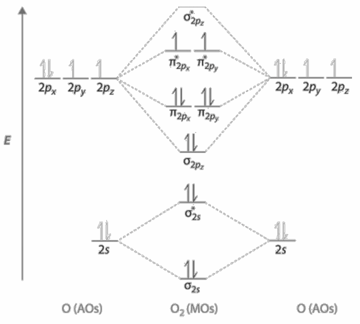
Chapter 5: Advanced Theories of Bonding



[Core electrons]

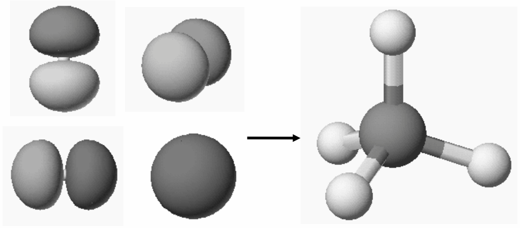
Chemistry 221
Professor Michael Russell
http://mhchem.org/221

Last update: 7/7/25

MAR

5.1 - Valence Bond Theory

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



MAR

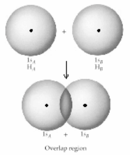
Two Theories of Bonding

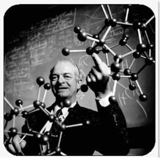
VALENCE BOND (VB) THEORY - **Linus Pauling**

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

half-filled atomic orbitals overlap to form bonds.

electrons stabilized by 2 nuclei

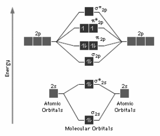


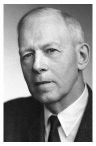


Linus Pauling

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

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





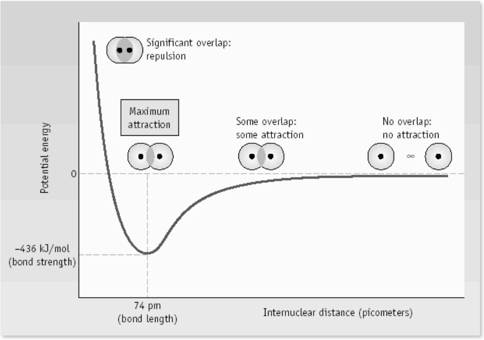
Robert Mulliken

MA

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)



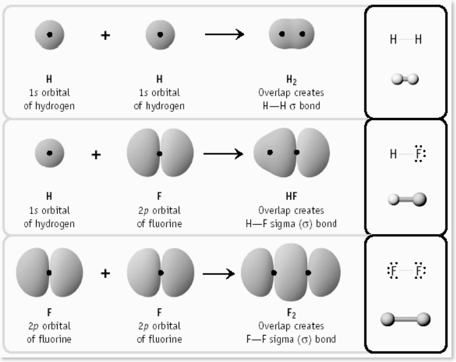
MAR

Other Types of Sigma Bonds

Two s orbitals overlap

One s & one p overlap

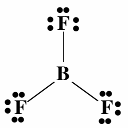
Two p orbitals overlap



MAR

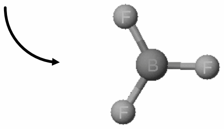
5.2 - Hybrid Atomic Orbitals

Bonding in BF_3



Boron configuration

↑↓	↑↓	↑ ☐ ☐
1s	**2s**	**2p**



trigonal planar
angle = 120°

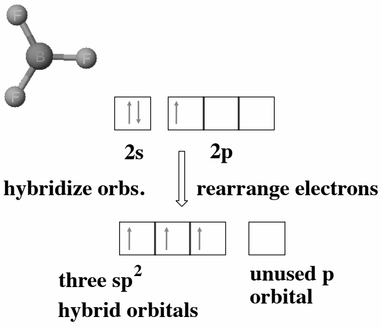
We can use BF_3 to discus Valence Bond Theory.

The question:

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

MAR

Valence Bond Theory: Bonding in BF_3



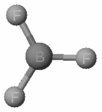
Pauling said to modify Valence Bonds with Orbital Hybridization

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

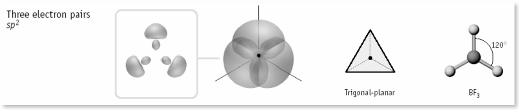
one s and 2 p atomic orbitals gives 3 sp^2 orbitals

MAR

Valence Bond Theory: Bonding in BF_3



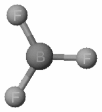
The three hybrid orbitals are made from 1 s orbital and 2 p orbitals create 3 sp^2 hybrid orbitals

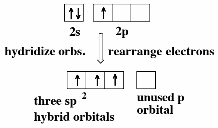


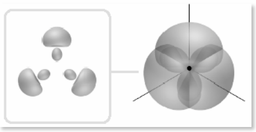
Now we have 3, half-filled HYBRID orbitals that can be used to form *planar* B-F sigma bonds.

MAR

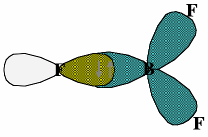
Valence Bond Theory: Bonding in BF_3







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

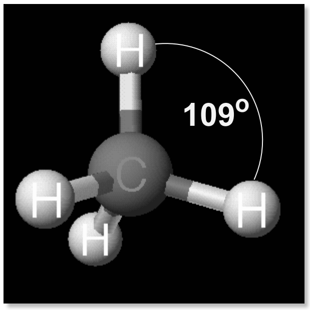


MAR

Valence Bond Theory: Bonding in CH_4

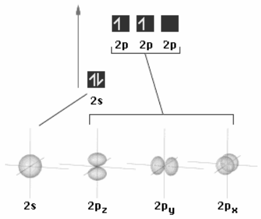
How do we account for 4 C-H sigma bonds 109° apart?

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.



MAR

Bonding in a Tetrahedron - Formation of Hybrid Atomic Orbitals

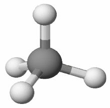


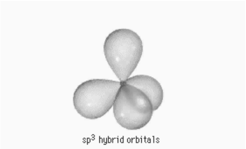
4 C atom orbitals hybridize to form four equivalent sp^3 hybrid atomic orbitals.

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

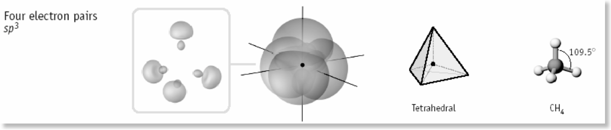
MAR

Bonding in a Tetrahedron - Formation of Hybrid Atomic Orbitals



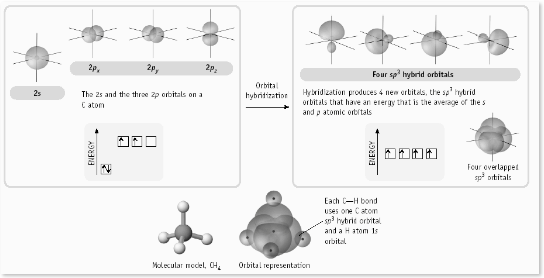


4 C atom orbitals hybridize to form four equivalent sp^3 hybrid atomic orbitals.



MAR

Bonding in CH_4



The 2*s* and the three 2*p* orbitals on a C atom

Hybridization produces 4 new orbitals, the sp^3 hybrid orbitals that have an energy that is the average of the *s* and *p* atomic orbitals

Each C—H bond uses one C atom sp^3 hybrid orbital and a H atom 1*s* orbital

Valence Bond Theory: Summary

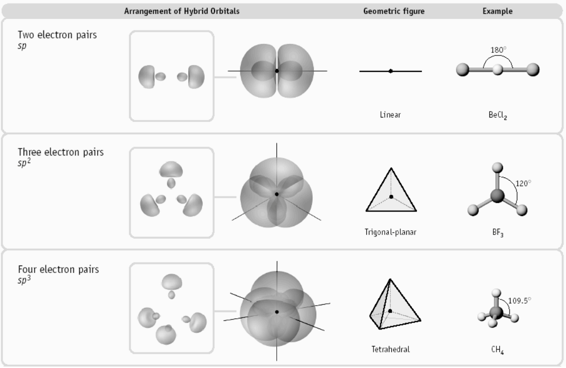
To form a covalent bond, an atom must have an **unpaired electron**.

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.

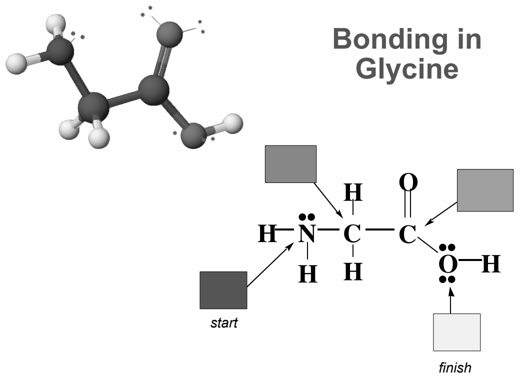
Bonds	*EPG*	*Hybrid*	*Remaining p orbs?*
2	linear	**sp**	2 p
3	trigonal planar	**sp^2**	1 p
4	tetrahedral	**sp^3**	none
5	trigonal bipyramid	**sp^3d**	---
6	octahedral	**sp^3d^2**	---

All tetrahedral EPG = sp^3 hybridized, etc.



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

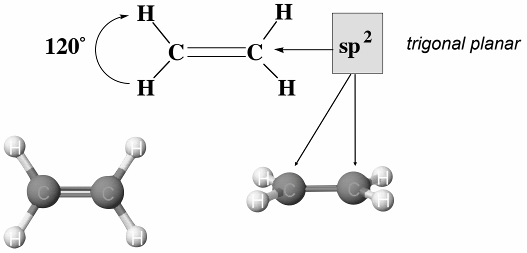
Bonding in Glycine



5.3 - Multiple Bonds

How to multiple bonds work with valence bond theory?

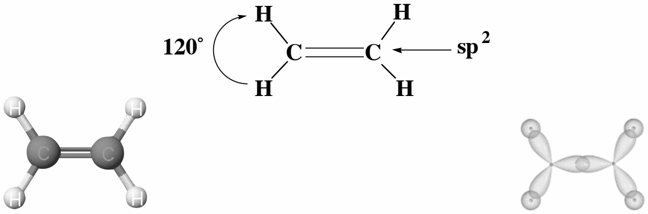
Consider ethylene, C_2H_4



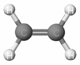
Sigma Bonds in C_2H_4

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

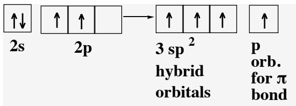


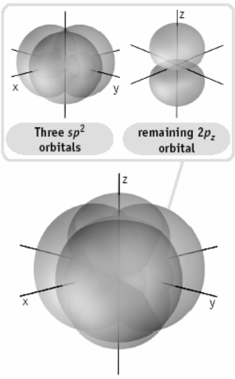
Pi (π) Bonds in C_2H_4



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

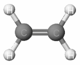
π bonds are 'above and below' the sigma bond



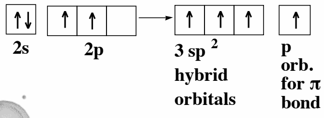


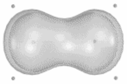
MAR

Pi (π) Bonds in C_2H_4



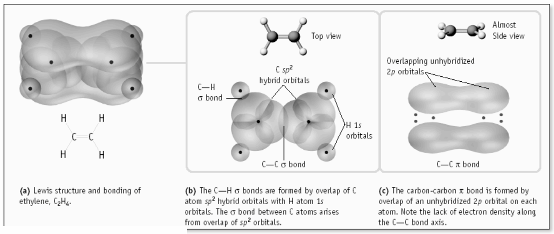
The unused p orbital on each C atom contains an electron, and this p orbital overlaps the p orbital on the neighboring atom to form the π bond.





MAR

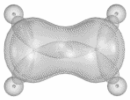
Multiple Bonding in C_2H_4



(a) Lewis structure and bonding of ethylene, C_2H_4.

(b) The C—H σ bonds are formed by overlap of C atom sp^2 hybrid orbitals with H atom 1*s* orbitals. The σ bond between C atoms arises from overlap of sp^2 orbitals.

(c) The carbon-carbon π bond is formed by overlap of an unhybridized 2*p* orbital on each atom. Note the lack of electron density along the C—C bond axis.

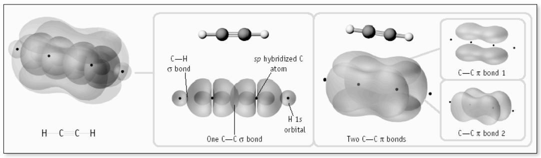


Notice how a double bond contains one sigma and one pi bond!

MAR

σ and π Bonding in C_2H_2

$H-C\equiv C-H$



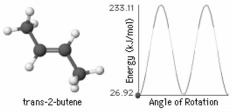
C_2H_2 has a *triple bond*

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

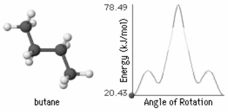
MAR

Consequences of Multiple Bonding

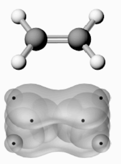
C=C bonds do not rotate well, but C-C bonds rotate easily



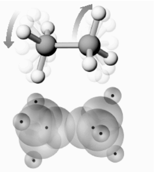
trans-but-2-ene



n-butane



(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.

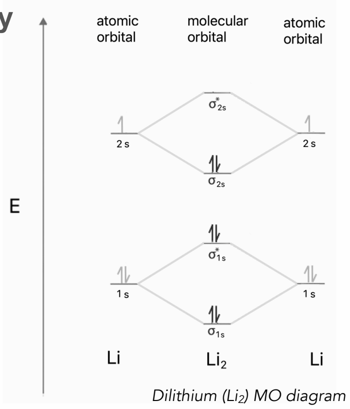


(a) Free rotation can occur around the axis of a single (σ) bond.

MAR

5.4 - Molecular Orbital Theory

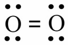
- Molecular Orbital Theory (MO) extends quantum mechanical wave functions to molecules
- MO accounts for paramagnetism, color, bonding
- Atomic orbitals delocalize into molecular orbitals
- Bonding and Antibonding orbitals
- ***Quite complicated,*** **need computers; we will only look at diatomics (*2 atom systems*) from the first and second periods *only***



Dilithium (Li_2) MO diagram

MAR

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

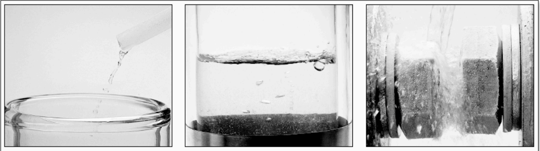


Figure 10.16 Liquid oxygen. Oxygen gas condenses to a liquid at −183 °C (*left*). Notice that liquid oxygen is very pale blue (*middle*). Oxygen in the liquid state is paramagnetic and clings to the poles of a magnet (*right*). *(Charles D. Winters)*

MAR

Four Principles of MO Theory

Principle #1:
Number of Molecular Orbitals =
Number of Atomic Orbitals

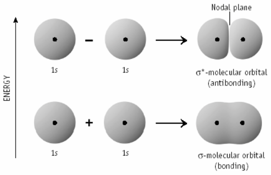
Two 1s orbitals from two hydrogen atoms create two molecular orbitals in H_2

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

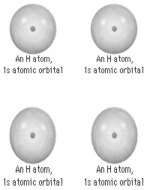
MAR

MO Theory and Waves

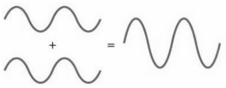
When two atomic 1s H orbitals combine, a **bonding (σ)** and **antibonding (σ*)** molecular orbital forms



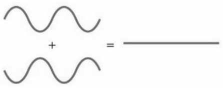
antibonding σ*



bonding σ



constructive (bonding)



destructive (antibonding)

MAR

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

MAR

MO Diagram for H_2

ENERGY

Molecular Orbital Theory

Antibonding MO

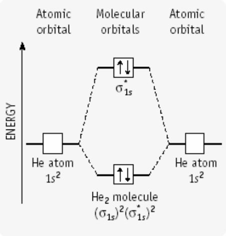
Atomic Orbitals

Bonding MO

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

MAR

MO Diagram for He_2



Antibonding MO

Atomic Orbitals

Bonding MO

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

MAR

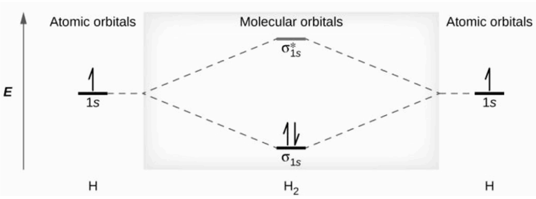
Bond Order for H_2

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

Bond Order = $^{1}/_{2}$ (# bonding e^- - # antibonding e^-)

Bond Order **> 0,**
stable **molecule (exists)**

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



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

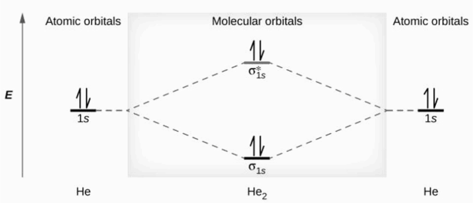
Bond Order for He_2

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

Bond Order = $^{1}/_{2}$ (# bonding e^- - # antibonding e^-)

Bond Order **> 0,**
stable **molecule (exists)**

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



In He_2,
Bond Order =
$^{1}/_{2}$ (2 - 2) = 0;
unstable
∴ He_2 does not exist

More on Bond Order

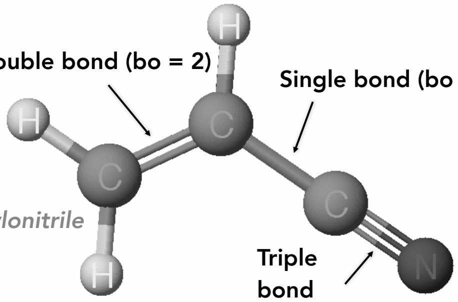
A Molecular Orbital bond order is similar in theory

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



Double bond (bo = 2)

Single bond (bo = 1)

Triple bond (bo = 3)

Acrylonitrile

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. ...

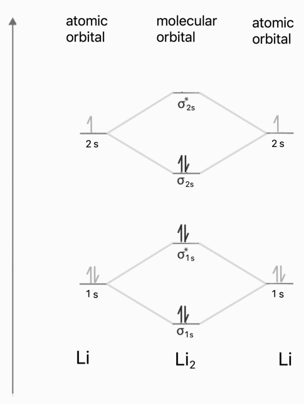
MAR

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?

MAR

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!

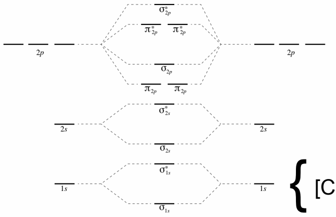
MAR

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



lowest to highest:
2π:1σ:$2\pi^*$:$1\sigma^*$
"2:1:2:1"

[Core electrons]

MAR *See <u>MO Diagram (B_2 - N_2) Handout</u>*

2p orbitals, σ and π bonds for "NBC"

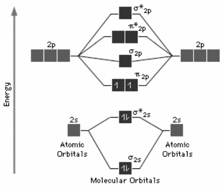
For B, C and N *("NBC")*,

π orbitals lower energy than σ orbital

π^* orbitals lower energy than σ* orbital

***Example:* B_2**

***Bond Order* = 1**



[Core electrons]

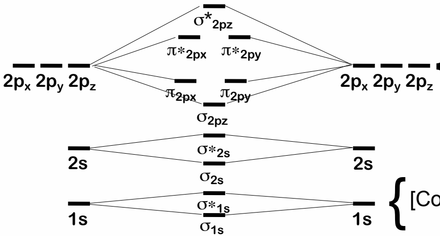
MAR *See <u>MO Diagram (B_2 - N_2) Handout</u>*

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



lowest to highest:
1σ:2π:$2\pi^*$:$1\sigma^*$
"1:2:2:1"

[Core electrons]

MAR *See <u>MO Diagram (O2 - Ne2) Handout</u>*

2p orbitals, σ and π bonds for "FONe"

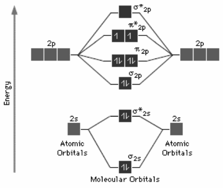
For F, O and Ne *("FONe")*,

σ orbital lower energy than π orbitals

π^* orbitals lower energy than σ* orbital

***Example:* O_2**

***Bond Order* = 2**



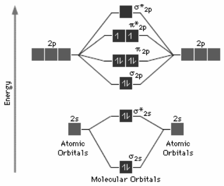
[Core electrons]

MAR *See <u>MO Diagram (O2 - Ne2) Handout</u>*

Paramagnetism

Paramagnetism exists when unpaired electrons found in MO diagram

O_2 is paramagnetic;
unpaired electrons
in two π^* orbitals



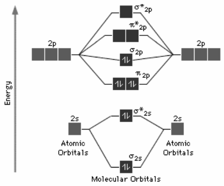
[Core electrons]

MAR

Paramagnetism

Paramagnetism exists when unpaired electrons found in MO diagram

N_2 is diamagnetic;
all electrons paired



[Core electrons]

MAR

Ionic Diatomic Molecules

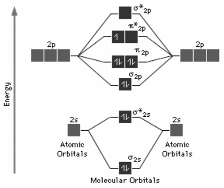
Predicting Ionic Diatomic MO diagrams simple: start with neutral molecule, then add or subtract electrons as necessary

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

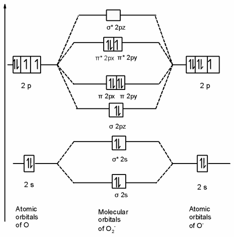
Predicting Ionic Diatomic MO diagrams simple: start with neutral molecule, then add or subtract electrons as necessary

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]

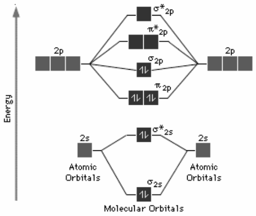
MAR

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

MAR

Sigma and Pi Bonds

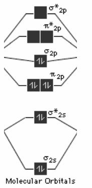
Determine sigma and pi bonds using:

 # 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



[Core electrons]

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

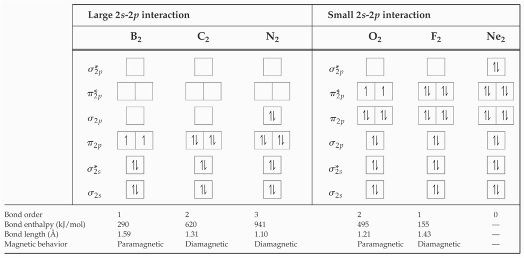
 # σ bonds = $^1/_2$(4 - 2) = 1 σ bond

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

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

MAR

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}	☐	☐	☐	σ^*_{2p}	☐	☐	↑↓
π^*_{2p}	☐ ☐	☐ ☐	☐ ☐	π^*_{2p}	↑ ↑	↑↓ ↑↓	↑↓ ↑↓
σ_{2p}	☐	☐	↑↓	π_{2p}	↑↓ ↑↓	↑↓ ↑↓	↑↓ ↑↓
π_{2p}	↑ ↑	↑↓ ↑↓	↑↓ ↑↓	σ_{2p}	↑↓	↑↓	↑↓
σ^*_{2s}	↑↓	↑↓	↑↓	σ^*_{2s}	↑↓	↑↓	↑↓
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	—

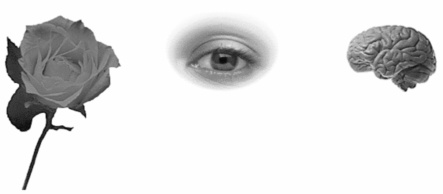
Note: all should have [core electrons]

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

MAR

MO Application: Vision

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

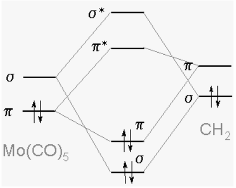


MAR

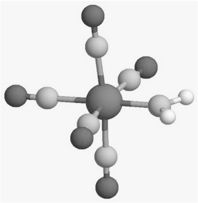
End of Chapter 5

See:

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



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

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.

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^{3}d^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