Chapter 10 – Chemical Bonding II: Molecular Shapes, Valence Bond Theory, and Molecular Orbital Theory

"No theory ever solves all the puzzles with which it is confronted at a given time; nor are the solutions already achieved often perfect"

– Thomas Kuhn (1922-1996)

Suggested Problems

- Chapter 10
  35, 37, 47, 49, 51, 53, 57, 67, 71, 75, 81, 83, 87, and 109
- Chapter 11 (Sections 11.1 and 11.3)
  49, 51, 53, and 55
- Also available at
  http://www.western.edu/faculty/dorth

Chapter 10 Outline (and 11.3)

- Molecular Shape – VSEPR
- Valence Bond Theory
- Molecular Orbital Theory
- Shape and Polarity
- Intermolecular forces (Section 11.3)

Molecular Shape -VSEPR

- The two-dimensional Lewis structure does NOT represent the actual shape of the molecule
- Valence Shell Electron Pair Repulsion
- Electron groups tend to arrange themselves so as to minimize the repulsion between themselves
- Each bond (single, double, or triple) and each lone pair counts as an "electron group"

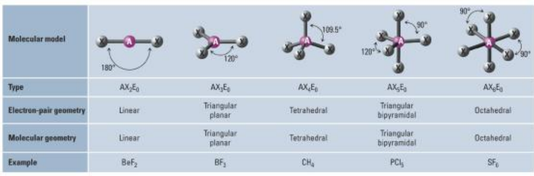
Two things to keep straight

- Molecular shapes are <u>determined</u> by the repulsion of various electron groups
- Molecular shapes are <u>named</u> by the resultant locations of the nuclei

Rules for determining molecular shape

- Determine number of electron groups around the central atom
- Arrange groups to minimize electron group - electron group repulsion
- Ignore the electron groups and name the molecular shape by looking at the nuclei

Idealized VSEPR Geometries



Molecular model					
Type	AX_2E_0	AX_3E_0	AX_4E_0	AX_5E_0	AX_6E_0
Electron-pair geometry	Linear	Triangular planar	Tetrahedral	Triangular bipyramidal	Octahedral
Molecular geometry	Linear	Triangular planar	Tetrahedral	Triangular bipyramidal	Octahedral
Example	BeF_2	BF_3	CH_4	PCl_5	SF_6

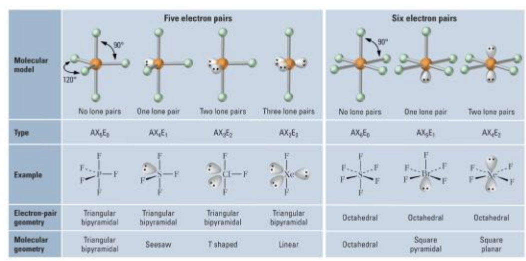
Common Molecular Shapes

- 2 electron groups, bond angle = 180°
  - linear
- 3 electron groups, bond angle = 120°
  - no lone pairs: Triangular planar
  - one lone pair: Bent
- 4 electron groups, bond angle = 109.5°
  - no lone pairs: Tetrahedral
  - one lone pair: Triangular pyramidal
  - two lone pairs: Bent

More Molecular Shapes

- Five electron groups, bond angle 90°, 120°
  - no lone pairs: Triangular bipyramidal
  - one lone pair: See-saw
  - two lone pairs: T-shaped
  - three lone pairs: Linear
- Six electron groups, bond angle 90°
  - no lone pairs: Octahedral
  - one lone pair: Square pyramidal
  - two lone pairs: Square planar
  - three lone pairs: T-shaped

VSEPR Theory Five and Six Electron Pairs



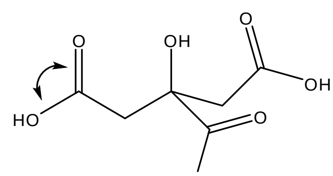
	Five electron pairs				Six electron pairs		
Molecular model	No lone pairs	One lone pair	Two lone pairs	Three lone pairs	No lone pairs	One lone pair	Two lone pairs
Type	AX_5E_0	AX_4E_1	AX_3E_2	AX_2E_3	AX_6E_0	AX_5E_1	AX_4E_2
Example	P	S	Cl	Xe	S	Br	Xe
Electron-pair geometry	Triangular bipyramidal	Triangular bipyramidal	Triangular bipyramidal	Triangular bipyramidal	Octahedral	Octahedral	Octahedral
Molecular geometry	Triangular bipyramidal	Seesaw	T shaped	Linear	Octahedral	Square pyramidal	Square planar

What shape are each of the following molecules?

- H_2O
- CO_2
- PCl_3
- SO_3
- XeF_4

What is the approximate angle of the O—C—O bond in the citric acid molecule below?

(A) 120°
(B) 109.5°
(C) 180°
(D) 90°

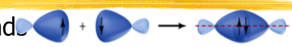


Valence Bond Theory

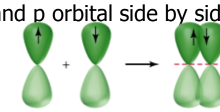
- Covalent bonds are formed by the overlap of ½ filled atomic orbitals from two separate atoms
- Bond strength is proportional to orbital overlap
- Two types of overlap leads to two types of bonds

Bond types in VB Theory

- Sigma (σ) bonds



  - Overlap along the bond axis
  - between s orbital and s orbital or s orbital and p orbital or two p orbitals directly
- Pi (π) bonds
  - Overlap off axis (above and below)
  - p orbital and p orbital side by side



Valence Bond picture of H_2O without hybridization

- Atomic orbitals
  - O: $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$
  - H: $1s^1$
- The 1s orbital of each H will overlap with a different 2p orbital of O
- 2 sigma bonds (direct overlap)
- Bond angle predicted to be 90°

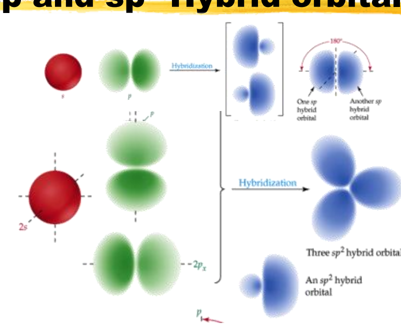
Orbital Hybridization

- Atomic orbitals are solutions to Schroedinger equation, $H\Psi = E\Psi$
- Linear combinations of orbitals are also solutions
- Resulting combinations are called hybrid orbitals (hybrids)
- Hybrids form because they increase the amount of overlap that can directly form when making sigma bonds

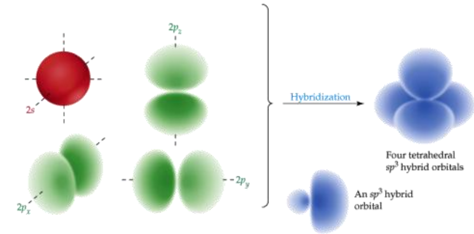
Forming Hybrids

- Number of atomic orbitals contributed = number of equivalent hybrid orbitals formed
- Hybrid orbitals only form sigma bonds
- Hybrid orbitals are named by listing atomic orbitals contributed (superscripts indicate multiples)
- Common hybrids: sp^3, sp^2, sp, sp^3d, sp^3d^2

sp and sp^2 Hybrid orbitals



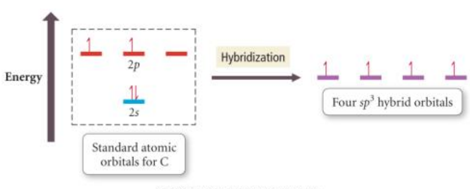
sp^3 Hybrid Orbitals



Hybridization of Carbon

- 4 single bonds
  - sp^3 hybridization, tetrahedral
- 2 single bonds and one double bond
  - sp^2 hybridization, trigonal planar
- 1 single bond and 1 triple bond or 2 double bonds
  - sp hybridization, linear

sp^3 Hybridization of C



Hybrid Orbital Geometries

TABLE 9.2 Hybrid Orbitals and Their Geometries

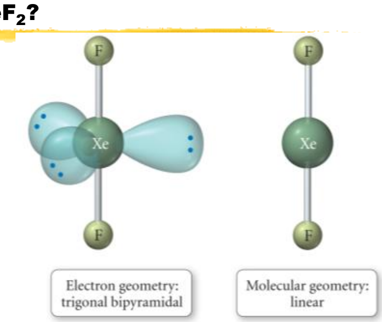
	Linear	Trigonal planar	Tetrahedral
Atomic orbitals mixed	One *s* and one *p*	One *s* and two *p*	One *s* and three *p*
Hybrid orbitals formed	Two *sp*	Three sp^2	Four sp^3
Unhybridized orbitals remaining	Two *p*	One *p*	None

Other hybrid orbitals

- sp^3d – leads to triangular bipyramidal geometry
- sp^3d^2 – leads to octahedral geometry

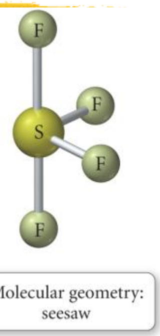
What is the hybridization of the central atom in XeF_2?

(A) *sp*
(B) sp^2
(C) sp^3d
(D) sp^3d^2



Which orbitals overlap to form the sigma bond between the sulfur and fluorine atoms in the molecule SF_4?

(A) sp^3d hybrid of S and $2p$ of F
(B) sp^3 hybrid of S and $2p$ of F
(C) sp^2 hybrid of S and $3p$ of F
(D) sp^3d^2 hybrid of S and $2p$ of F



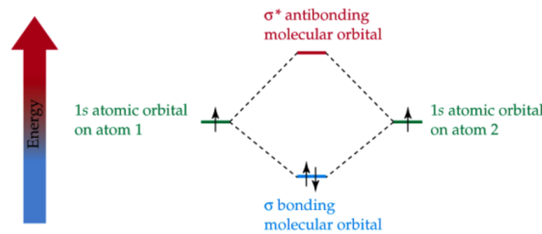
Problems with Valence Bond Theory

- VB theory predicts many properties better than Lewis Theory
  - bonding schemes, bond strengths, bond lengths, bond rigidity
- however, there are still many properties of molecules it doesn't predict perfectly
  - magnetic behavior of O_2

Molecular Orbital Theory

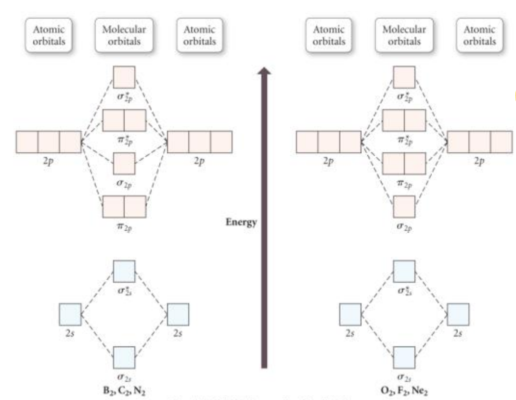
- Solve $H\Psi = E\Psi$ to obtain molecular orbitals
- Molecular orbitals
  - analogous to atomic orbitals (1s, 2s, etc)
  - sigma and pi molecular orbitals can be considered combinations of atomic orbitals
  - two classes of orbitals
    - bonding: σ &π orbitals concentrate e^- density between atoms, lower in energy than corresponding atomic orbitals
    - antibonding: σ^* & π^* orbitals concentrate e^- density away from volume between atoms, higher in energy than corresponding atomic orbitals
  - orbitals still fill using Aufbau principle and Hund's rule

MO diagram for H_2



Bond order

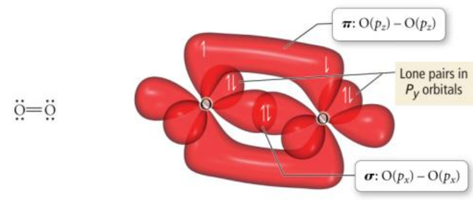
- Bond order = [(# of e^- in bonding orbitals) – (# of e^- in antibonding orbitals)] /2
- single, double, triple bonds have Bond order = 1, 2, 3
- If predicted bond order is greater than zero, molecule is stable



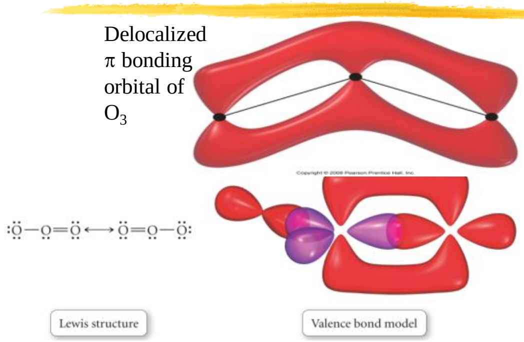
Magnetism

- Paramagnetism
  - unpaired electrons are present
  - attracted to a magnet
- Diamagnetism
  - all electrons are paired
  - slight repulsion to magnets

O_2 as described by Lewis and VB theory



Different models of Ozone, O_3



Theories of Bonding

- Lewis structures (with VSEPR)
  - simple, intuitive
- Valence bond theory
  - uses atomic orbitals as basis
  - hybridization is powerful concept to explain bond strength and geometry
  - difficulty with resonance
- Molecular Orbital theory
  - $H\Psi = E\Psi$
  - least intuitive and most exact

Polar Covalent Bonding

- The sharing of electrons in most covalent bonds is NOT equal
- The atom which better attracts the bonding electrons attains a partial negative charge
- The other atom attains a partial positive charge

Bond polarity and molecular polarity

- A polar bond is one with an unequal sharing of electrons
  - separation of charge indicated by bond dipole arrow
- A polar molecule has a net separation of charge indicated by a molecular dipole moment, μ

Polarity of Molecules

- in order for a molecule to be polar it must
  1) have polar bonds
     - electronegativity difference - theory
     - bond dipole moments - measured
  2) have an unsymmetrical shape
     - vector addition
- polarity affects the intermolecular forces of attraction
  - therefore boiling points and solubilities
    - like dissolves like

What holds solids and liquids together?

- Intermolecular forces
  - Dipole-dipole attractions
  - Hydrogen "bonding"
  - London dispersion forces

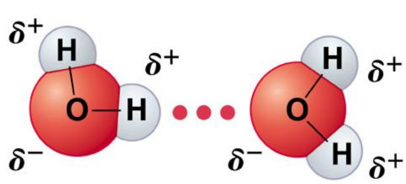
Dipole-dipole attractions

- Attraction between partially positive portion of one molecule and partially negative portion of a different molecule
- 3-4 kJ/mol

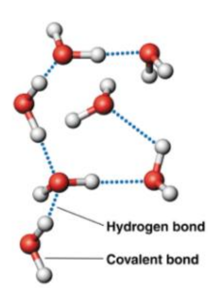
Hydrogen bonding

- Special case of dipole-dipole interaction
  - name reserved for when H is bonded to nitrogen, oxygen, and fluorine
- Fairly strong interaction, 10-40 kJ/mol
- Very important in living animals
  - holds proteins in their 3-dimensional shape

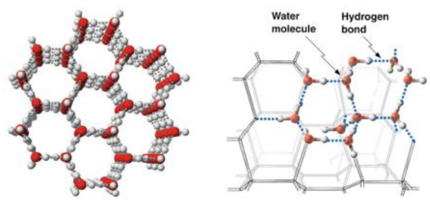
Hydrogen bonding



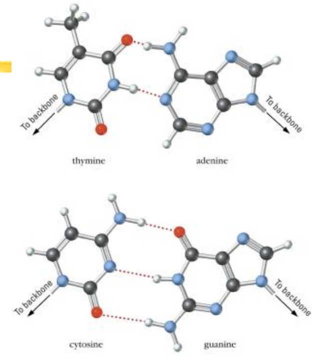
Example of Hydrogen bonding in liquid water



Structure of Ice



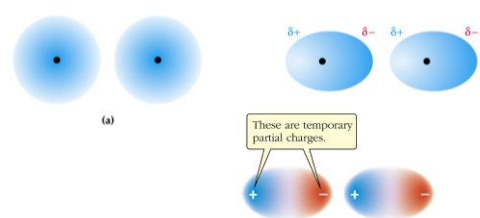
Hydrogen Bonding in DNA



London Dispersion Forces

- When all else fails …
- Attraction between a temporary dipole and the resulting induced dipole
- Fleeting attraction and weak, 1-10 kJ/mol
- Bigger molecules have stronger London dispersion forces

London Dispersion Forces visualized



More to say about London dispersion forces

- Most important for large molecules
- Only interaction available for nonpolar compounds
- $I_2 > Br_2 > F_2$
- Xe > Kr > Ar > Ne
- The greater the attraction, the higher the boiling and melting points

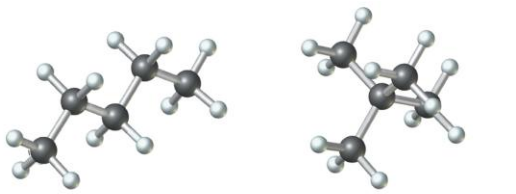
Boiling Points of Nonpolar Substances

TABLE 9.5 Effect of Numbers of Electrons on Boiling Points of Nonpolar Molecular Substances

Noble gases			Halogens			Hydrocarbons		
	No. e's	bp (°C)		No. e's	bp (°C)		No. e's	bp (°C)
He	2	−269	F_2	18	−188	CH_4	10	−161
Ne	10	−246	Cl_2	34	−34	C_2H_6	18	−88
Ar	18	−186	Br_2	70	59	C_3H_8	26	−42
Kr	36	−152	I_2	106	184	C_4H_{10}*	34	0

* Butane.

Structures & Boiling Points



pentane, bp = 36.0 °C   2,2-dimethylpropane, bp = 9.5 °C

Determining IM Forces

- Does the compound have a metal and non-metal?
  - YES – Ionic
  - NO -- Is the molecule polar?
    - NO – London Dispersion Forces
    - YES – Does the compound have hydrogen bonded to N, O, or F?
      - YES – Hydrogen Bonding
      - NO – Dipole-dipole interactions

What is the chief IM force in the following?

- SO_2
- CO_2
- NH_3
- H_2O
- PCl_3
- SO_3
- XeF_4

Physical properties depend upon intermolecular interactions

- Viscosity
  - liquid's resistance to flow
  - increases with strength of intermolecular interaction
- Surface tension
  - liquid's resistance to spreading
  - molecules on surface have less intermolecular interactions