bond Theory.

The question:

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

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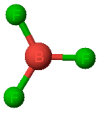
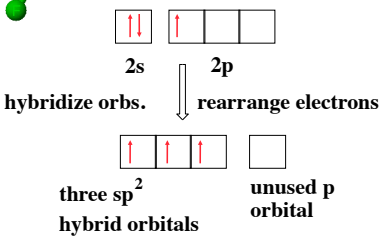
Valence Bond Theory: Bonding in BF_3





Pauling said to modify Valence Bonds with Orbital Hybridization

Mix available atomic orbitals to form a new set of orbitals - *Hybrid* Orbitals - that will give the maximum overlap in the correct geometry.

one s and 2 p atomic orbitals gives 3 sp^2 orbitals

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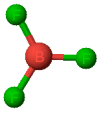
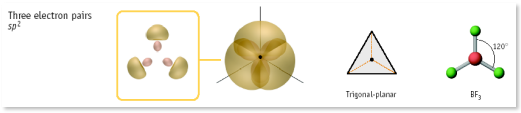
Valence Bond Theory: Bonding in BF_3



The three hybrid orbitals are made from 1 s orbital and 2 p orbitals create 3 sp^2 hybrid orbitals



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

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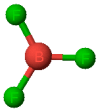
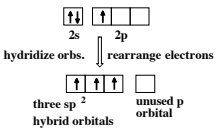
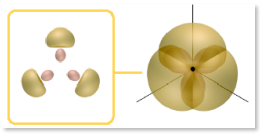
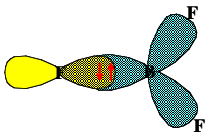
Valence Bond Theory: Bonding in BF_3







An atomic orbital from each F overlaps one of the sp^2 hybrids to form a B-F σ bond.



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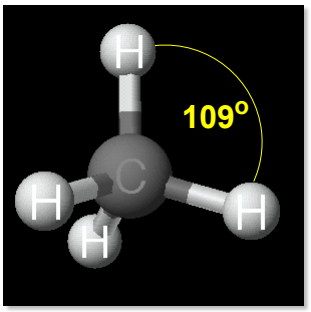
Valence Bond Theory: Bonding in CH_4

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

Need to use 4 atomic orbitals - s, p_x, p_y, and p_z - to form 4 new hybrid orbitals pointing in the correct direction.



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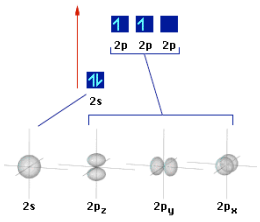
Bonding in a Tetrahedron - Formation of Hybrid Atomic Orbitals



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

one s and 3 p atomic orbitals gives 4 sp^3 orbitals

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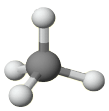
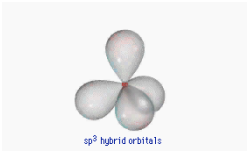
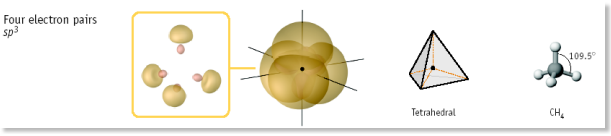
Bonding in a Tetrahedron - Formation of Hybrid Atomic Orbitals





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



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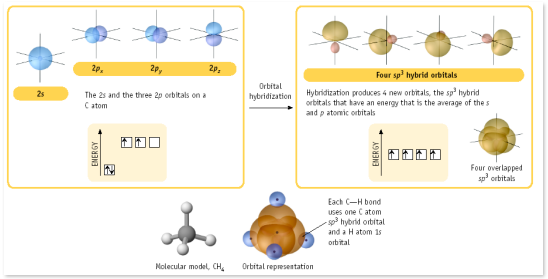
Bonding in CH_4



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Valence Bond Theory: Summary

To form a covalent bond, an atom must have an **unpaired electron**.

Number of bonds formed by an atom is **determined by the number of unpaired electrons**.

VB works well for explaining the bonding in diatomic molecules and for explaining the lack of bonding by the noble gases.

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**	---

All tetrahedral EPG = sp^3 hybridized, etc.

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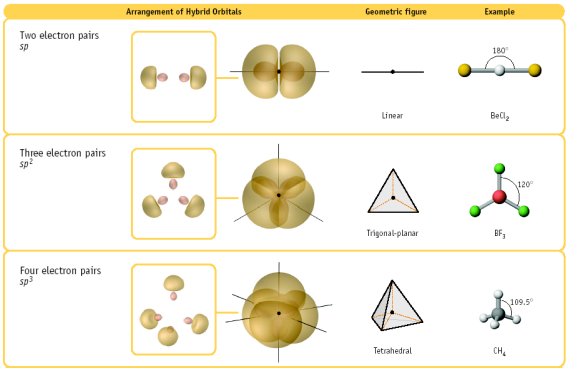

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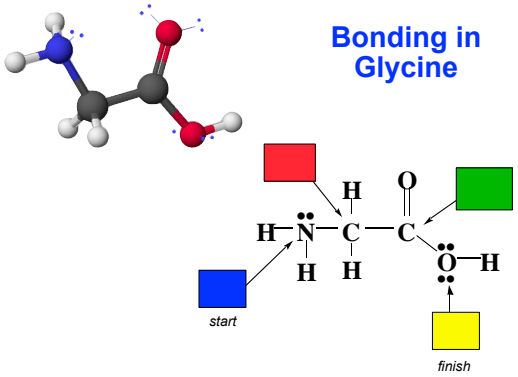
Bonding in Glycine



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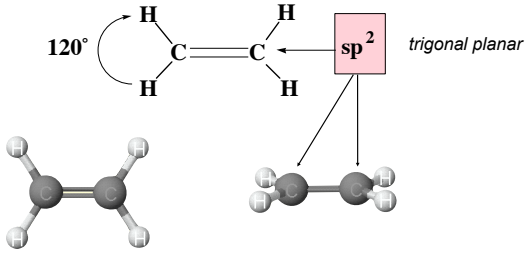
5.3 - Multiple Bonds

How to multiple bonds work with valence bond theory?

Consider ethylene, C_2H_4



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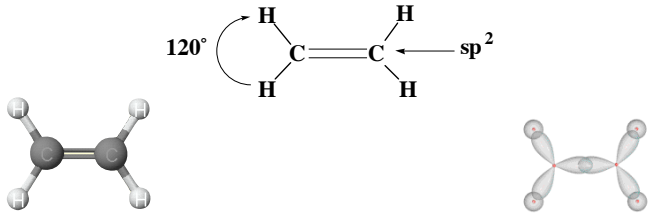
Sigma Bonds in C_2H_4

Sigma bonds *('single bonds')* **operate through 'head to head' overlap of singly occupied orbitals in each atom**

Ethylene has sigma bonds between the C and H atoms as well as a sigma bond between the two C atoms



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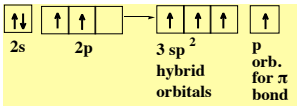
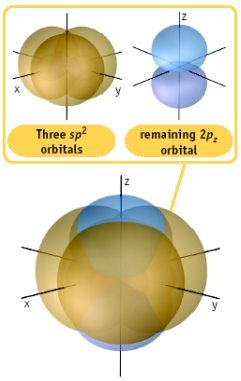
Pi (π) Bonds in C_2H_4

The unused p electrons on each C overlap in a 'side-by-side' sharing of 'regular' atomic p orbitals to make a π bond

π bonds are 'above and below' the sigma bond





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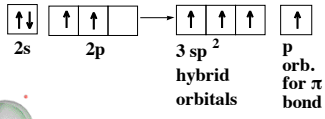
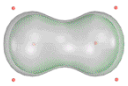
Pi (π) Bonds in C_2H_4

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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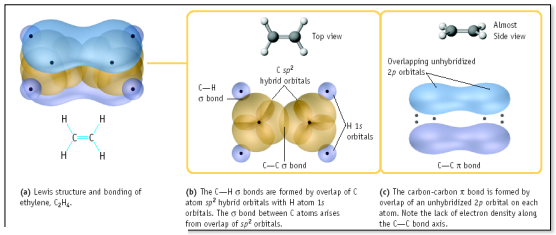
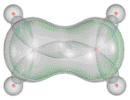
Multiple Bonding in C_2H_4





Notice how a double bond contains one sigma and one pi bond!

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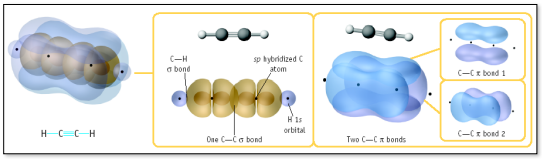
σ and π Bonding in C_2H_2

H—C≡C—H



C_2H_2 has a *triple bond*

Notice how a triple bond contains one sigma and two pi bonds!

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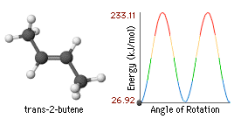
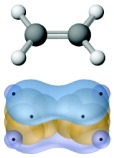
Consequences of Multiple Bonding

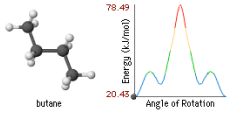
C=C bonds do not rotate well, but C-C bonds rotate easily



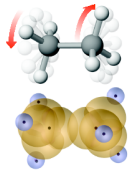
trans-but-2-ene



(b) In contrast, rotation is severely restricted around double bonds because doing so would break the π bond, a process generally requiring a great deal of energy.



n-butane



(a) Free rotation can occur around the axis of a single (σ) bond.

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5.4 - Molecular Orbital Theory

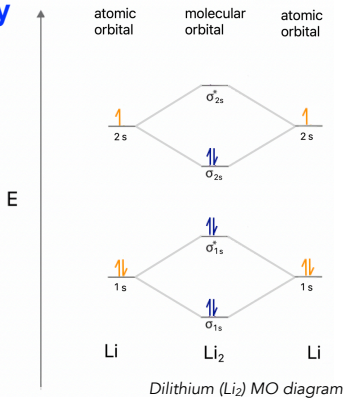
Molecular Orbital Theory (MO) extends quantum mechanical wave functions to molecules

MO accounts for paramagnetism, color, bonding

Atomic orbitals delocalize into molecular orbitals

Bonding and Antibonding orbitals

Quite complicated, need computers; we will only look at diatomics (*2 atom systems*) from the first and second periods *only*



Dilithium (Li_2) MO diagram

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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_2

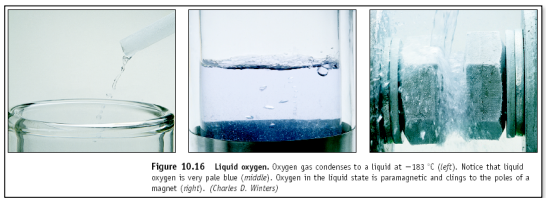

Figure 10.16 Liquid oxygen. Oxygen gas condenses to a liquid at −183 °C (*left*). Notice that liquid oxygen is very pale blue (*middle*). Oxygen in the liquid state is paramagnetic and clings to the poles of a magnet (*right*). *(Charles D. Winters)*

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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_2

Two 1s orbitals and two 2s orbitals from two lithium atoms create four molecular orbitals in Li_2

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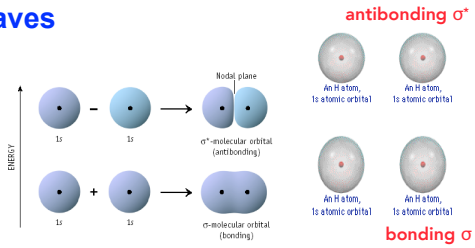
MO Theory and Waves

When two atomic 1s H orbitals combine, a **bonding (σ)** and **antibonding (σ*)** molecular orbital forms



constructive (bonding) destructive (antibonding)

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Principles #2 and #3 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

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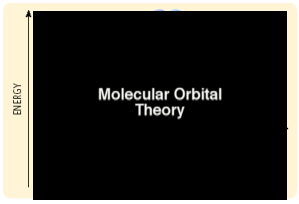
MO Diagram for H_2



Antibonding MO

Atomic Orbitals

Bonding MO

Two 1s electrons from two H atoms occupy the σ orbital in H_2

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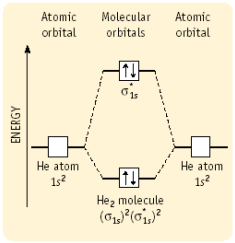
MO Diagram for He_2



Antibonding MO

Atomic Orbitals

Bonding MO

Two 1s electrons in σ,
Two 1s electrons in σ*

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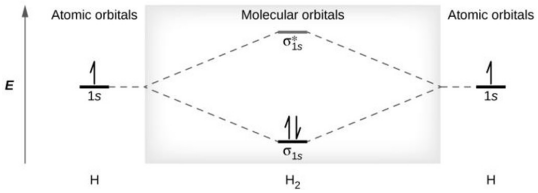
Bond Order for H_2

Bond Order = $^1/_2$ (# bonding e$^-$ - # antibonding e$^-$)

Bond Order **> 0**,
stable molecule (exists)
Bond Order **= 0** *(or < 0)*,
unstable molecule (does not exist)



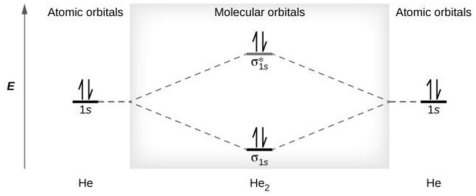
Scientists use **bond order** to tell if a molecule can exist (or not)

In H_2,
Bond Order =
$^1/_2$ (2 - 0) = 1;
stable

Bond Order for He_2

Bond Order = $^1/_2$ (# bonding e$^-$ - # antibonding e$^-$)

Bond Order **> 0**,
stable molecule (exists)
Bond Order **= 0** *(or < 0)*,
unstable molecule (does not exist)



Scientists use **bond order** to tell if a molecule can exist (or not)

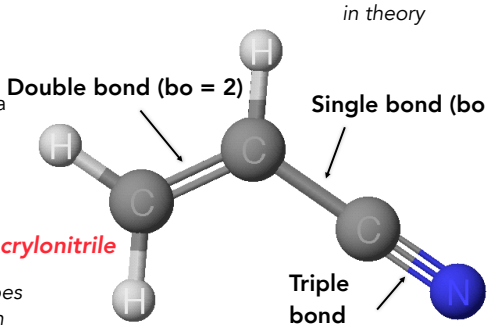
In He_2,
Bond Order =
$^1/_2$ (2 - 2) = 0;
unstable
$\therefore$ He_2 does not exist

More on Bond Order

In a **Lewis structure:**

* a single bond has a bond order of 1
* a double bond has a bond order of 2
* a triple bond has a bond order of 3

A Molecular Orbital bond order is similar in theory



As bond order goes up, bond length goes down

MAR

Principle #4 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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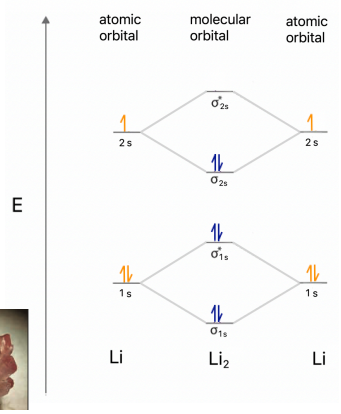
MO Diagram for Dilithium, Li_2

Note: no overlap between 1s and 2s

Bond Order = $^1/_2$ (4 - 2) = 1

Stable molecule



Would you expect Be_2 to exist? Why?

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2p orbitals, σ and π bonds

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

Two p orbitals create 2 σ MO bonds

Four remaining p orbitals create 4 π MO bonds

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

... but there's a catch!

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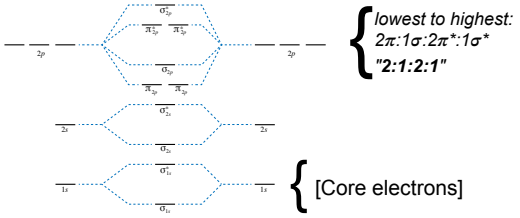
2p orbitals, σ and π bonds for "NBC"

For B, C and N *("NBC")*,
π orbitals lower energy than σ orbital
π* orbitals lower energy than σ* orbital



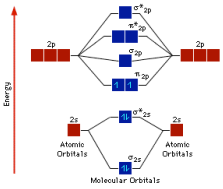
MAR See MO Diagram (B_2 - N_2) Handout

2p orbitals, σ and π bonds for "NBC"

For B, C and N *("NBC")*,
π orbitals lower energy than σ orbital
π* orbitals lower energy than σ* orbital

Example: B_2

Bond Order = 1

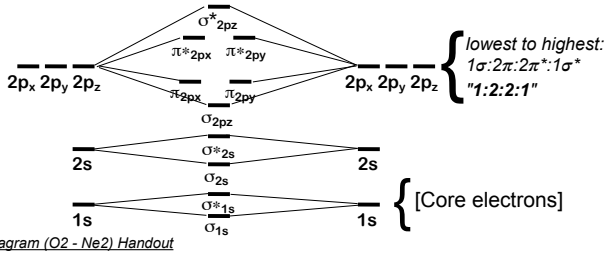


[Core electrons]

MAR See MO Diagram (B_2 - N_2) Handout

2p orbitals, σ and π bonds for "FONe"

For F, O and Ne *("FONe")*,
σ orbital lower energy than π orbitals
π* orbitals lower energy than σ* orbital



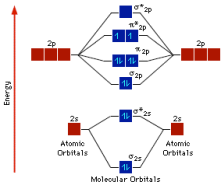
MAR See MO Diagram (O2 - Ne2) Handout

2p orbitals, σ and π bonds for "FONe"

For F, O and Ne *("FONe")*,
σ orbital lower energy than π orbitals
π* orbitals lower energy than σ* orbital

Example: O_2

Bond Order = 2



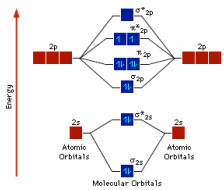
[Core electrons]

MAR See MO Diagram (O2 - Ne2) Handout

Paramagnetism

Paramagnetism exists when unpaired electrons found in MO diagram

O_2 is paramagnetic;
unpaired electrons
in two π* orbitals



[Core electrons]

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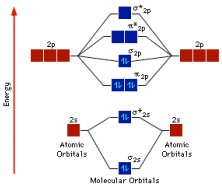
Paramagnetism

Paramagnetism exists when unpaired electrons found in MO diagram

N_2 is diamagnetic;
all electrons paired



[Core electrons]

MAR

Ionic Diatomic Molecules

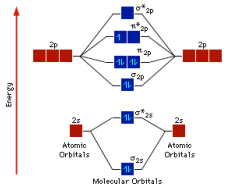
Predicting Ionic Diatomic MO diagrams simple: start with neutral molecule, then add or subtract electrons as necessary

Use Hund's rule and Pauli exclusion principle; re-check magnetism, bond order, etc.

Example: O_2^{1+}

Remove electron from π^*_{2p} orbital

bond order = 2.5, paramagnetic



[Core electrons]

MAR

Electrons are removed from the Highest Occupied Molecular Orbital (**HOMO**) in the molecule

Ionic Diatomic Molecules

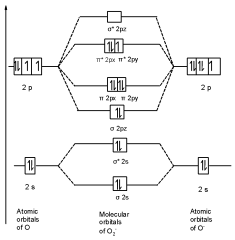
Predicting Ionic Diatomic MO diagrams simple: start with neutral molecule, then add or subtract electrons as necessary

Use Hund's rule and Pauli exclusion principle; re-check magnetism, bond order, etc.

Example: O_2^{1-}

Add electron to π^*_{2p} orbital

bond order = 1.5, paramagnetic



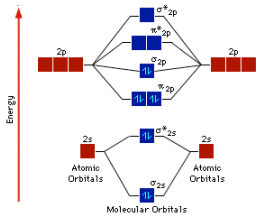
[Core electrons]

MAR

Electrons are added from the Lowest Unoccupied Molecular Orbital (**LUMO**) in the molecule

Molecular Orbital Shorthand Notation

Used to abbreviate the MO diagrams



[Core electrons]

- Ignore core electrons (all 1s interactions *only*) by writing **[core electrons]**
- combine π_{2px} and π_{2py} into one π_{2p} parentheses *(same with antibonding)*
- Write in order of **increasing energy**

For N_2:

[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:

 # σ bonds = $^1/_2$ (# σ bonding e$^-$ - # σ antibonding e$^-$)

 # π bonds = $^1/_2$ (# π bonding e$^-$ - # π antibonding e$^-$)

and

bond order = # σ bonds + # π bonds

For N_2: [core electrons]$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^4(\sigma_{2p})^2$

σ bonds = $^1/_2$(4 - 2) = 1 σ bond
π bonds = $^1/_2$(4 - 0) = 2 π bonds

bond order = $^1/_2$(8 - 2) = 3 = 1 σ + 2 π bonds

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MO Diagram for Diatomics

Large 2*s*-2*p* interaction				Small 2*s*-2*p* interaction		
	B_2	C_2	N_2	O_2	F_2	Ne_2
σ^*_{2p}						
π^*_{2p}						
σ_{2p}						
π_{2p}						
σ^*_{2s}						
σ_{2s}						
Bond order	1	2	3	2	1	0
Bond enthalpy (kJ/mol)	290	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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MO Application: Vision

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

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End of Chapter 5

See:

- *Chapter Five Study Guide*
- *Chapter Five Concept Guide*
- *Important Equations (following this slide)*
- *End of Chapter Problems (following this slide)*

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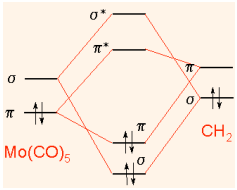
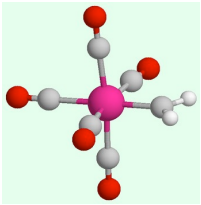


MO Diagram for $Mo(CO)_5=CH_2$



Important Equations, Constants, and Handouts from this Chapter:

- *the* **bond order, bond energy and bond length** *relationships*
- *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^2, 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*

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

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End of Chapter Problems: *Test Yourself*

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_3 b. CO_2 c. CH_2Cl_2 d. XeF_4
2. Use MO theory to tell which has the largest bond order: C_2 or F_2. Are either species paramagnetic?
3. Use MO theory to speculate on the existence of dilithium.
4. Which compound is stronger by MO theory: Be_2 or B_2^{+1}.
5. Describe the hybridization change on carbon as methane (CH_4) is burned to create carbon dioxide.

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End of Chapter Problems: *Answers*

1. a. trigonal planar, trigonal planar, sp^2. b. linear, linear, sp. c. tetrahedral, tetrahedral, sp^3. d. octahedral, square planar, sp^3d^2
2. $BO(C_2) = 2$, diamagnetic. $BO(F_2) = 1$, diamagnetic.
3. By MO theory, dilithium (Li_2) should exist (BO = 1, diamagnetic.)
4. MO theory would predict that B_2^{+1}(bond order = 0.5, paramagnetic) is stronger than Be_2 (bond order = 0, this should not exist at all.)
5. sp^3 to sp

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