

Chemical Bonding and Molecular Structure: Orbital Hybridization and Molecular Orbitals

A Look Back - What do our current models say about REAL LIFE?

- **Atomic Structure Models:** (Bohr/Quantum Mechanical)

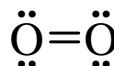
- **Bonding Model:** (Lewis Structures/VSEPR)

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Conflicts with Models and REAL LIFE.

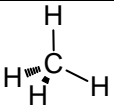
A couple of examples:

1. O₂: 12 valence e⁻, Lewis Structure:



- What does the bond look like?
 - BUT: Experiment shows that O₂ is paramagnetic
 - LEWIS STRUCTURE DOESN'T WORK!

2. Methane, CH₄

C: 1s ² 2s ² 2p ² H: 1s ¹	
<u>Expectations (theory):</u> Electron Energies:	<u>Observations (REAL LIFE):</u> Shape:
Orbital Distribution:	Bond Characteristics:

When theory breaks down, what do you do?

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Two “New” Complementary Theories:

1. Valence Bond Theory (Linus Pauling)
2. Molecular Orbital Theory (Robert Mulliken)

Valence Bond Theory

- Three main points:
 1. Covalent bonding is a result of **overlap** of atomic orbitals present in each of the components of the bond.
 2. These overlapping orbitals must contain two e⁻ of opposite spin.
 3. As a result of overlap, the probability of finding electrons in the space between the nuclei is increased.

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Valence Bond Theory

Examples:

- Bonding in H₂ (simplest example)

H: 1s¹

H₂: H-H single bond

- How does this bonding occur? What do the individual H atoms "see" as they approach one another?
- Bond formed results from the overlap of a single orbital from each atom: **sigma bond (σ bond)**



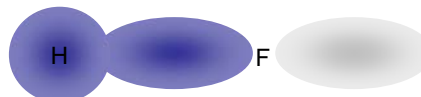
- Bonding in HF

H: 1s¹

F: 1s²2s²2p⁵

H-F single bond

- Each atom has one unpaired e⁻
- H's is in s-orbital
- F's is in p-orbital
- Form a sigma bond by overlapping s & p orbitals



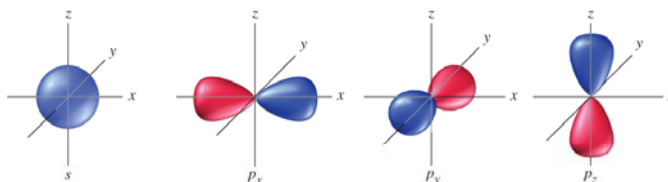
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Valence Bond Theory

We start running into problems if molecules become more complex!

- More than one bonding electron
- Valence electrons in more than one type of subshell (s,p,d?)
- Need to extend the model

Let's look back at methane again and consider carbon's atomic orbitals:



- Given electronic structure, there is NO WAY that CH_4 can be tetrahedral based on the overlap of atomic orbitals!
- How do we modify the model to account for REAL LIFE?

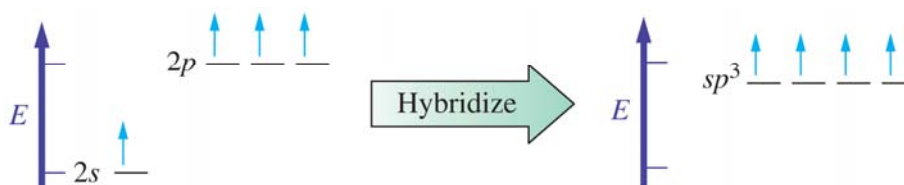
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V. B. Theory: Orbital Hybridization

Linus Pauling: In forming bonds, atoms must allow the combination of their atomic orbitals to form **hybrid orbitals** that have an orientation that matches the geometry of the compound

- **Hybrid Orbitals**: mixture of s, p, and d orbitals to form a new set of hybrid orbitals, all at the same energy, *but new geometry*.

of hybrid orbitals = # of atomic orbitals used



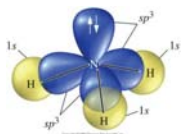
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V. B. Theory: Orbital Hybridization

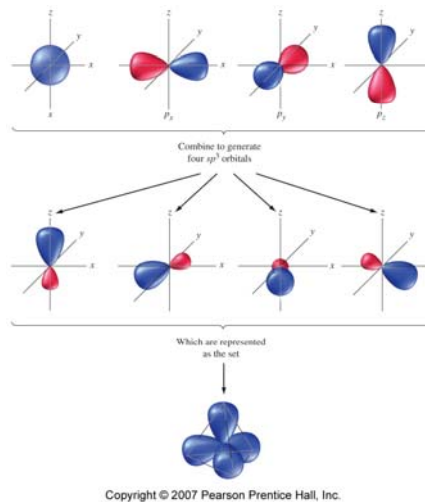
Compare CH₄, NH₃, and H₂O

- All have tetrahedral e- pair geom.
- Varying molecular geometry.
- sp³ hybridization:
1 s-orbital + 3 p-orbitals



How about other molecules?

- H₃C-CH₃ (ethane)
- Each carbon has tetrahedral geom.
- sp³ hybridization works

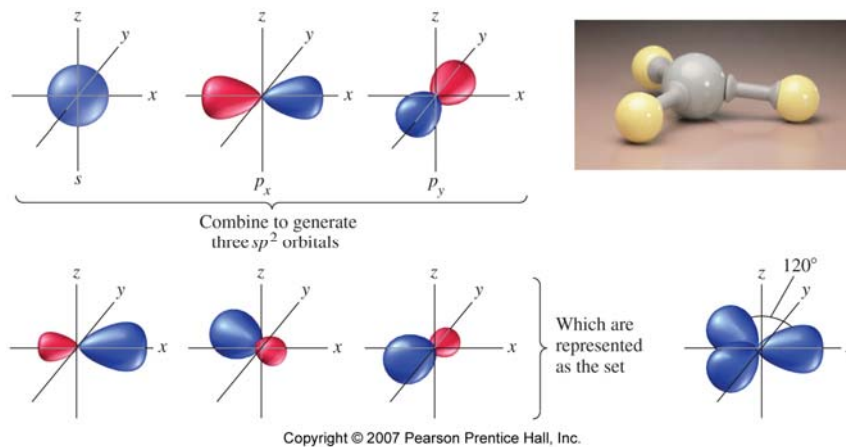


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V. B. Theory: Orbital Hybridization

Trigonal planar e-pair geometry:

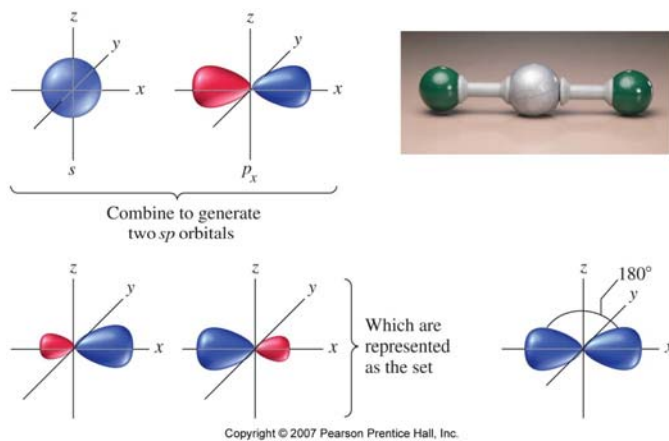
- sp² hybridization



V. B. Theory: Orbital Hybridization

Linear e⁻-pair geometry:

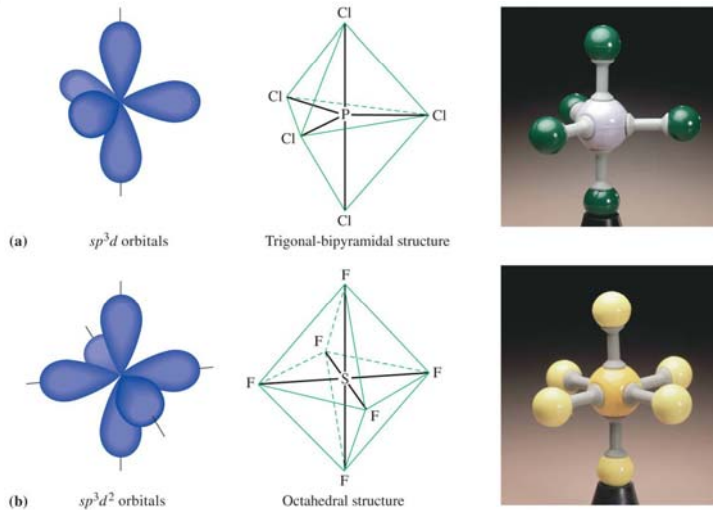
- sp hybridization



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V. B. Theory: Orbital Hybridization

Expanded octets and transition metals



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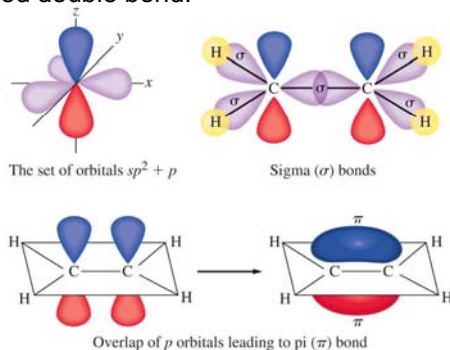
V. B. Theory: Orbital Hybridization

Multiple bond formation

- Need more than one orbital (hybrid or unhybridized) to interact

$\text{H}_2\text{C}=\text{CH}_2$ (ethene)

- Each carbon has trigonal planar geometry... sp^2 hybridization.
- Also need double bond!

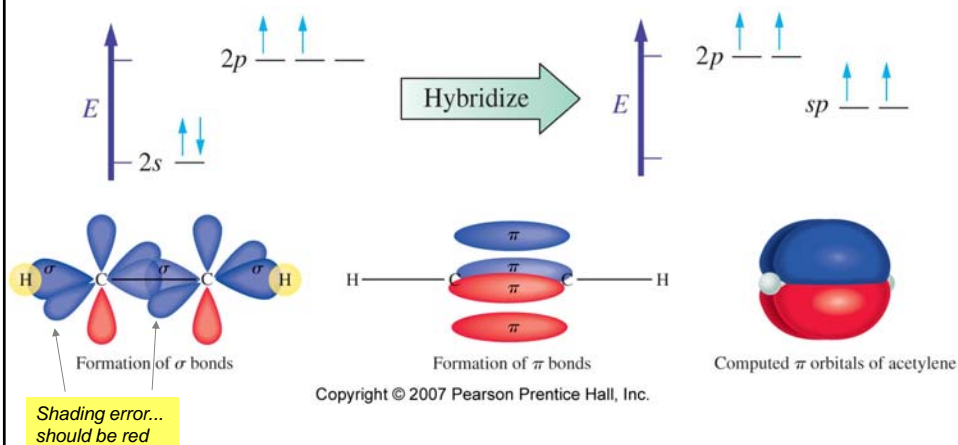


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V. B. Theory: Orbital Hybridization

How about Acetylene ($\text{HC}\equiv\text{CH}$)

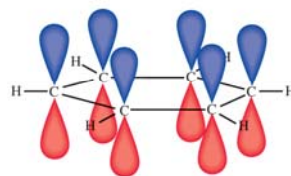
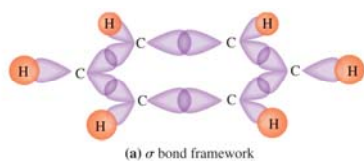
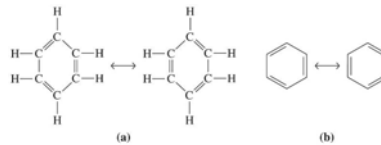
- Linear e^- pair configuration, sp^3 and sp^2 are no good.
- Also need triple bond formation



V. B. Theory: Shortcomings

Benzene: C_6H_6

- Ring
- All 6 C-C bonds are identical!
- Very stable molecule!
- Highlights limitations of valence bond theory!



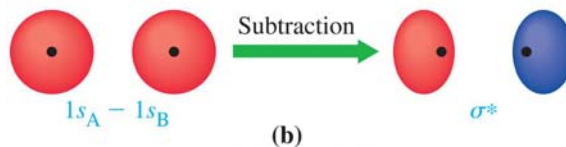
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Molecular Orbital (MO) Theory

Mathematical combinations of atomic orbitals (AO) yield molecular orbitals (MO)

- "Linear Combination of Atomic Orbitals"
- Orbitals can combine constructively (bond) or destructively (no bond).



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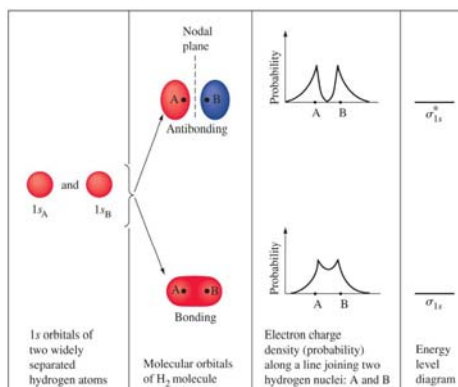
Key Principles of MO Theory

- Total # of MOs formed = Total # AOs combined
 - Form both bonding and antibonding orbitals

- For any parent orbitals, bonding MOs are of lower energy (more stable) than antibonding MOs.

- Electrons are assigned to MOs of successively higher energy, following the Pauli exclusion principle.

- AOs combine to form MOs best when AOs are of similar energy
 - Same n and l



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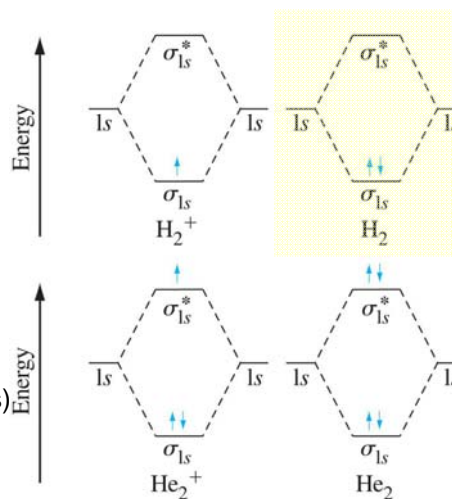
Filling MO's

Consider Hydrogen (H_2)

- Electrons are in $1s$ orbitals
- Form bonding and antibonding orbitals by "adding" and "subtracting" $1s$ orbitals
- Orbitals fill following Pauli Exclusion Principle

Bond Order:

- $BO = \frac{1}{2}(\# \text{ of } e^- \text{ in bonding MOs} - \# \text{ of } e^- \text{ in antibonding MOs})$



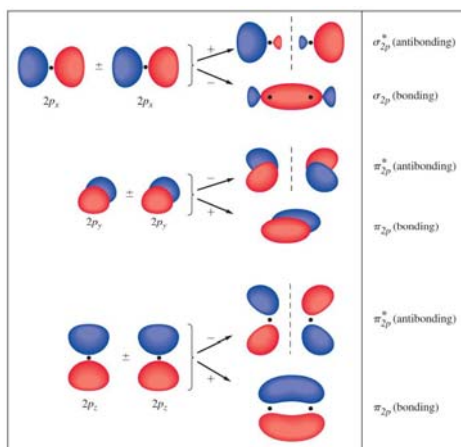
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MO's Involving p-electrons

Keep in mind 4th "Key Principle"

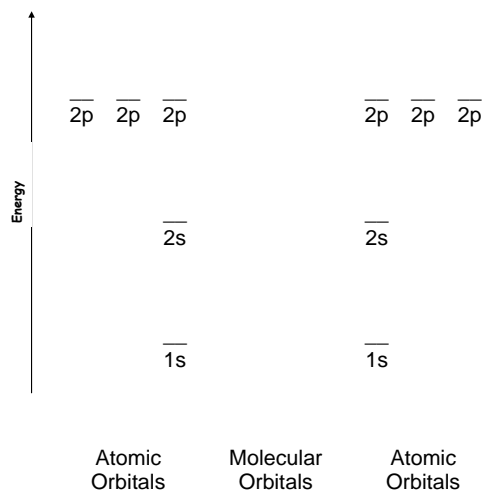
- Expect primary contribution will be from combining orbitals of the same n and ℓ .



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MO Diagrams

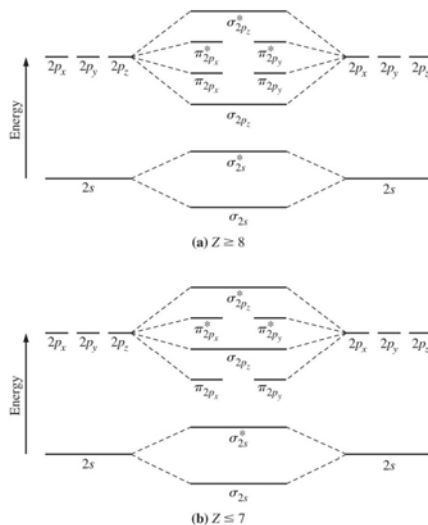
- We can attempt some generalizations...must fit real life!



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“Generalized” MO Diagrams

- In order to fit real life, order of energies of “p” MO’s can take one of two forms.
- Why?
 - In real life, O_2 and B_2 are paramagnetic (have unpaired e⁻)
 - B $1s^2 2s^2 2p^1$
 - O $1s^2 2s^2 2p^4$



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“Generalized” MO Diagrams

σ_{2p}^*	□	□	□	□	□
π_{2p}^*, π_{2p}^*	□ □	□ □	□ □	□ □	□ □
σ_{2p}	□	□	□	□	↑↓
π_{2p}, π_{2p}	□ □	□ □	↑ ↓	↑↓ ↑↓	↑↓ ↑↓
σ_{2s}^*	□	↑↓	↑↓	↑↓	↑↓
σ_{2s}	↑↓	↑↓	↑↓	↑↓	↑↓
	Li_2	Be_2	B_2	C_2	N_2
Bond order	1	0	1	2	3
Magnetism	Dia-magnetic	-	Para-magnetic	Dia-magnetic	Dia-magnetic

σ_{2p}^*	□	□	↑↓
π_{2p}^*, π_{2p}^*	↑ ↓	↑↓ ↑↓	↑↓ ↑↓
π_{2p}, π_{2p}	↑↓ ↑↓	↑↓ ↑↓	↑↓ ↑↓
σ_{2p}	↑↓	↑↓	↑↓
σ_{2s}^*	↑↓	↑↓	↑↓
σ_{2s}	↑↓	↑↓	↑↓
	O_2	F_2	Ne_2
Bond order	2	1	0
Magnetism	Para-magnetic	Dia-magnetic	-

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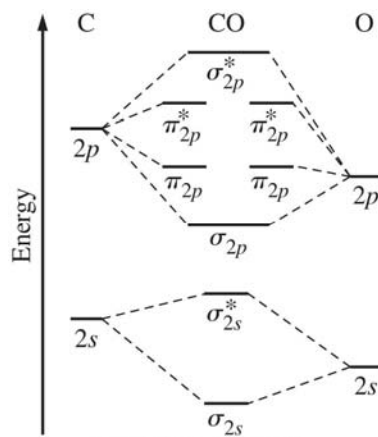
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MO's for Heteronuclear Diatomics

- AO's for atoms may not contribute equally
 - Depends on energies of AO's & properties of atoms
- Consider CO

C: $1s^2 2s^2 sp^2$

O: $1s^2 2s^2 sp^4$



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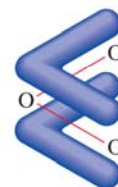
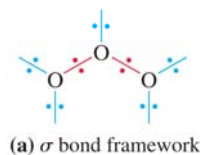
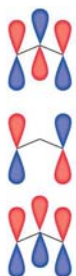
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MO's Beyond Diatomics: Ozone and Benzene

- The picture gets a little more clouded...Math gets tougher!
- Dealing with resonance/delocalized bonding.

Ozone:

Lewis	Valence Bond	MO



(b) Delocalized π molecular orbital

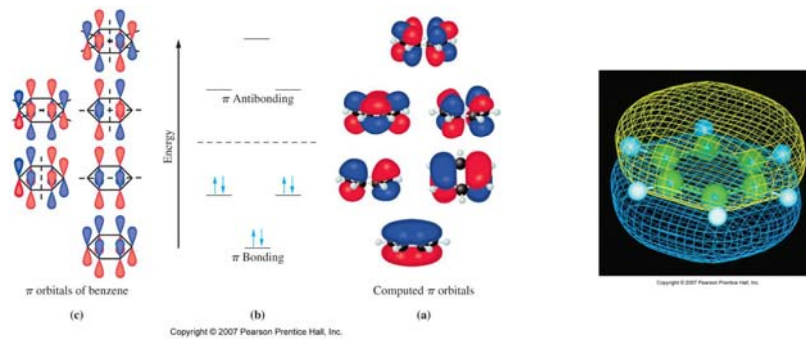
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MO's Beyond Diatomics: Ozone and Benzene

Benzene:

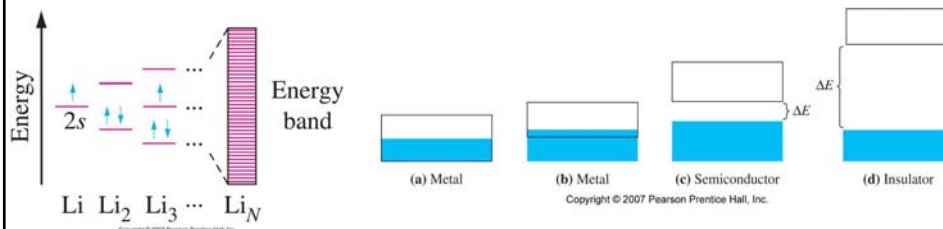
Lewis	Valence Bond	MO



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“Bonding” in Metals

- Discrete MO's don't work
 - Too many e⁻ involved (AO's for all atoms!)
- **Band Theory** analog for metals
 - Valence band vs. Conduction band



- Semiconductors and doping

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