

CHEMISTRY 112 LECTURE

EXAM II Material

CHEMICAL BONDING

Part I Chemical Bonding I – Lewis Theory Chapter 9 pages 376-386

A. Drawing electron dot structures

HOW TO:

1. Write e⁻ dot structure for the individual atoms.
2. a) Add together the number of valence electrons for all the atoms
(If it is an ion, you must add or subtract electrons accordingly)
b) Divide the total number of e⁻ by 2: This will give you the number of e⁻ pairs available for bonding.
3. Determine which is the central atom
 - a. The least represented atom that is **not H**
 - b. Usually, the **first** atom in the chemical formula that is **not H**.
4. Arrange atoms symmetrically around the central atom.
5. Draw a single line (or 2 dots) between the central and outer atoms.
6. From the total number of valence electrons subtract 2 electron for each bond made.
7. Attempt to place the remaining electron pairs around the outer atoms to make an octet or duet (for H)
8. Additional electrons are placed on the central atom
9. If the central atom still has less than an octet ; then, a double or triple bond must be formed.
Warning: Do not use a double or triple bond unless you have to!

HONC, a general rule(a help)

Examples:

B. Specific Electron Dot Cases:

1. Ions:

2. Oxy Acids

3. Carbon chains

C. Exceptions to the Octet Rule

1. Electron deficient molecules: Molecules where the central atom does not have an octet. Usually a group IIIA atom
Example: BCl_3

2. Expanded valence shell: Molecules where the central atom has more than 8 valence around the central atom. The central atom would belong to the 3rd, 4th, 5th, 6th, or 7th period.
Example: SF_6

3. Molecules with an odd number of electrons: There are an odd number of valence electrons in the molecule
Example: NO_2

Practice:

SO₂

CH₂O

IF₅

H₃PO₄

NO₃⁻

SCl₂

HBrO

CO

CH₃COCH₃

OH⁻

PF₅

SO₃²⁻

H₃O⁺

HClO

SO₃

CO₃²⁻

IOCl₅

IF₃

NF₃⁺

XeCl₂

BH₃

H₂PO₃⁻

Part II Resonance Structures

Some molecules can be drawn with more than one lewis dot structure.

None of the lewis dot structure depicts the molecule accurately. **Resonance structures** are two or more electron dot structures for a molecule or ion that have the same arrangement of atoms.

Ozone:

Experiments have shown that the two lewis dot structures are equivalent and that the bond strength characteristics are a hybrid of the two structures. The actual molecule is a **resonance hybrid** with two of the electrons being **delocalized** (spread over the entire molecule).

Examples:

1.. Given: NO_3^{1-}

2. Given: SCN^{1-}

Part III Formal Charges

The **Formal Charge** of an atom is the hypothetical charge you obtain by assuming that the bonding electrons are equally shared.

Formal charges, when assigned, can be used to determine the most important lewis dot structure.

Formal Charge How To :

1. All of the unshared (nonbonding) electrons are assigned to the atom on which they are found
2. Half of the bonding electrons are assigned to each atom in the bond.

Formal Charge = valence electrons - unshared valence electrons - 1/2 shared electrons]

Selection of the most important lewis structure:

1. Smaller formal charges (+ or -) are better than larger formal charges

2. like charges on adjacent atoms are not desirable

3. The more negative formal charge should be assigned to the more electronegative atom.

Practice Problem: NNO

Part IV Chemical Bonding II: Molecular Shapes, Valence Bond Theory, and Molecular Orbital Theory

Chapter 9 & 10

Pages 398-409, 424-470

Molecular geometry describes the three-dimensional arrangement of atoms in a molecule. Molecular geometry is an important factor in determining physical and chemical properties of molecules as well as reactions molecules will or will not undergo.

For simple molecules molecular geometry can be predicted using: **VSEPR** - VALENCE-SHELL-ELECTRON-PAIR-REPLUSION THEORY

Valence shell electron pairs are arranged about each atom so that electrons are as far apart from each other to minimize electron-pair repulsion.

LONE PAIR-LONE PAIR > LONE PAIR-BONDING PAIR > BONDING PAIR-BONDING PAIR

PART A. ELECTRON PAIR GEOMETRY

**Number of Electron Pairs
around the Central Atom**

Electron Pair Geometry

2	Linear
3	Trigonal Planar
4	Tetrahedral
5	Trigonal Bipyramidal
6	Octahedral

PART B. MOLECULAR GEOMETRY

Valence shell electron pairs, bonding and nonbonding, are arranged around the central atom to minimize repulsion between pairs

The **Molecular Geometry** is determined by the relative positions of the bonding pairs around the central atom

LONE PAIR-LONE PAIR > LONE PAIR-BONDING PAIR > BONDING PAIR-BONDING PAIR

ELECTRON PAIRS			ARRANGEMENT OF ELECTRON PAIRS	MOLECULAR GEOMETRY	EXAMPLE
Total	Bonding	Lone Pair			

Linear

<u>2</u>	2	0	Linear	Linear	BeF ₂
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CO

Trigonal Planar

<u>3</u>	3	0	Trigonal Planar	Trigonal Planar	BF ₃
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	2	1		Bent/Angular	SO ₂
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Remember: LONE PAIR-LONE PAIR > LONE PAIR-BONDING PAIR > BONDING PAIR-BONDING PAIR Repulsion

ELECTRON PAIRS			ARRANGEMENT OF ELECTRON PAIRS	MOLECULAR GEOMETRY	EXAMPLE
Total	Bonding	Lone Pair			

Tetrahedral

<u>4</u>	4	0	Tetrahedral	Tetrahedral	CH ₄
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	3	1		Trigonal Pyrimidal	NH ₃
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	2	2		Bent/Angular	H ₂ O
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Remember: LONE PAIR-LONE PAIR > LONE PAIR-BONDING PAIR > BONDING PAIR-BONDING PAIR Repulsion

ELECTRON PAIRS			ARRANGEMENT OF	MOLECULAR GEOMETRY	EXAMPLE
Total	Bonding	Lone Pair	ELECTRON PAIRS		

Trigonal Bipyramidal

<u>5</u>	5	0	Trigonal Bipyramidal	Trigonal Bipyramidal	PCl ₅
	4	1		Seesaw/Distorted Tetrahedron	SF ₄
	3	2		T-shaped	ClF ₃
	2	3		Linear	XeF ₂

Remember: LONE PAIR-LONE PAIR > LONE PAIR-BONDING PAIR > BONDING PAIR-BONDING PAIR Repulsion

ELECTRON PAIRS			ARRANGEMENT OF ELECTRON PAIRS	MOLECULAR GEOMETRY	EXAMPLE
Total	Bonding	Lone Pair			

Octahedral

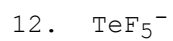
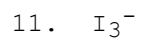
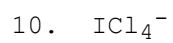
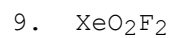
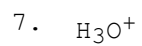
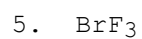
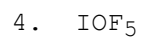
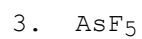
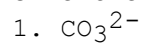
<u>6</u>	6	0	Octahedral	Octahedral	SF ₆
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	5	1		Square Pyramidal	IF ₅
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	4	2		Square Planar	XeF ₄
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Problems:

Give the Molecular Geometry for the following:



Molecular Bond Theory

BACKGROUND

Quantum mechanics can be used to understand bonding and electronic structure. We will consider two theories derived from quantum mechanics: Valence Bond Theory (VB) and Molecular Orbital Theory (MO). Both theories use quantum mechanics but use different simplifying assumptions

PART I VALENCE BOND THEORY: Orbital Overlap as a Chemical Bond

According to Valence Bond Theory (VB) A bond forms between two atoms when orbitals (electron clouds) overlap and a pair of electrons occupies the region between both nuclei.

The following conditions must be met:

1. There must be maximum overlap in a region between the two nuclei of the bonding atoms.
2. The total number of electrons in the same region of space (overlap) is no more than two. According the Pauli Exclusion Principle, the two electrons must have opposite spin.

A. HYBRID ORBITALS

To apply the Valence Bond theory to polyatomic molecules both the formation of electron-pair bonds (shared electrons) and the observed geometries of the molecules must be shown.

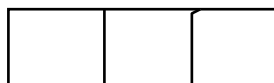
1. The number of hybrid orbitals obtained always equals the number of atomic orbitals mixed
2. The type of hybrid orbitals obtained varies with the types of atomic orbitals mixed.

sp Hybrid Orbitals

1. Linear/ 180°
2. 2 Hybrid orbitals from the hybridization of one "s" and one "p" orbital

Consider BeF_2 :

Energy Diagram/Electron Box Diagram:



Ground State
(Central atom)

Excited State
(Central atom)

Bonded state
in molecule

Contour Diagram:



+



Hybridize
→



=



s orbital

p orbital

Two sp hybrid orbitals

sp hybrid orbitals shown together
(large lobes only)

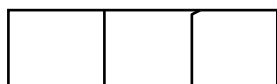
sp² Hybrid Orbitals

1. Trigonal Planar/120°

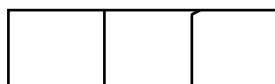
2. 3 Hybrid orbitals from the hybridization of one "s" and two "p" orbitals

VSEPR for: BF₃:

Energy Diagram:



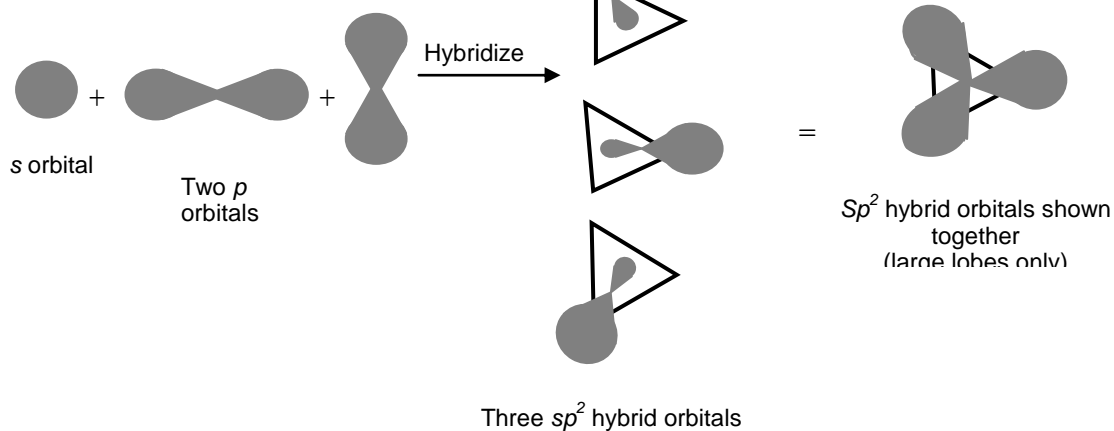
Ground State
(Central atom)



Excited State
(Central atom)

Bonded state
in molecule

Contour Diagram:



sp³ Hybrid Orbitals

1. Tetrahedral/109.5°
2. 4 Hybrid orbitals from the hybridization of one "s" and three "p" orbitals

VSEPR for: CH₄

Energy Diagram:



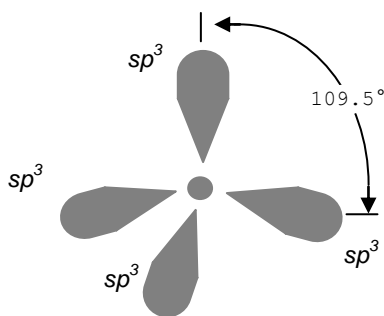
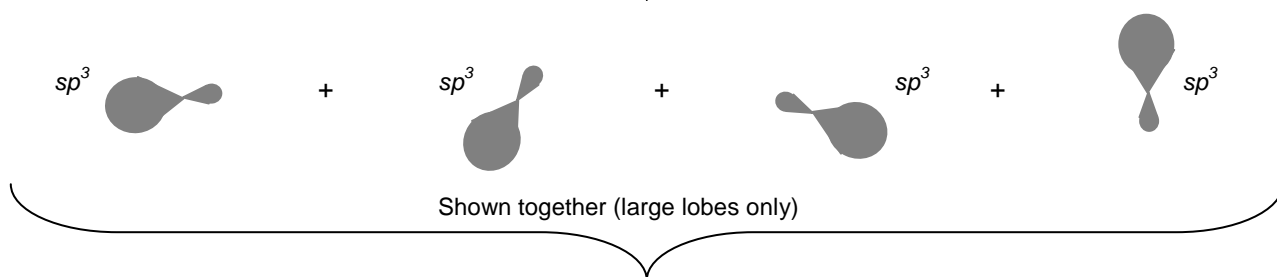
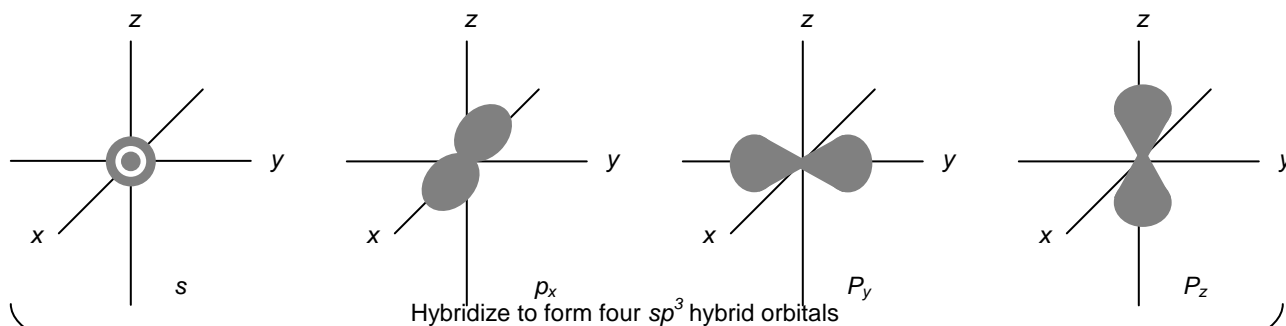
Ground State
(Central atom)



Excited State
(Central atom)

Bonded state
in molecule

Contour Diagram:



sp³d Hybrid Orbitals

1. Trigonal Bipyramidal/120° and 90°
2. 5 Hybrid orbitals from the hybridization of one "s", three "p" and one "d" orbitals

VSEPR for: PI₅

Energy Diagram:

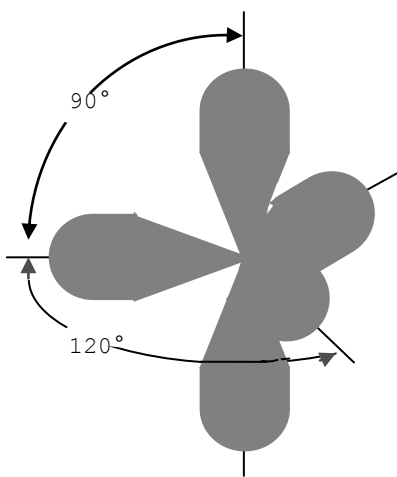


Ground State
(Central atom)

Excited State
(Central atom)

Bonded state
in molecule

Contour Diagram:



Trigonal
Bipyramidal

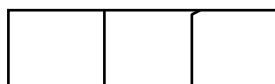
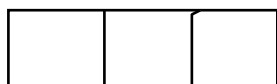
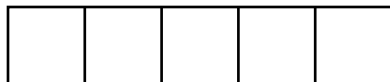
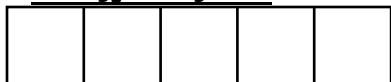
sp³d² Hybrid Orbitals

1. Octahedral/ 90°

2. 6 Hybrid orbitals from the hybridization of one "s", three "p" and two "d" orbitals

VSEPR for: SBr₆

Energy Diagram:

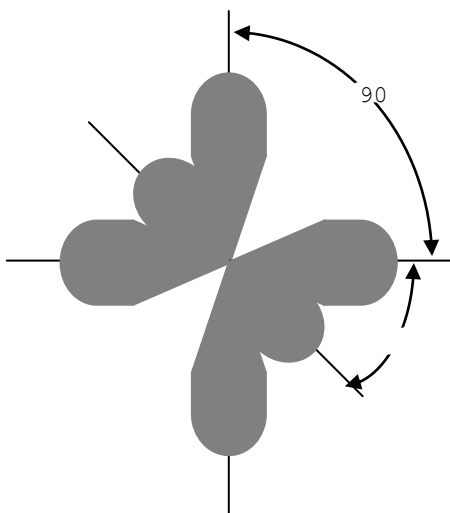


Ground State
(Central atom)

Excited State
(Central atom)

Bonded state
in molecule

Contour Diagram:



Octahed
ral

Hybrid Orbitals	Number of Orbitals	Geometric Arrangement
sp	2	
sp ²	3	
sp ³	4	
sp ³ d	5	
sp ³ d ²	6	

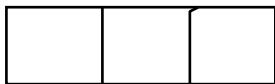
Problems:

NH₃

VSPER:

The hybrid orbitals

Energy Diagram:



Ground State
(Central atom)

Bonded state
in molecule

Molecular Geometry Name

Bond angle

State reason for the observed bond angle

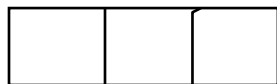
Lone Pairs? Which orbital do they occupy?

Contour Diagram:

H₂O
VSEPR:

The hybrid orbitals

Energy Diagram:



Ground State
(Central atom)

Excited State
(Central atom)

Bonded state
in molecule

Molecular Geometry name

Bond angle

State reason for the observed bond angle

Lone Pairs? Which orbital do they occupy?

Contour Diagram

ClF₃
VSEPR:

The hybrid orbitals

Energy Diagram:



Ground State
(Central atom)

Excited State
(Central atom)

Bonded state
in molecule

Molecular Geometry Name

Bond angle

State reason for the observed bond angle

Lone Pairs? Which orbital do they occupy?

Contour Diagram:

IF₅
VSEPR:

The hybrid orbitals

Energy Diagram:



Ground State
(Central atom)

Excited State
(Central atom)

Bonded state
in molecule

Molecular Geometry Name

Bond angle

State reason for the observed bond angle

Lone Pairs? Which orbital do they occupy?

Contour Diagram:

PART II MULTIPLE BONDS

a. Sigma Bonds σ

Sigma Bonds are bonds where the electron density is concentrated symmetrically about the internuclear axis.

b. Pi Bonds π

Pi Bonds are bonds results from the overlap between two p orbitals oriented perpendicular to the internuclear axis. This sideways overlap of p orbitals produces a pi bond (π)

Use the Valence Bond Theory to explain the bonding in C_2H_4
VSEPR:

The hybrid orbitals

Energy diagram:

Ground State
(Central atom)

Excited State
(Central atom)

Bonded state
in molecule

Molecular Geometry Name

Bond angle

Lone Pairs? Which orbital do they occupy?

Use the Valence Bond Theory to explain the bonding in C_2H_2
VSEPR:

The hybrid orbitals

Electron box diagram

Ground State
(Central atom)

Excited State
(Central atom)

Bonded state
in molecule

Molecular Geometry Name

Bond angle

Lone Pairs? Which orbital do they occupy?

Double Bonds

Triple Bonds

VBT problems

For the following compounds:

- Give the VSEPR structure
- Determine the hybridization of the central atom
- Draw the electron box diagram, fully labeled
- Draw the VBT contour diagrams, fully labeled (include bond angles, also)

- BH₃
- ICl₃
- C₂Cl₂
- AsI₅
- PH₃
- SI₆
- H₂Se
- H₂Se
- FCCF
- ClBr₂F
- BrI₅
- Br₂CCBr₂
- SiN⁻
- NCl₃
- NCl₃
- NO₂

PART III MOLECULAR ORBITAL THEORY (MO): Electron Delocalization

Pages 458-470

In the molecular orbital theory electrons in molecules exists in allowed energy states called molecular orbitals. The MO theory views the entire molecular orbitals extending over the entire molecule.

Background:

Addition of waves

The Hydrogen Molecule:

When the two separate atomic orbitals from each hydrogen overlap two molecular orbitals are produced.

The higher energy orbital has none/very little electron density between the nuclei and is called the **antibonding orbital**

The lower energy orbital concentrates its electron density between the two hydrogen nuclei and is called the **bonding orbital**

$$\text{BOND ORDER} = \frac{1}{2} (\# \text{ Bonding electrons} - \# \text{ Antibonding electrons})$$

A bond order of = 1 is a single bond

A bond order of = 2 is a double bond

A bond order of = 3 is a triple bond

Note: With this theory bond orders of 1/2, 3/2 and etc can occur

Electron Configuration:

(MO style!)

Draw the Molecular Orbital Energy level diagram for the following:
(First Row)



a. Bond Order:

b. Number of unpaired electrons and magnetic properties



a. Bond Order:

b. Number of unpaired electrons and magnetic properties

Molecular Orbital (MO) Energy-Level Diagrams

1. The number of molecular orbitals formed always equals the number of atomic orbitals combined.
2. Atomic orbitals combine into Molecular Orbitals most effectively with other atomic orbitals of similar energy.
3. The effectiveness of the atomic orbitals combining into molecular orbitals is dependent on the amount of overlap of the orbitals. As the overlap increases, the bonding orbital energy (ex σ_{1s}) is lowered and the antibonding (ex. σ^*_{1s}) is raised in energy.
4. Each molecular orbital can have a maximum of two electrons with paired spins (Pauli exclusion principle)
5. When Molecular orbitals have the same energy (degenerate), one electron enters each separate orbital (with the same spin-Hunds rule!) before spin pairing occurs.

Contour representations of molecular orbitals formed by by the 2p orbitals on two atoms.

2nd Row Elements - p orbitals

MO Energy Level Diagram for homonuclear diatomic molecules

Draw the Molecular Orbital Energy level diagram for F_2
- Small 2s-2px interaction

- a. Electron Configuration:
- b. Bond Order:
- c. Number of unpaired electrons and magnetic properties:
- d. Bond Length:
- e. Bond Dissociation Energy:
- f. Bond Strength:

Draw the Molecular Orbital Energy level diagram for O_2
- Small $2s-2p_x$ interaction

- a. Electron Configuration:
- b. Bond Order:
- c. Number of unpaired electrons and magnetic properties:
- d. Bond Length
- e. Bond Dissociation Energy:
- f. Bond Strength:
- g. Compare the O_2 molecule to O_2^{2-} ion
- h. Compare the O_2 molecule to O_2^{1+}

Draw the Molecular Orbital Energy level diagram for N_2

- Large 2s-2px interaction

a. Electron Configuration:

b. Bond Order:

c. Number of unpaired electrons and magnetic properties:

d. Bond Length

e. Bond Dissociation Energy:

f. Bond Strength:

MO Energy Level Diagram for a Heteronuclear diatomic molecules

Draw the Molecular Orbital Energy level diagram for CN^- (If similar to a homonuclear diatomic molecule)

- Large $2s$ - $2p_x$ interaction

- a. Electron Configuration:
- b. Bond Order:
- c. Number of unpaired electrons and magnetic properties:
- d. Bond Length
- e. Bond Dissociation Energy:
- f. Bond Strength:

Problems:

1. Which has the Highest Bond Energy? Why?

a. B_2 or B_2^{2+}

b. C_2 or C_2^{2-}

2. Which has the Shortest Bond Length? Why?

a. Ne_2 or Ne_2^-

b. F_2 or F_2^{+1}

3. Which has the Lowest Bond Dissociation Energy? Why?

a. C_2 or C_2^{2-}

b. C_2 or C_2^{2-}