Chapter 10
Molecular Geometry and Chemical Bonding Theory

I) VSEPR Model

Valence-Shell Electron-Pair Repulsion Model

A) Model predicts

Predicts electron arrangement and molecular shapes by assuming electron groups want to minimize repulsions

B) Model does not address

- nature of the orbitals involved with bonding
- how the atomic orbitals predict shapes of molecules

C) Electron Arrangement

- includes all shared pair of electrons and lone pairs of electron on the central atom
- gives the positions of the electron density regions around the central atom

D) Molecular Shape

- only includes shared pair of electron (no lone pairs for electrons)
- gives the general shape of the atoms in the molecule

E) Method for determining e^- arrangement or molecular shapes

1) Draw the Lewis structure
2) Determine total electron density regions on the central atom
   electron density regions (sometimes referred to as legs of e^-) are:
    a) shared pair of e^- (single bond or multiple bond)
    b) lone pair of e^-
3) Electron Arrangement counts both shared e^- and lone pair e^-
4) Molecular shape
    a) depends on the e^- arrangement
    b) count only shared pair of e^- (no lone pairs)

Table of electron arrangements and molecular shapes.

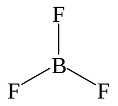
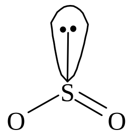
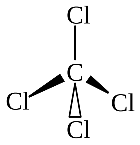
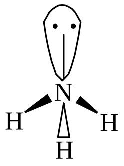
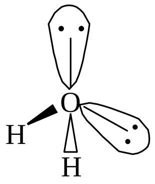
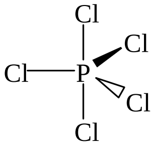
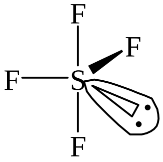
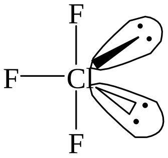
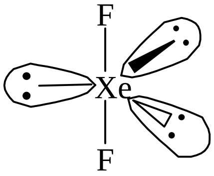
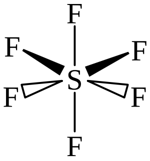
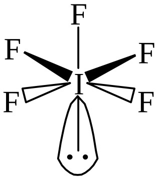
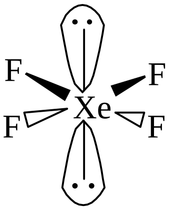
e^- pairs							
Total	shared pair of e^-	lone pair of e^-	e^- arrangement	molecular shape	bond angle	example	
2	2	0	linear	linear	180°	BeF_2	F—Be—F
3	3	0	trigonal planar	trigonal planar	120°	BF_3	
	2	1	"	bent		SO_2	
4	4	0	tetrahedral	tetrahedral	109.5°	CCl_4	
	3	1	"	trigonal pyramidal		NH_3	
	2	2	"	bent		H_2O	

Table of electron arrangements and molecular shapes.

	e^- pairs						
Total	shared pair of e^-	lone pair of e^-	e^- arrangement	molecular shape	bond angle	example	
5	5	0	trigonal bipyramidal	trigonal bipyramidal	90°/120°	PCl_5	
	4	1	"	seesaw		SF_4	
	3	2	"	T-shape		ClF_3	
	2	3		linear		XeF_2	
6	6	0	octahedral	octahedral	90°	SF_6	
	5	1		square pyramid		IF_5	
	4	2		square planar		XeF_4	

Note:
In the trigonal bipyramidal electron arrangement, the lone pair of electrons have two locations it could take. An axial position is on the axis of the molecule. An equatorial position is located on the molecule's "equator." A lone pair of electrons will reside on the equatorial position which exhibits a smaller amount of electron pair repulsion. An axial lone pair repels 3 other electron pairs at 90° angles, whereas an equatorial lone pair only has 2 electron pairs at 90° angles.

II) Dipole moments

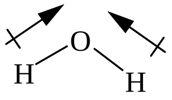
A) Polar bonds

A covalent bond involves the sharing of an electron pair between two atoms. If the electron pair is unequally shared between the two atoms, the bond is called a polar covalent bond. Which atom the electron pairs spend more time around is determined by the atoms' electronegativity.

An unequal sharing of an electron pair results in one atom in the bond experiencing an partial negative charge ($\delta-$) while the other atom has a partial positive charge ($\delta+$). For example, the bond between oxygen and hydrogen is polar covalent. The oxygen is more electronegative than hydrogen and gains a greater share of the electron pair. Partial charges on O and H are represented in the following fashion; $^{\delta+}\text{H—O}^{\delta-}$.

Dipole moment is a measure of the magnitude of the partial charges in a molecule.

- usually measured in units of *debyes*(D)
- represented by an arrow that has a positive sign on one end (+⟶)
- dipole-moment arrows points from the positive partial charge towards the negative partial charge



B) Polar Molecules

A polar molecule is a molecule with an nonzero dipole moment.
A nonpolar molecule is a molecule with a zero dipole moment.

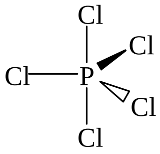
1) diatomic molecules built with
   - the same atoms is nonpolar
   - different atoms is polar

2) polyatomic molecule with individual polar bonds

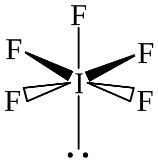
   - is nonpolar if the dipole moments of the individual bonds cancel out. The canceling of the bonds dipole occurs when the shape of a molecule is symmetrical around the central atom.

   - is polar if the shape of the molecule is nonsymmetrical around the central atom. The molecule has an overall net dipole moment.

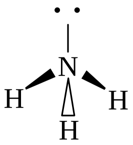
Examples:



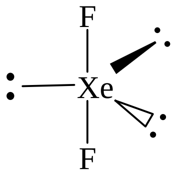
PCl_5 is nonpolar



IF_5 is polar



NH_3 is polar



XeF_2 is nonpolar

III) Valence Bond Theory

explains the electron pair or covalent bond with quantum mechanics

A) Bonds

A bond forms between two atoms when

1) orbitals overlap (occupy the same space)
2) no more than 2 e^- occupy the overlapping orbitals

Strength of the bond depends on the amount of orbital overlap

1) more orbital overlap results in a stronger bond
2) depends on the shape and direction of the orbitals

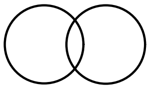
Bonds formed from orbital overlap

1) sigma bond (σ)

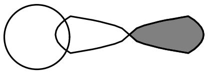
end-to-end or head-on overlap on the bond axis

an s-bond can be formed by overlapping

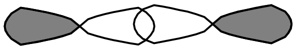
a) two *s* orbitals



b) one *s* and one *p* orbital

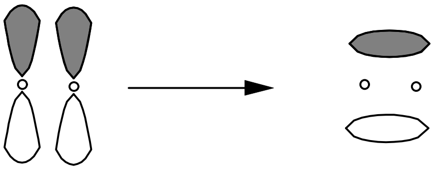


c) two *p* orbitals



2) pi bond (π)

side-to-side overlap of orbitals above and below the bond axis



Note: the σ bond is stronger than the π bond, because the σ bond experiences more overlap directly on the bond axis.

3) Multiple bonds
The "first" bond to form between two atoms is of the Sigma type. Whenever multiple bonds (such as double or triple) are present between two atoms, one is always a Sigma and the remaining bond(s) is(are) of the Pi type.

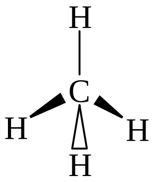
Bond	consist of
single	1 σ-bond
double	1 σ-bond and 1 π-bond
triple	1 σ-bond and 2 π-bonds

B) Hybrid Orbitals

hybridization is the process of orbital mixing

Linus Pauling proposed
the valence atomic orbitals in a molecule are different from those of an isolated atom.
The carbon atom in methane, CH_4, has valence e^- in the 2*s* and 2*p* subshell. The 2*s* orbital and all three 2*p* orbitals are used in bonding with the four hydrogen atoms. A closer look at the bonds in CH_4 shows that all four bonds are identical even though totally different atomic orbitals are used. This shows that some hybridization of the orbitals have occurred.

i.e. the four bonds in CH_4 are identical



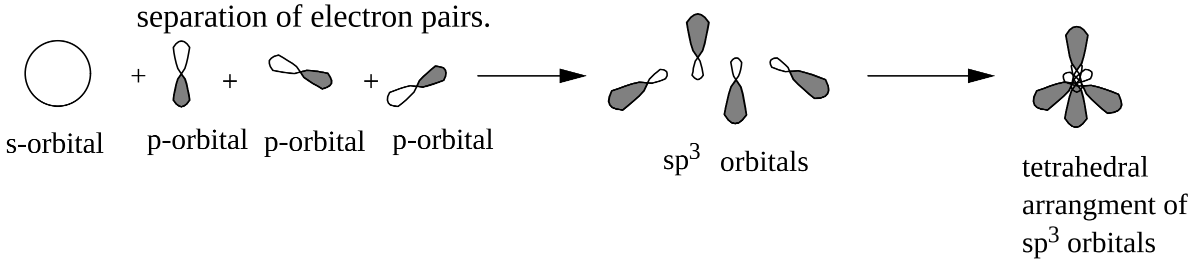
C) Forming Hybrid Orbitals

2 key points
1) The number of hybrid orbitals equals the number of atomic orbitals mixed
   e.g. if 1 *s*-orbital and 3 *p*-orbital are mixed, 4 hybrid orbitals are produced.

2) The type of hybrid orbital depends on the type of atomic orbital mixed together.

   e.g. the mixture of 1 *s*-orbital and 3 *p*-orbitals are called sp^3 hybrid orbitals.

The hybrid orbitals on the central atom are arranged to provide the maximum separation of electron pairs.



Types of hybrid orbitals

hybrid orbital	geometric arrangement	number of orbitals	examples
sp	linear	2	BeF_2
sp^2	trigonal planar	3	BF_3
sp^3	tetrahedral	4	CH_4
sp^3*d*	trigonal bipyramidal	5	PCl_5
sp^3*d*^{2}	octahedral	6	SF_6

Function of a hybrid orbital is

1) form σ-bonds
2) house lone pairs of e^-

D) Assigning hybridization state on the central atom

1) Draw Lewis structure of the molecule
2) Predict overall arrangement of e^- pairs by determining number σ-bonds and lone pairs.
3) Deduce hybridization state of central atom by setting the number of hybrid orbitals equal to the number of e^- density regions on the central atom.
4) Set-up orbital box diagrams to match hybrid state of the central atom

sets of orbital box diagrams need to represent hybridization

- a) ground state
- b) excited state
  - involves promoting an e^- from the ground state to another orbital giving an excited state
- c) hybridized state
  - involves combining the orbital being mixed to form hybrid orbitals.

Examples:

A) $BeCl_2$

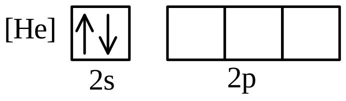
1) 

2) 2 σ-bonds + 0 lone pairs = 2 e^- density regions

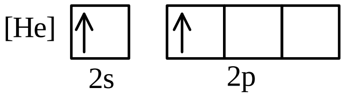
3) 2 e^- density regions needs two orbitals: *sp*

4) orbital box diagram for Be, [He] $2s^2$

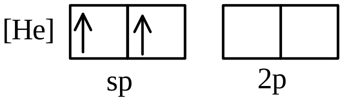
a) ground state



b) excited state
promote one of the 2*s*
electrons to a 2*p* orbital

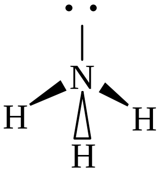


c) hybrid state



B) NH_3

1)

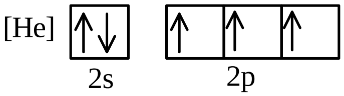


2) 3 σ-bonds + 1 lone pairs = 4 e⁻ density regions

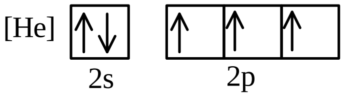
3) 4 e⁻ density regions need four orbitals: sp^3

4) orbital box diagram for N, [He] $2s^2 2p^3$

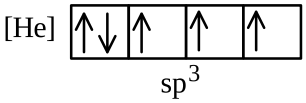
a) ground state



b) excited state
no electrons need to be promoted. The paired e⁻ are the lone pair of e⁻ and the 3 single e⁻ can form the σ-bonds.

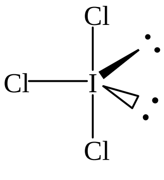


c) hybrid state



C) ICl_3

1)

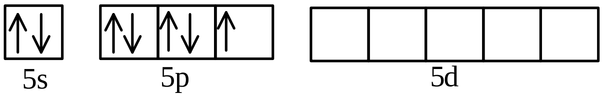


2) 3 σ-bonds + 2 lone pairs = 5 e⁻ density regions

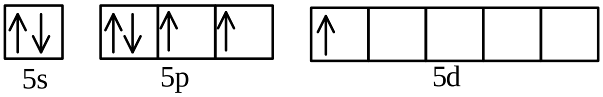
3) 5 e⁻ density regions need five orbitals: sp^3d

4) orbital box diagram for I, [Kr] $4d^{10}5s^2 5p^5$

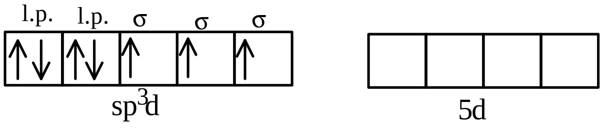
a) ground state



b) excited state
one electron needs to be promoted. The two pair of e$^-$ are the lone pairs and the 3 single e$^-$ can form the σ-bonds.

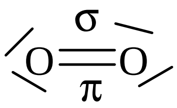


c) hybrid state



D) O_2

1)

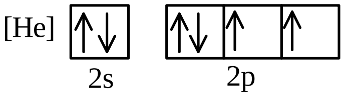


2) on one oxygen atom: 1 σ-bonds + 2 lone pairs = 3 e$^-$ density regions

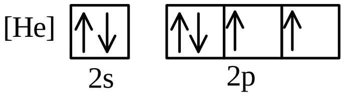
3) 3 e$^-$ density regions need three orbitals: sp^2

4) orbital box diagram for O, [He] $2s^22p^4$

a) ground state



b) excited state
no electrons need to be promoted. The two pair of e$^-$ are the lone pairs and the 1 of the single e$^-$ can form the σ-bond the other single e$^-$ will form the π-bond.



c) hybrid state