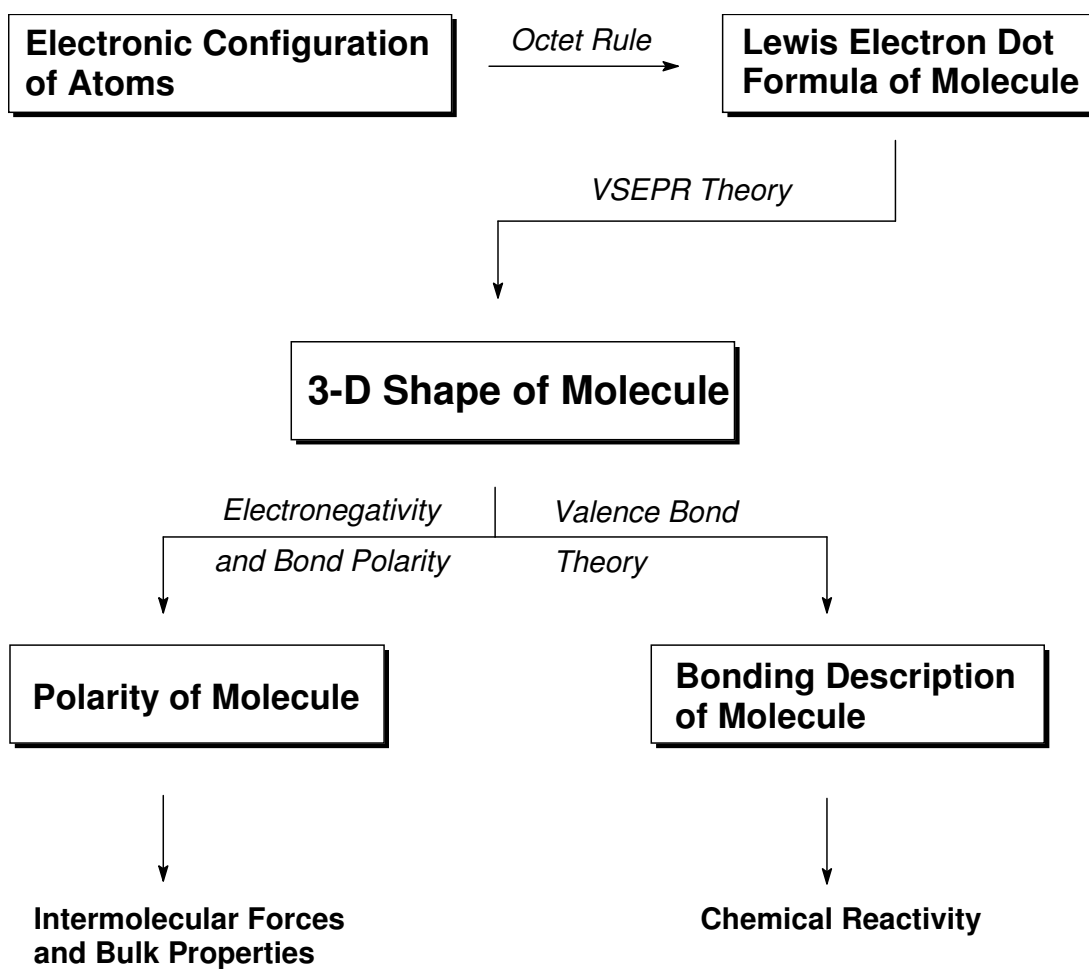


Chemical Bonding and Molecular Structure (Chapter 10)

Molecular Structure

1. General Summary -- Structure and Bonding Concepts


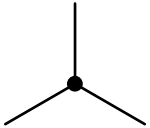
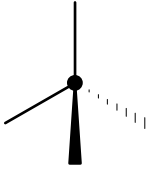
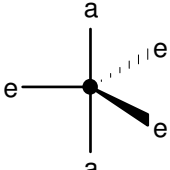
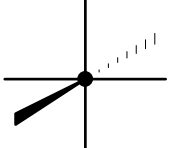


2. **VSEPR Theory** -- simple prediction of molecular shapes

Valence Shell Electron Pair Repulsion Theory

Hypothesis -- The structure of a molecule is that which minimizes the repulsions between pairs of electrons on the central atom.

"**Steric Number**" (SN) = # of atoms attached to central atom
 (aka "electron groups") + # of lone pairs on central atom

SN	Electron Pair Arrangement (aka "electron geometry")	Molecular Shape	Examples
2		linear 180°	AX ₂ linear BeCl ₂ , CO ₂
3		trigonal planar 120°	AX ₃ trigonal planar AEX ₂ bent BCl ₃ , CH ₃ ⁺ SnCl ₂ , NO ₂ ⁻
4		tetrahedral 109.5°	AX ₄ tetrahedral AEX ₃ pyramidal AE ₂ X ₂ bent CH ₄ , PO ₄ ³⁻ NH ₃ , ClO ₃ ⁻ H ₂ O, SeF ₂
5		trigonal bipyramidal 120° & 90°	AX ₅ trig bipyramid AEX ₄ "see saw" AE ₂ X ₃ T-shaped AE ₃ X ₂ linear PF ₅ , SeCl ₅ ⁺ SF ₄ , BrF ₄ ⁺ ClF ₃ , XeO ₃ ²⁻ XeF ₂ , ICl ₂ ⁻
6		octahedral 90°	AX ₆ octahedral AEX ₅ square pyramid AE ₂ X ₄ square planar SF ₆ , PCl ₆ ⁻ BrF ₅ , SF ₅ ⁻ XeF ₄ , IF ₄ ⁻

(A = central atom, X = terminal atom, E = lone pair)

Related aspects:

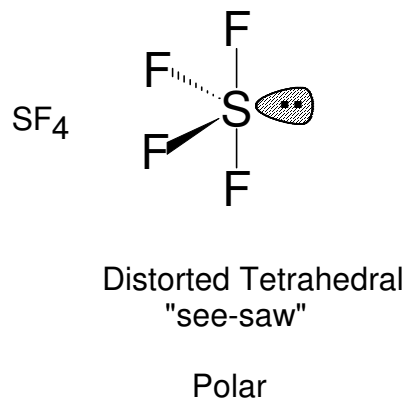
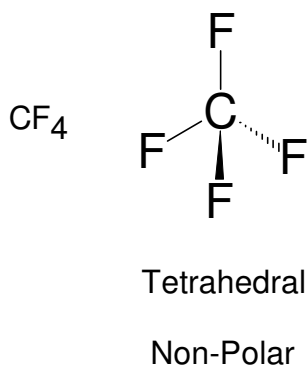
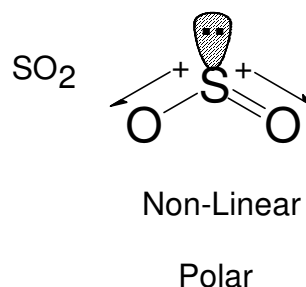
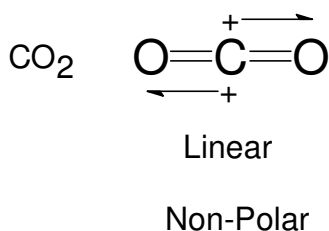
- In *trigonal bipyramid* structures, lone e⁻ pairs adopt equatorial positions (e)
- Order of repulsions: Lp - Lp > Lp - Bp > Bp - Bp
 (Predicts distortions from ideal geometries)

3. Polarity of Molecules -- can predict from molecular shape

Polar or Non-Polar?

In **very symmetrical structures** (e.g., CO_2 or CF_4), the individual bond dipoles effectively cancel each other and the molecule is **non-polar**.

In **less symmetrical structures** (e.g., SO_2 and SF_4), the bond dipoles do not cancel and there is a net dipole moment which makes the molecule **polar**.



Other examples for practice:

Polar: H_2O SnCl_2 NH_3 SeF_2 PF_3 BrF_5 XeO_3

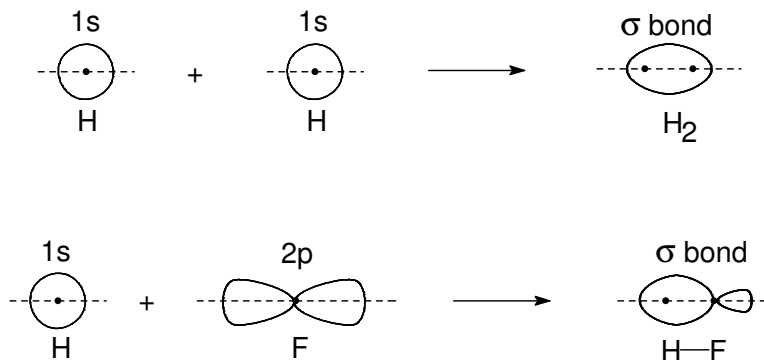
Non-Polar: BeCl_2 CH_4 PF_5 XeF_2 XeF_4 SO_3

Valence Bond Theory

1. Basic Concept

Covalent Bonds result from **overlap of atomic orbitals**

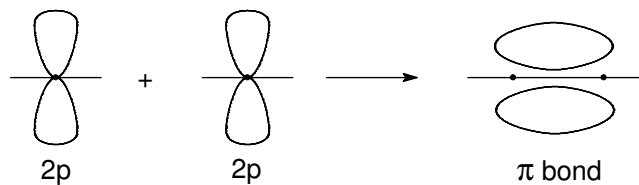
for example, consider the H₂ and HF molecules:



Two types of covalent bonds:

σ (sigma) bond "head-to-head" overlap along the bond axis

π (pi) bond "side-to-side" overlap of p orbitals:



single bond -- always a σ bond

double bond -- combination of one σ bond and one π bond

triple bond -- combination of one σ bond and two π bonds

2. Hybrid Atomic Orbitals

Question: Description of bonding in CH₄ molecule?

experimental fact -- CH₄ is **tetrahedral** (H-C-H angle = 109.5°)

VSEPR theory "explains" this -- 4 e⁻ pairs, ∴ tetrahedral

however, if only *s* and *p* orbitals are used, the angles ought to be 90° since the *p* orbitals are mutually perpendicular!

Solution: modify the theory of atomic orbitals and use:

Hybridization: combination of 2 or more atomic orbitals on the same atom to form a new set of "Hybrid Atomic Orbitals" used in bonding.

Types of Hybrid Orbitals

Atomic Orbitals	Hybrid Orbitals	Geometry	Unhybridized <i>p</i> Orbitals
one <i>s</i> + one <i>p</i>	two <i>sp</i>	Linear (180°)	2
one <i>s</i> + two <i>p</i>	three <i>sp</i> ²	Trigonal planar (120°)	1
one <i>s</i> + three <i>p</i>	four <i>sp</i> ³	Tetrahedral (109.5°)	0

{ **Note:** combination of *n* AO's yields *n* Hybrid Orbitals }

Example: in CH₄, C is *sp*³ hybridized:

C $\uparrow\downarrow$ \uparrow \uparrow — *ground state* - valence shell orbital diagram
 2s 2p (predicts 90° angles -- wrong!)

C \uparrow \uparrow \uparrow \uparrow *hybridized state*
 sp^3 sp^3 sp^3 sp^3 (predicts 109.5° angles -- right!)

3. Examples

Use valence bond theory to describe the bonding in the following.

(Draw clear 3-D pictures showing orbital overlap, etc.)

H₂O, NH₃, CH₄, PF₃ (simple σ bonds and lone pairs)

H₂CNH double bond like H₂CCH₂ (ethene) and H₂CO (formaldehyde)

HCN triple bond like HCCH (ethyne) and N₂ (nitrogen)

Molecular Orbital Theory

1. Comparison of VB and MO Theory

Valence Bond Theory ("simple" but somewhat limited)

e⁻ pair bonds between two atoms using overlap of *atomic orbitals* on two atoms

Molecular Orbital Theory (more general but "complex")

all e⁻'s in molecule fill up a set of *molecular orbitals* that are made up of linear combinations of *atomic orbitals on two or more atoms*

MO's can be:

"localized" -- combination of AO's on two atoms,
as in the diatomic molecules

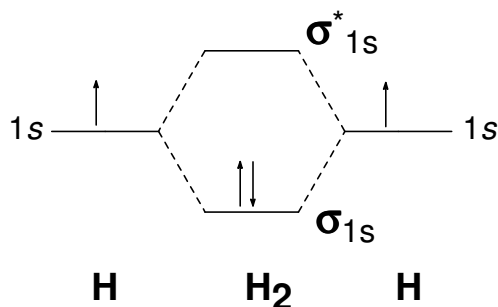
"delocalized" -- combination of AO's on three or more atoms
as in benzene (C₆H₆)

2. Molecular Orbitals for simple diatomic molecules (H₂ and He₂)

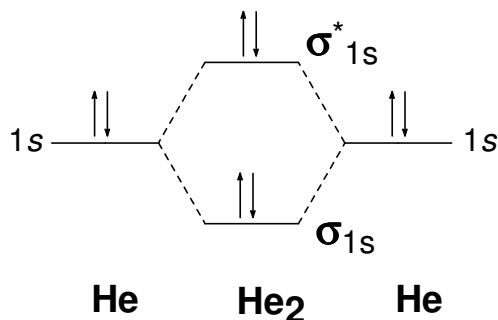
in H₂ the 1s atomic orbitals on the two H atoms are combined into:

a **bonding MO** -- σ_{1s} and an **antibonding MO** -- σ^*_{1s}

MO energy level diagram for H₂ (only the bonding MO is filled):



In contrast, the MO diagram for the nonexistent molecule, He₂ shows that both bonding and antibonding MO's are filled:



$$\text{Bond Order} = 1/2 [(\# \text{ bonding } e^{-}\text{'s}) - (\# \text{ antibonding } e^{-}\text{'s})]$$

$$\text{for H}_2 = 1/2 [2 - 0] = 1 \quad (\text{a single bond})$$

$$\text{for He}_2 = 1/2 [2 - 2] = 0 \quad (\text{no net bonding interaction})$$

3. MO's for 2nd Row Diatomic Molecules (e.g., N₂, O₂, F₂, etc.)

AO combinations -- from **s orbitals** and from **p orbitals**

MO energy level diagram -- Page 467

e.g., Fill in MO diagram for C₂, N₂, O₂, F₂, and Ne₂ and determine bond order for each:

molecule	C ₂	N ₂	O ₂	F ₂	Ne ₂
bond order	2	3	2	1	0

General "rules"

- electrons fill the lowest energy orbitals that are available
- maximum of 2 electrons, spins paired, per orbital
- Hund's rule of maximum unpaired spins applies*

***accounts for paramagnetism of O₂** (VB theory fails here!)

4. Delocalized Molecular Orbitals

By combining AO's from three or more atoms, it is possible to generate MO's that are "delocalized" over three or more atoms

Examples:

Resonance in species like **formate ion** HCO₂⁻ and **benzene** (C₆H₆) can be "explained" with a single MO description containing delocalized π bonds.