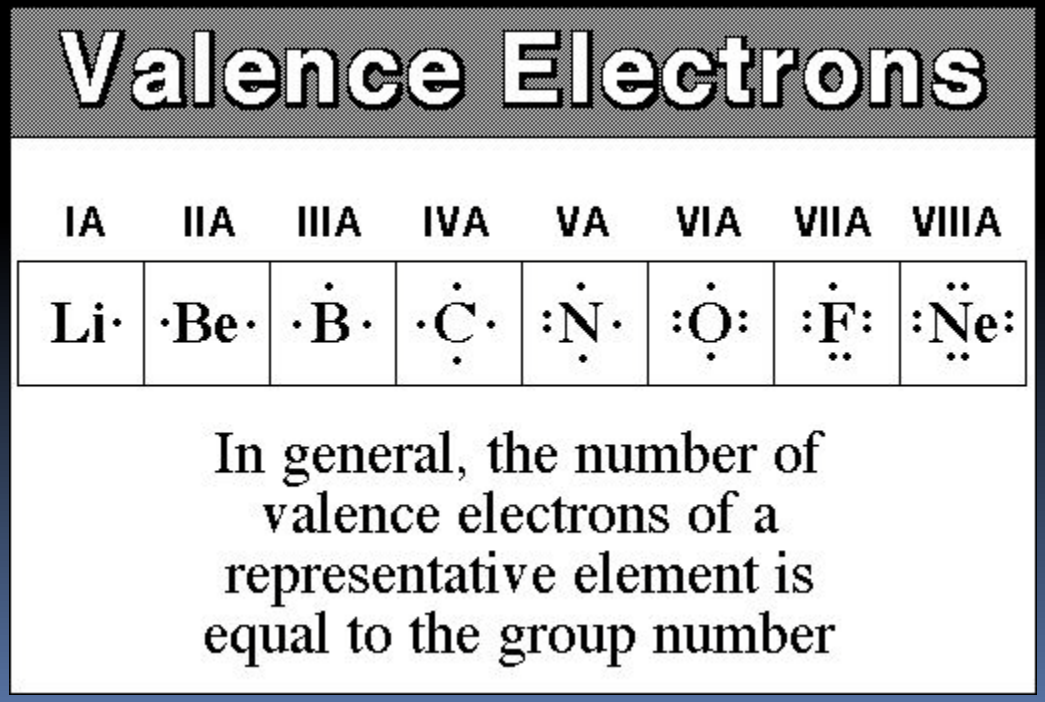
PART 3 – Chemical Bonds, Valence Bond Method, and Molecular Shapes

Reference: Chapter 9—10 in textbook

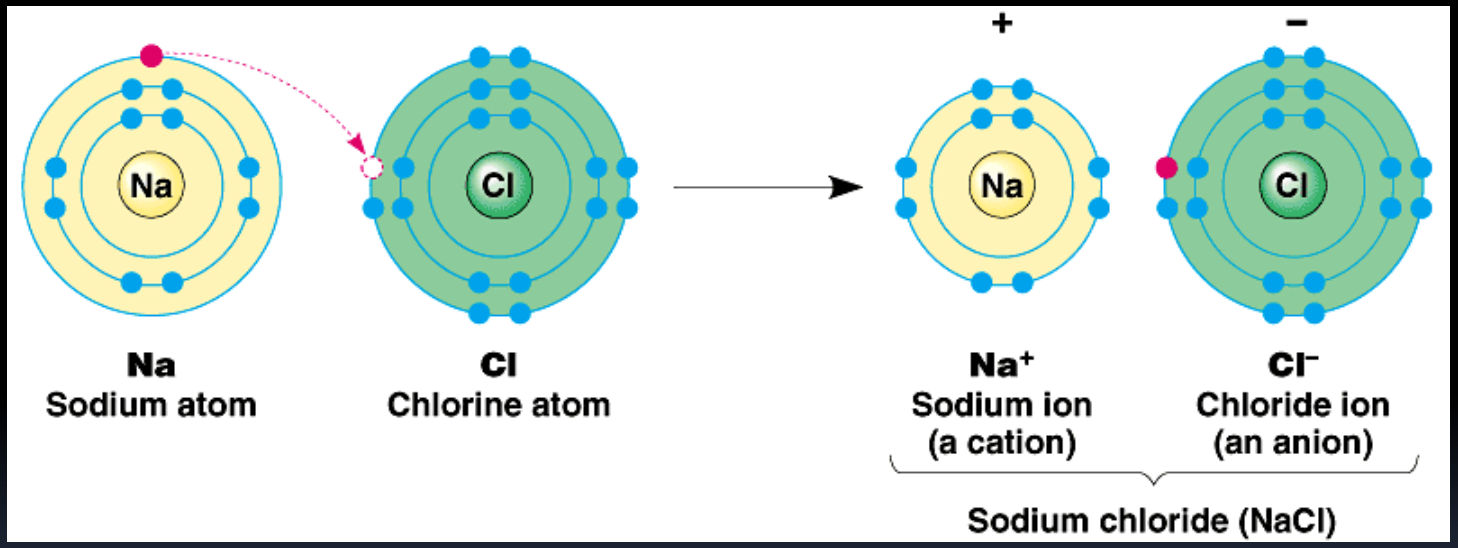
Valence Electrons

- Valence Electron
  - Define: the outer shell electrons
  - Important for determination of chemical properties



Ionic Bond

- Ionic bond
  - Define: Attraction between cation(s) and anion(s)



  - Usually ionic bond is formed between an active metal atom and an active non-metal atom.

Ionic Bonds

- Which compounds have ionic bonds?
  - Cation: formed from active metal atoms, (Group IA and IIA), e.g. Li, Na, Mg, K, Ca, …
  - Anion: formed from active non-metal atoms, (Group VIA and VIIA), e.g. O, F, S, Cl, Br, I, …
- How to represent ionic bonds?
  - Cation and anions are written in brackets, with the outmost shell of electrons and charges.

Covalent Bond

- Covalent bond:
  - formed between two (or more) non-metals, or one non-metal and one metal with low activity.
  - Atoms are connected by one pair (or more pairs) of shared electrons.
  - Examples:
    - H_2, O_2, N_2, HCl, H_2O, CO_2, CO, C_2Br_2.
    - GaAs, ZnSe, HgS

Lewis Structure & Octet Rule

- Lewis structure
  - A simple way to show valence electrons and molecular structure.
- Octet Rule (useful but not always true)
  - Octet rule: Groups of 8 electrons around each atom are most stable.
- Additional important concepts
  - Single bond, Double bond, Triple bond
  - Lone pair electrons (Nonbonding electrons)

How to Write Lewis Structures

- Steps: (see book, pg. 330)
  - (1) Write the atoms in the correct arrangement;
  - (2) Calculate the total valence electrons;
  - (3) Place one pair of e between each atoms;
  - (4) Beginning at structure outside, place e in pairs until reaching octet;
  - (5) Extra e are put in the central atoms; (Attention!)
  - (6) If not enough e, make double/triple bonds.
  - (7) *Check possible resonance structures.*

Questions

- Please write the following molecules with Lewis structure:
  - H_2, O_2, N_2, HCl, HClO, H_2O, CO_2, CO, C_2Br_2;
  - HNO_3, H_2CO_3;
  - H_2SO_4, H_3PO_4, $HClO_4$.

  (Does the octet rule work here? Why this rule can be broken?)

Additional Concepts in Lewis Structure

- Coordinate bond: a covalent bond in which both electrons are provided by one atom.
  - e.g. CO,
- Lone pair e: a valence e pair without bonding or sharing with other atoms.
  - e.g. H_2O, NH_3, CO_2.
- Bond order, Bond length, Bond energy
  - High bond order ↔ Short bond length ↔ High bond energy (requiring more energy to break a bond)

Bond Length, Energy & Order

- Bond order
- Bond length
  - Average distance between two bonding atoms.
- Bond energy
  - Energy required to break a given bond (in moles).

bond	Ave. Length	Ave. Energy/kJ mol^{-1}
H—H	74 pm	432
H—C	109 pm	415
H—N	101	390
H—O	96	460
H—Cl	127	428
H—Br	141	362
C—C	154	345
C=C	133	615
C≡C	120	835
N≡N	110	942
Cl—Cl	199	240
Br—Br	228	190
I—I	267	149

Organic Molecules

- Contain C and H, as well as O, N, S, etc.
- Carbon chain as the main framework
  - Alkyl (only C and H elements)
    - Alkane (single C-C bond only)
    - Alene (contains at least one C=C bond)
    - Alkyne (contains at least one C≡C bond)
  - Examples:
    - Write Lewis structures: CH_4 (methane), C_2H_6 (ethane), C_3H_8 (propane), C_2H_4 (ethylene), C_2H_2 (ethyne), C_2H_5OH (ethanol), CH_3COCH_3 (acetone).

Exception of Octet Rule in Lewis Structure

- More than 8 electrons in one of the atoms;
  - Example: SF_6, PCl_5.
- Fewer than 8 electrons in one of the atoms;
  - Example: $BeCl_2$, BF_3.
- Odd number of electrons in one of the atoms
  - Example: NO, NO_2.

Formal Charges

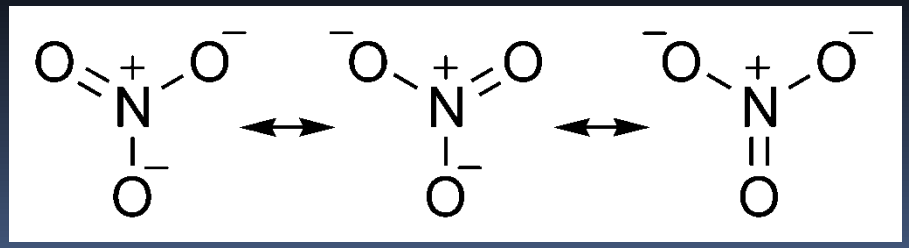
- Formal charges (FC): showing approximate distribution of electrons in molecules and ions.
- Calculate FC:
  - Assign each atom half of e in shared e-pairs;
  - Assign all unshared e as where they are;
  - Subtract the number of electrons assigned to each atom from the number of its valence electrons
- Example:
  - CO, ClO^-, NO_2, HNO_3.

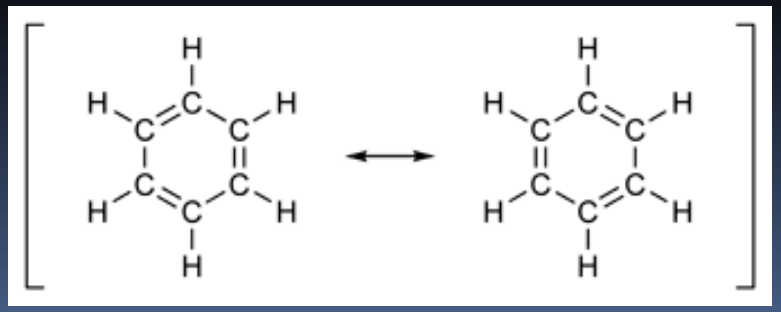
FC for Deciding the Best Lewis Structure

- Rules (Book, pg 324)
  - Small FC are better than large FC. (Zero FC is the best.)
  - Negative FC on atom(s) with higher electronegativity.
  - Opposite charges closer together are more likely than separating far apart;
  - Same charges in adjacent atoms are very unlikely.
- Examples:
  - (1) Decide which Lewis Structure of CO_2 is better?
  - (2) Decide formaldehyde (CH_2O) structure (Book pg. 324: Q 9.9).

Resonance Structure

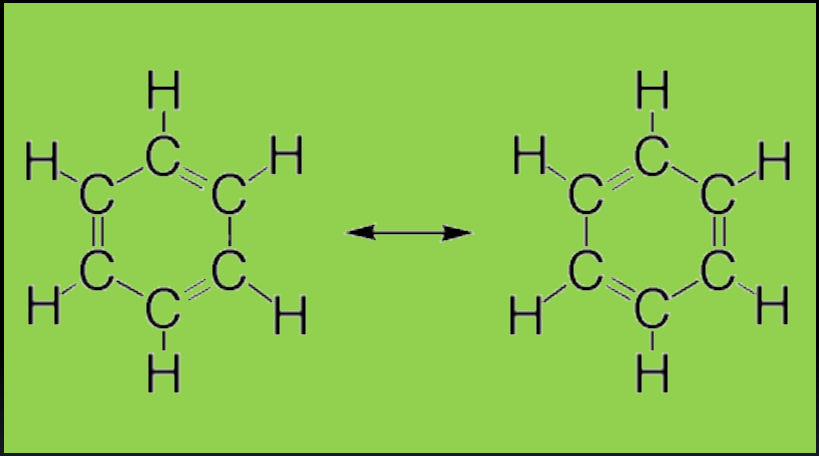
- Resonance structures
  - Possible electron structures of multiple identical Lewis structures
  - Arbitrary representation, not real
  - Examples:





Resonance Structure for Benzene

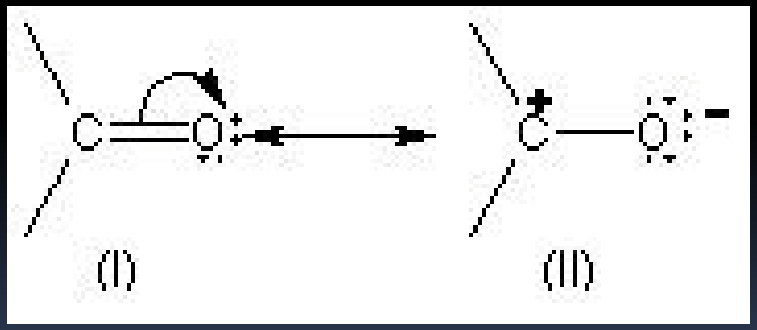
- Benzene (C_6H_6):
  - Distance between two adjacent C atoms is same, and longer than C=C but shorter than C-C.



  - All the bond angle is 120°, and the whole benzene molecule is in a plane.

Organic Molecule Reactivity

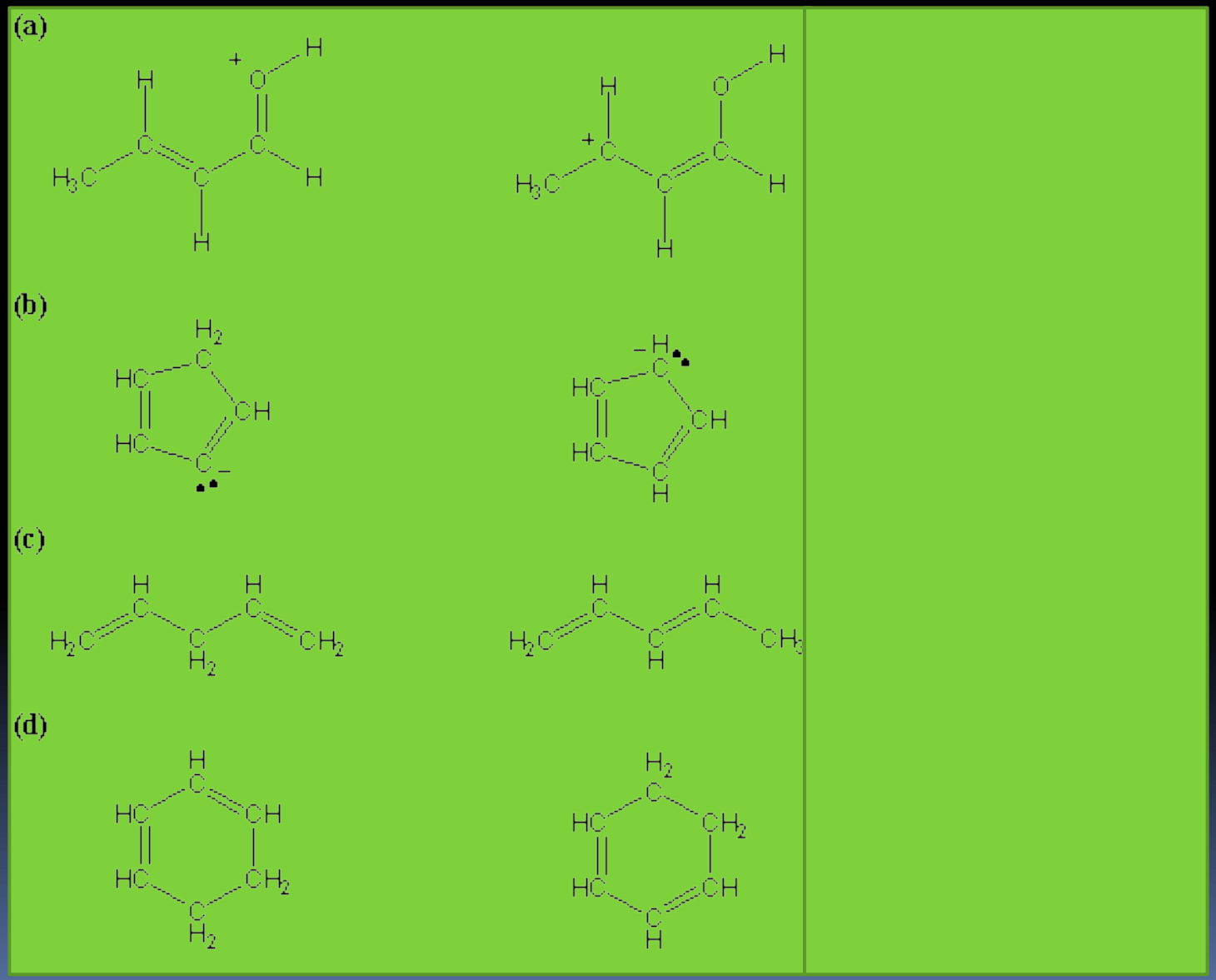
- Resonance structures are useful in predicting possible reactions, especially for organic reaction.
  - Example: carbonyl group



Q: Write the Resonance Structures

- Please write the following molecules with Lewis structure. Note that:
  - For those molecules with more than one stable resonance structures, write all of them.
  - Choose which one structure(s) is the best one(s).
- H_2, O_2, N_2, HCl, HClO, H_2O, CO_2, CO, C_2Br_2;
- HNO_3, H_2CO_3;
- H_2SO_4, H_3PO_4, $HClO_4$.

Q: Write the Resonance Structures

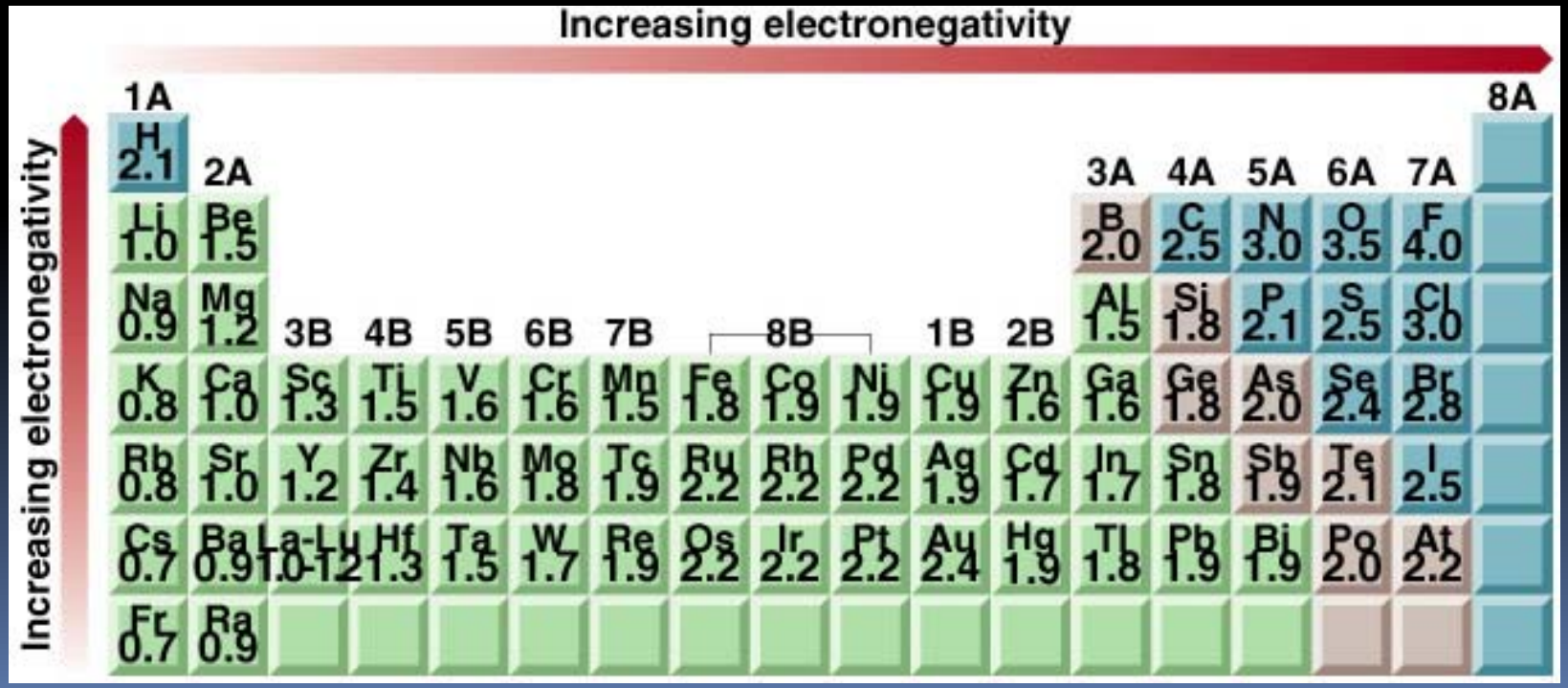


Lewis Structure is “Not Correct”

- Classical Lewis Structure provides a useful method for simple e configuration in molecules, however, it cannot explain:
  - Exception of the Octet Rule;
  - Why the bond length, order of some resonance structures (e.g. SO_2, NO_3^-) are the same?
  - The paramagnetism of O_2 molecule. (Try to write O_2 in Lewis structure?)

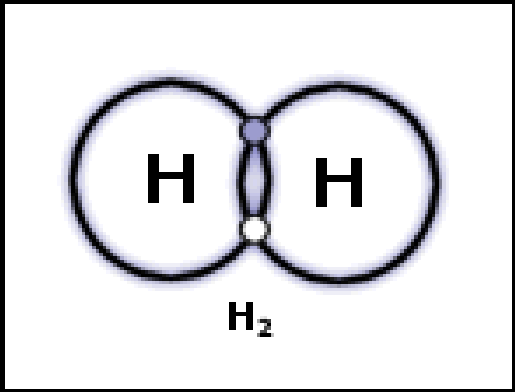
Electronegativity

- In hetero-nuclear molecule, electron cloud (bond) is not evenly distributed between two bonding atoms.
- Electronegativity: the ability of an atom to attract electrons towards itself.

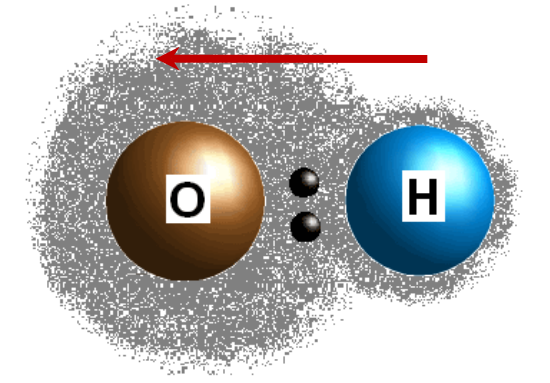


Nonpolar & Polar Covalent Bonds

- Nonpolar bond: between two identical atoms



- Polar bond: between two different atoms



- Dipole: from positive to negative charges

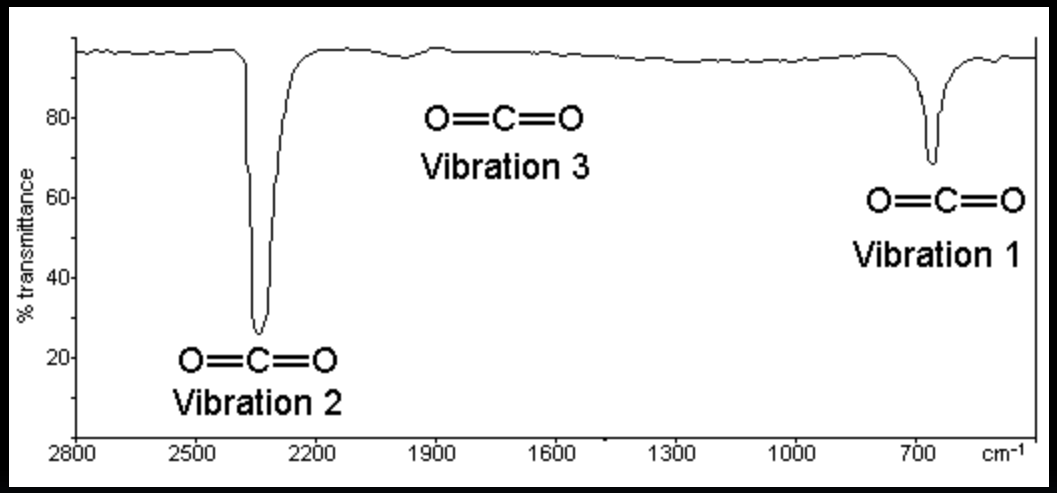
Questions

- Q1: Of the bonds Al-Cl, Cl-Cl, H-Cl, and K-Cl, (a) which bond is nonpolar? (b) Only one bond is ionic. Which one is it? (c) Arrange the bond in order of increasing polarity.

- Q2: Draw the dipole direction(s) of the following molecules: O_2, N_2, HCl, HClO, H_2O, CO_2, CO, C_2Br_2, HNO_3, H_2CO_3.

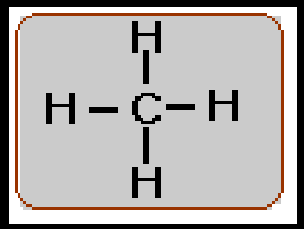
Dipole and IR-Spectrum

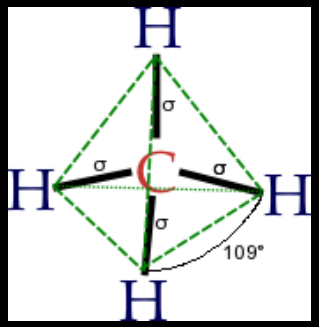
- Example: Infra-Red (IR) spectrum

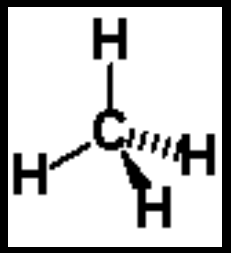


Bond Angle in 3D Space

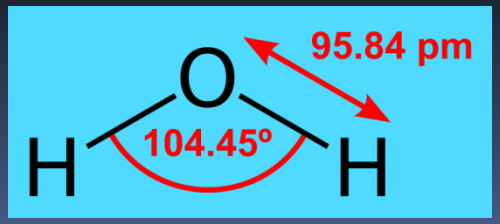
- Shape of polyatomic molecules or ions
  - How to draw positions of each atom in 3D space

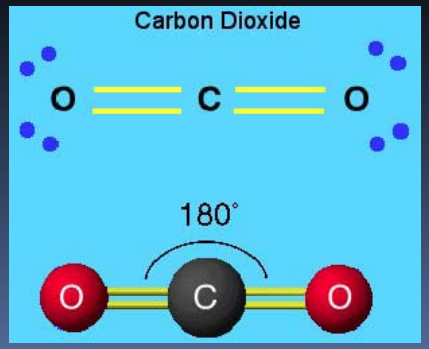


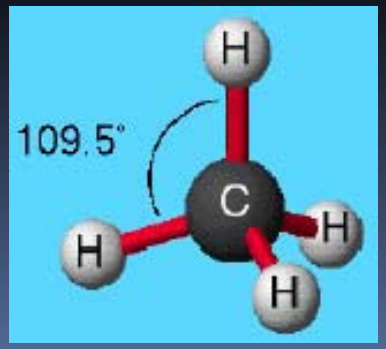




  - Bond angle





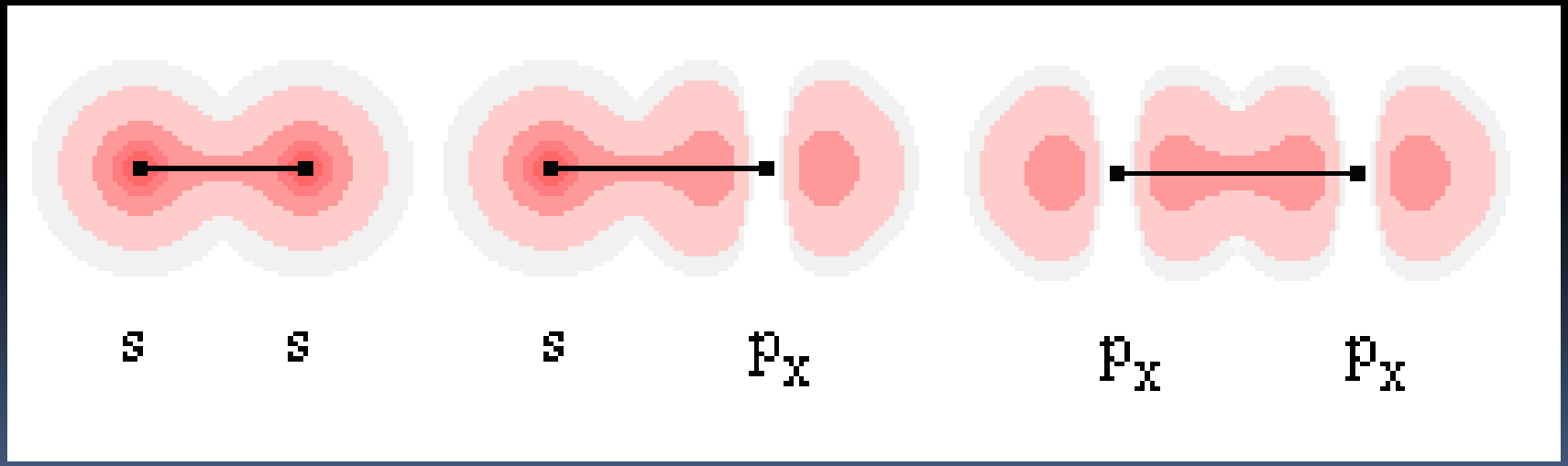


Valence Bond (VB) Method

- VB method:
  - The bonding between atoms are formed by overlap of atomic orbitals.
  - Two e^-_s need to have opposite spins to form a bond.
  - Refer to the binding energy curve of H_2 (book, pg 357).
- So, for a covalent bond, it has:
  - Saturation (i.e. the maximum number of e pairs)
  - Direction (i.e. to maximize the direction of orbitals)

Sigma (σ) Bond, Pi (π) Bond

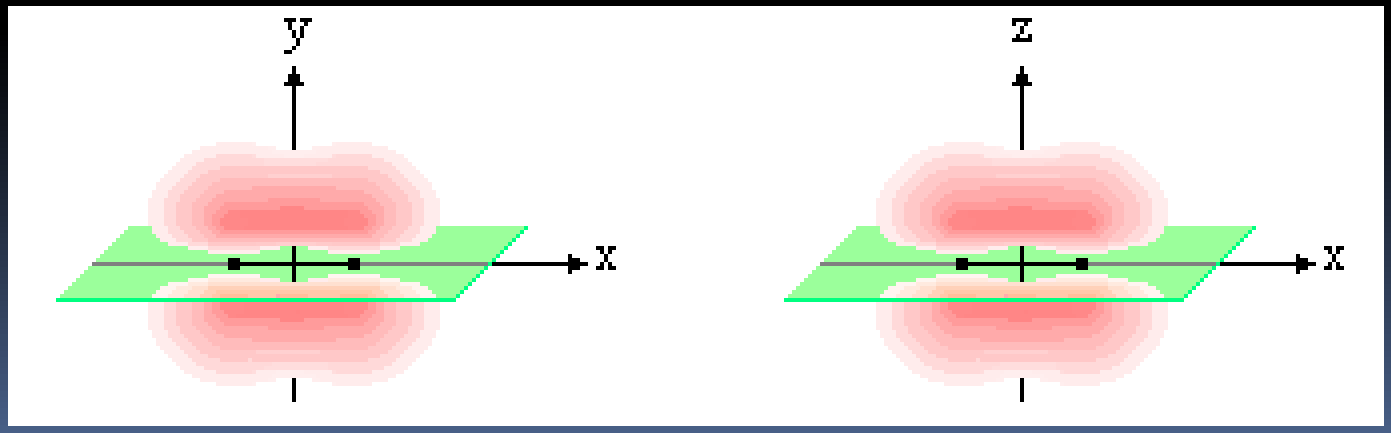
- σ bond:
  - Bonds formed by “head-on” overlap of atomic orbitals;
  - Symmetric about the internuclear axis.
  - Example: H_2, Cl_2, HCl, …



s-s σ bond **s-p_x σ bond** **p-p_x σ bond**

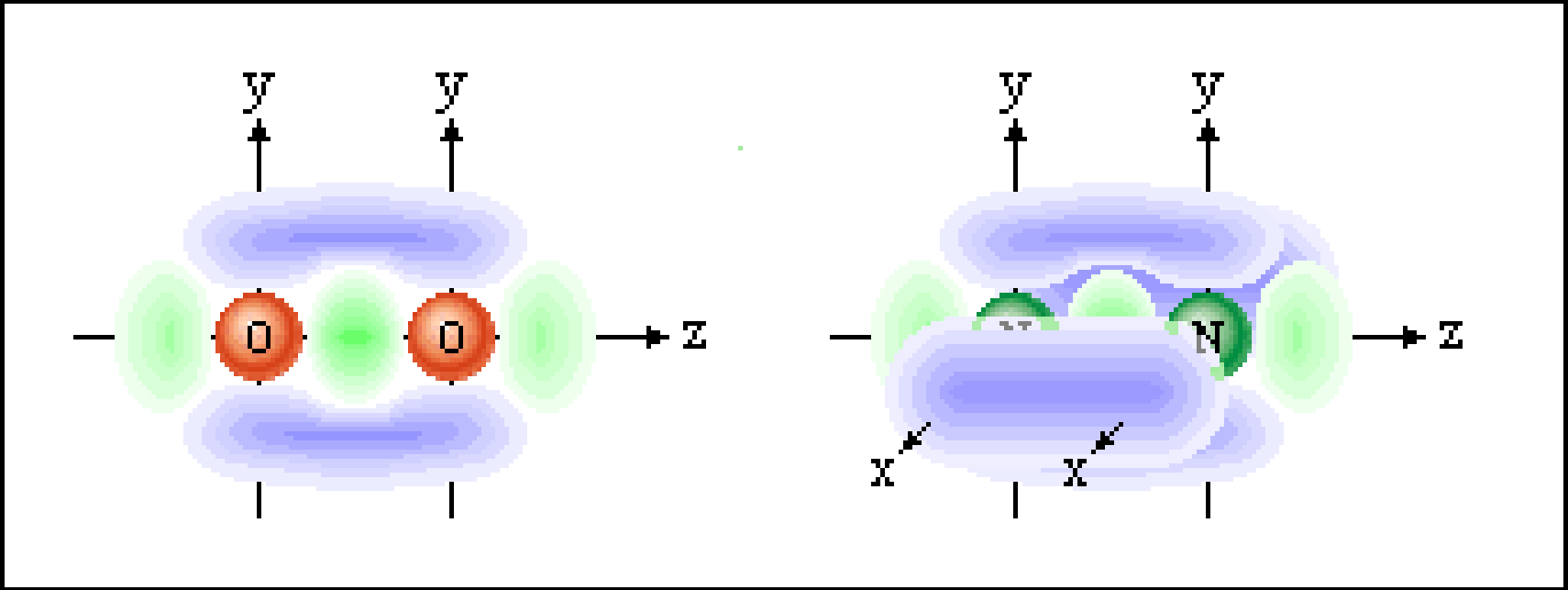
Sigma (σ) Bond, Pi (π) Bond

- π bond
  - Bonds formed by sidewise (“*shoulder-by-shoulder*”) overlap of atomic orbitals;
  - One part above, the other part below molecular plane.
  - Example: O_2, CO_2, N_2, …



p_y-p_y π bond **p_z-p_z π bond**

Examples: O_2, N_2

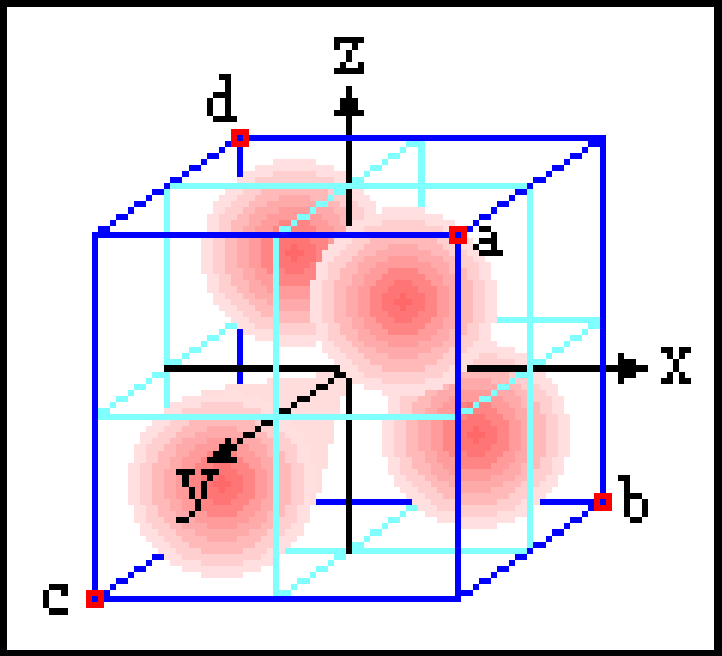


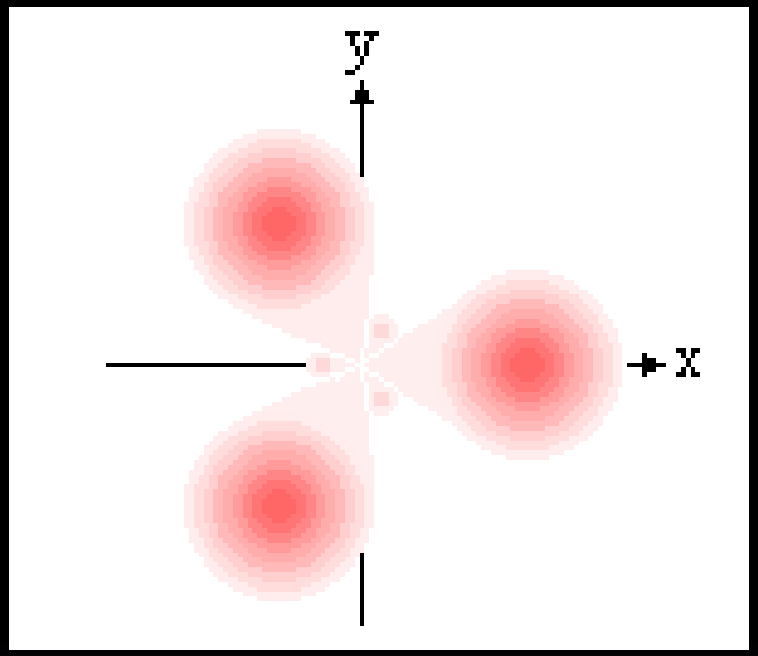
- Q: (1) How many σ bonds and π bonds are there in O_2 and N_2, respectively? (2) What are their bond orders? (3) Estimate which molecule is more stable? Why?

Hybrid Orbitals

- Define: New atomic orbitals pictured as resulting from combination of original atomic orbitals (e.g. s, p, d, …)
  - Same number of new orbitals formed as original ones;
  - Hybrid orbitals are identical (in length, direction, order, etc.)
- Examples:
  - **sp^3** hybrid: CH_4 (methane), CH_3CH_3 (ethane);
  - **sp^2** hybrid: CH_2CH_2 (ethylene), SO_2.
  - **sp** hybrid: CHCH (ethyne), CO_2.

Shape of sp^3, sp^2, sp hybrid orbitals





sp^3 hybrid orbital (4 orbitals);

bond angle is 109.5^o.

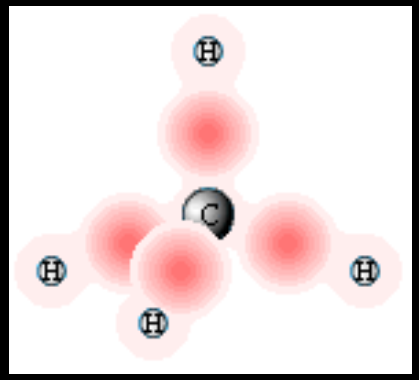
sp^2 hybrid orbital (3 orbitals);

bond angle is 120°.

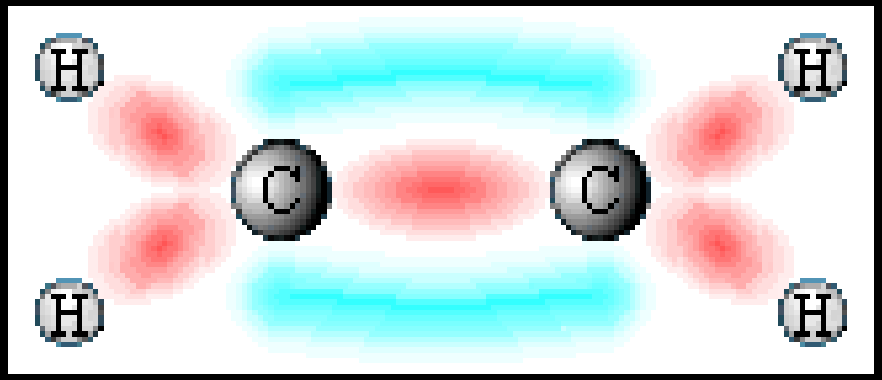
sp hybrid orbital (2 orbitals);

bond angle is 180°.

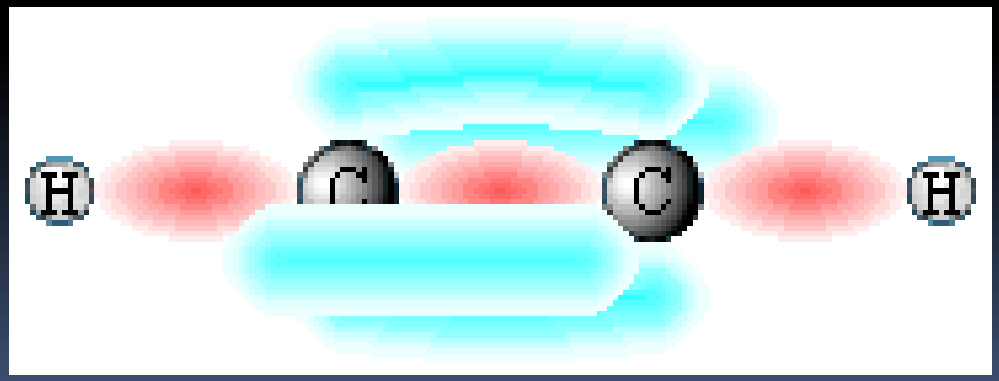
Shapes of a Few Molecules



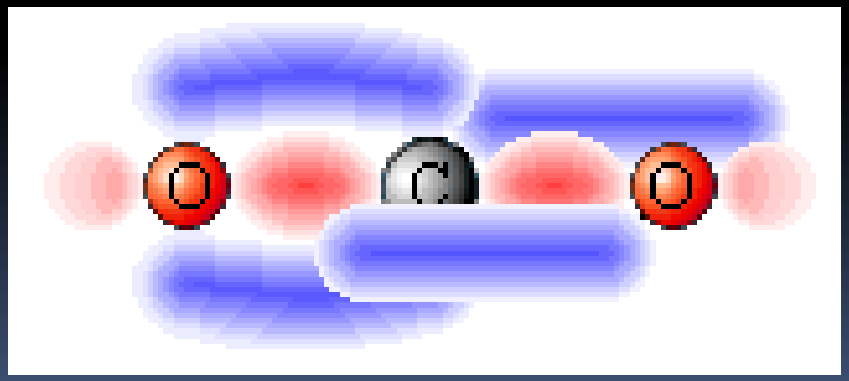
CH_4



C_2H_4



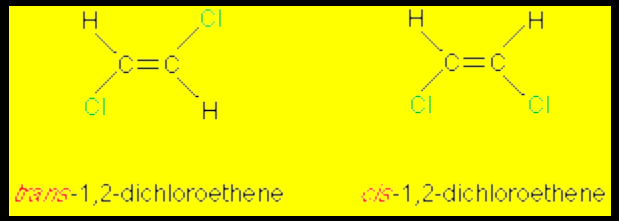
C_2H_2

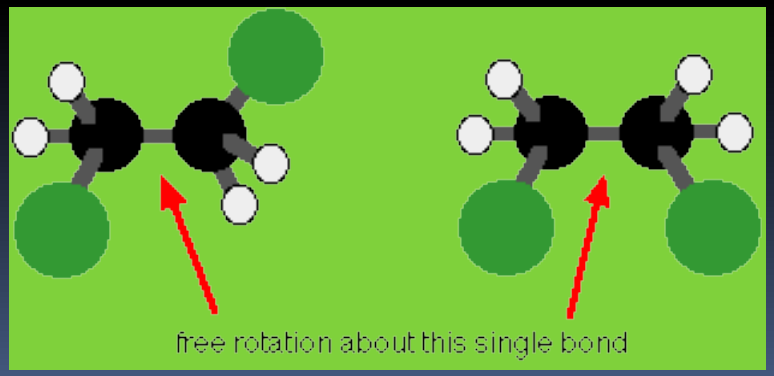


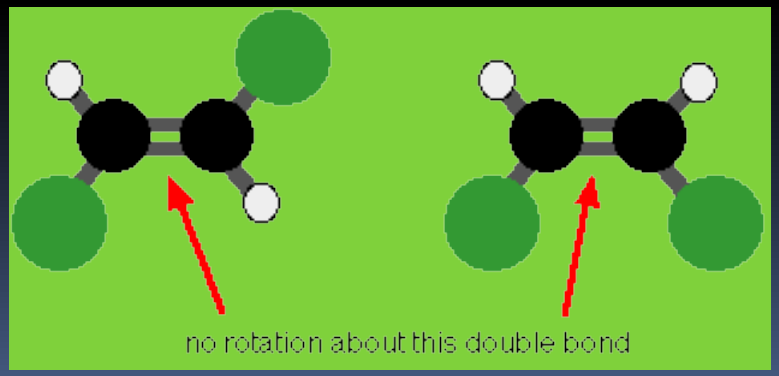
CO_2

Cis-Trans Isomerism (sp^2 hybrid)

- Cis-trans isomerism: a form of stereo-isomerism
- Existinrotate,g in molecules with a bond that cannot freely (such as sp^2-sp^2 C=C bond).

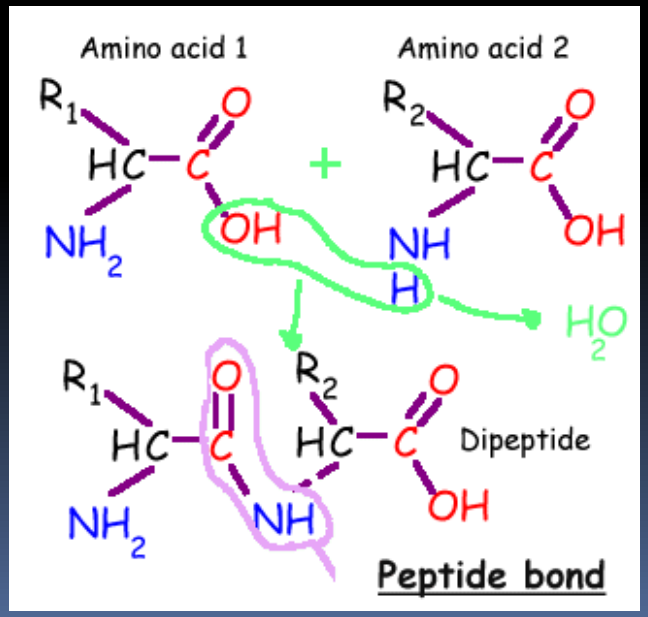


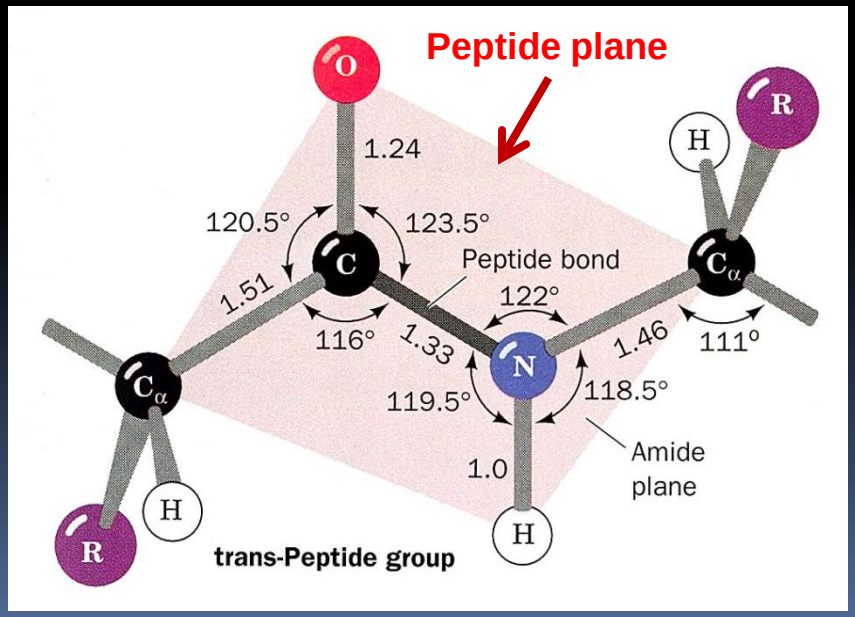




Example: Peptide Bond

- Peptide bond: a C-N bond formed between a carboxyl group (-COOH) of an amino acid, and an amino group (-NH_2) from another amino acid.
- Due to the sp^2 hybrid of C atom, peptide planes are formed with six atoms. (*This structure serves as a basic unit for constructing protein 3D conformation*).



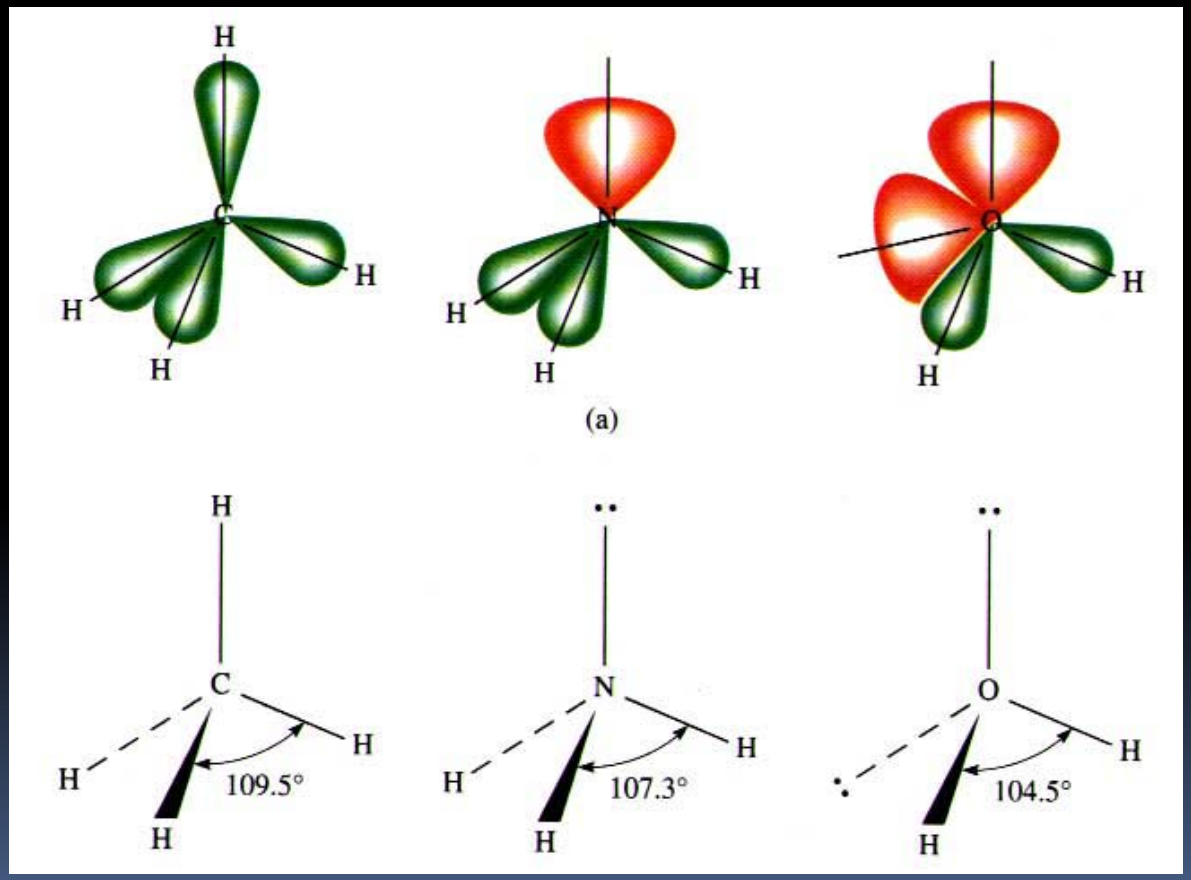


Advantage & Disadvantage of VB

- Advantages:
  - Explains the covalent bond's saturation and direction, very useful for many (organic) molecules;
  - Very useful in prediction of molecule shape.
- Disadvantages:
  - Cannot explain the equal bond length/energy in the resonance structures;
  - Cannot explain the paramagnetism in O_2 molecule.

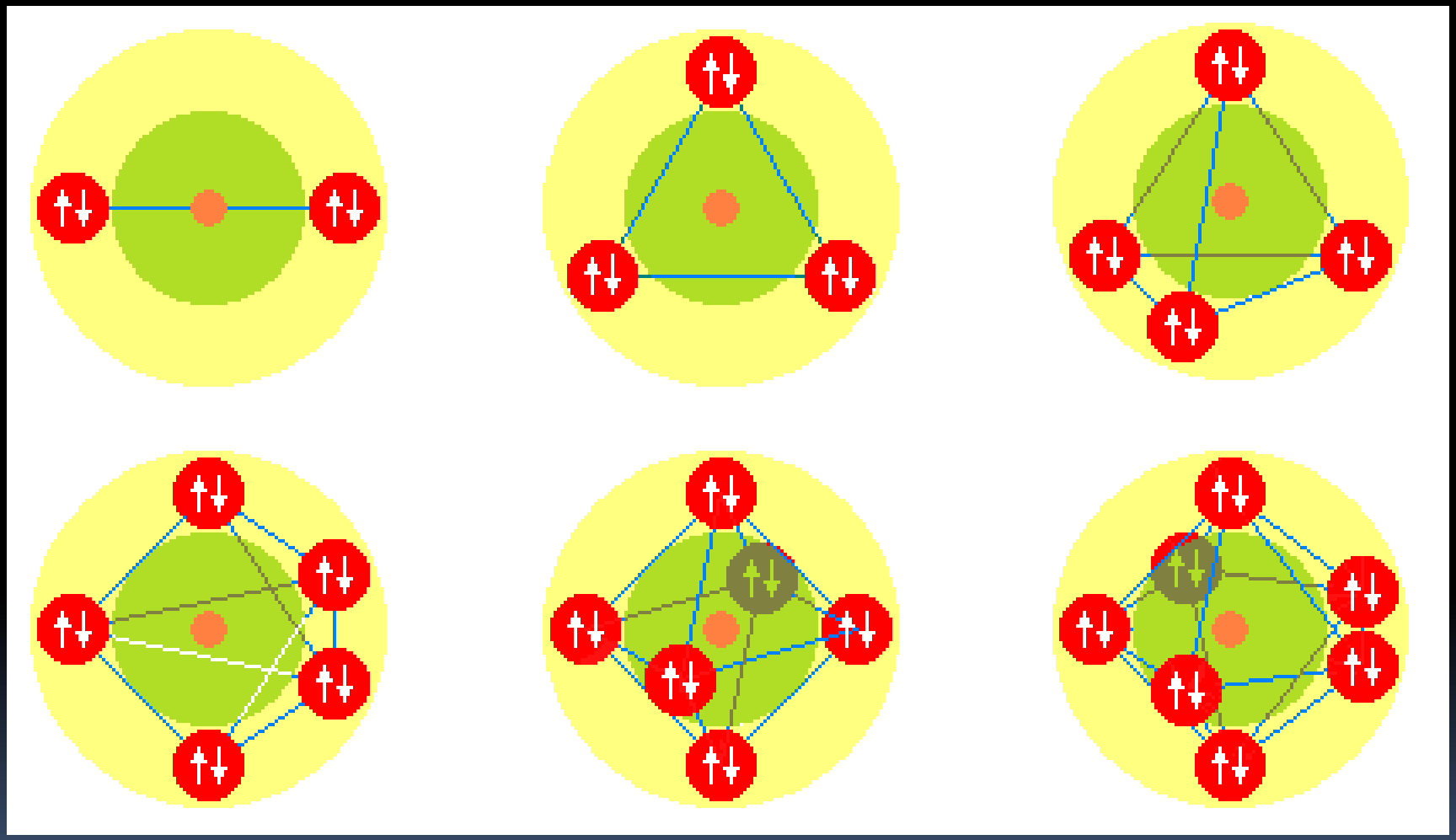
Molecular Shape

- Molecular shapes of CH_4, NH_3, H_2O & HF



Tetrahedral **Trigonal pyramid** **Bent**

Valence Shell Electron Pair Repulsion

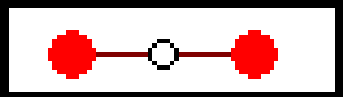
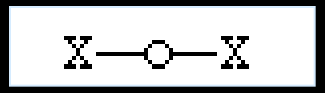
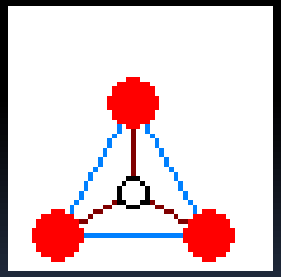
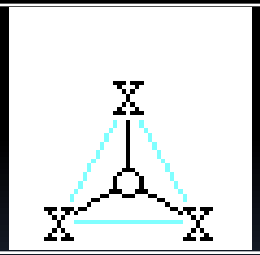
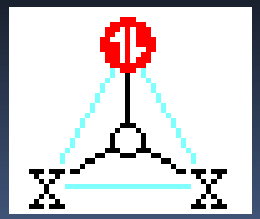


Molecule shape with different number of valence electron pairs (only consider the central atom)

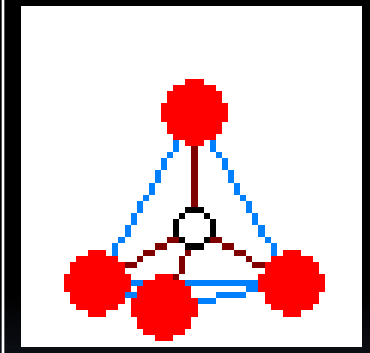
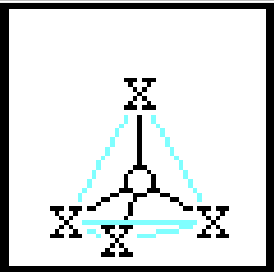
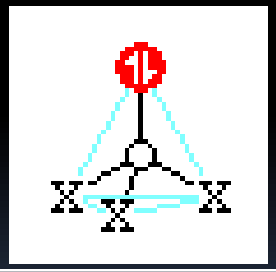
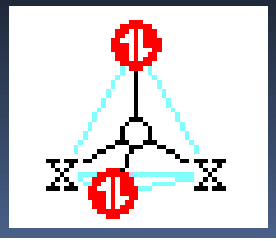
VSEPR Method

1. Consider all electron pairs of the central atom, (including bonding pairs and lone pairs)
2. Decide geometry of electron pairs of the molecule
   - # of e pairs = [(# of valence e) + (# of non-VIA atoms) + (charges)] * 0.5
3. Minimize the repulsion force:
   - Lone pair – Lone pair > Lone pair – Bonding pair > Bonding pair – Bonding –pair
   - Minimize the # of right angles of higher repulsion
   - Double, Triple bonds or unpaired electron is considered as single bond, but higher bond order has larger repulsion.

Shape of Electron Pairs, Molecules

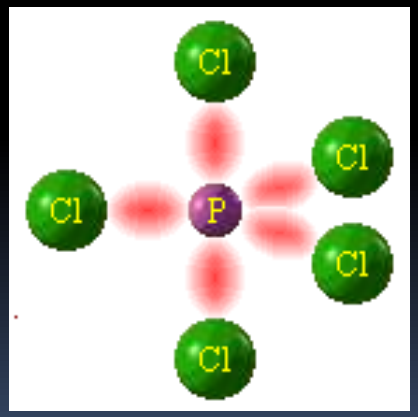
Valence Electron Pair Number	Electron Pair Shape	Formula	Molecule Shape	
2	 linear	AX_2	 linear	
3	 trigonal planar	AX_3		trigonal planar
		AX_2e		V-shaped

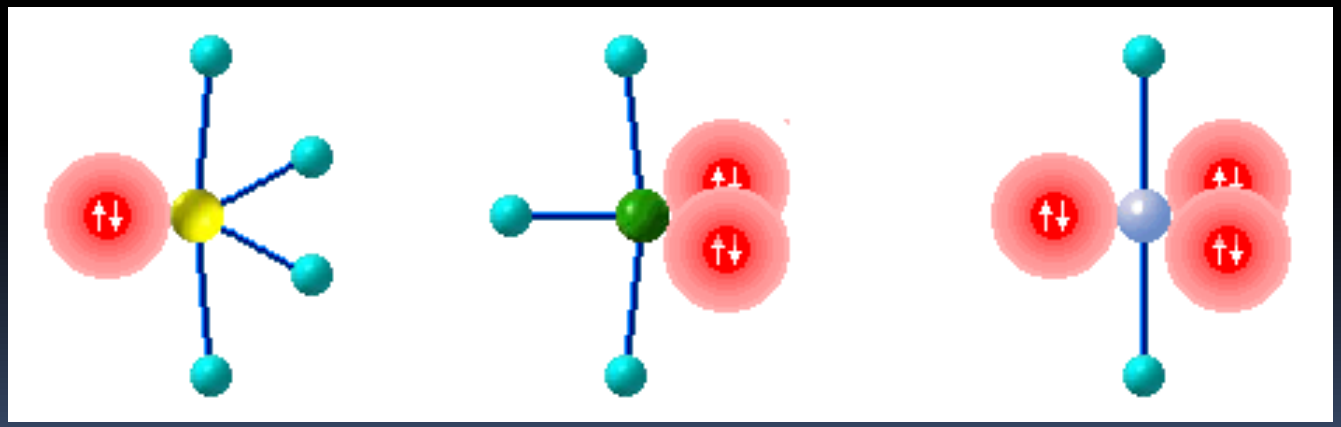
Shape of Electron Pairs, Molecules

Valence Electron Pair Number	Electron Pair Shape	Formula	Molecule Shape	
4	 tetrahedral	AX_4		tetrahe-dral
		AX_3E		trigonal pyramid
		AX_2E_2		V-shaped

Hybrid Orbital with d-orbital

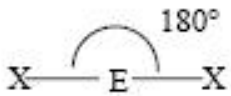
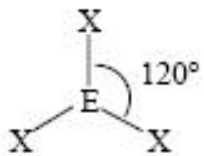
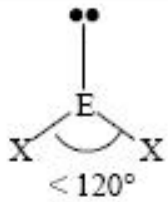
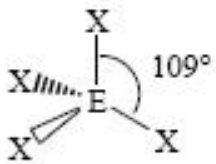
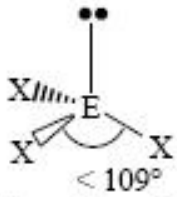
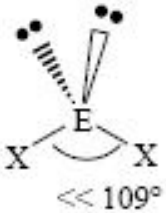
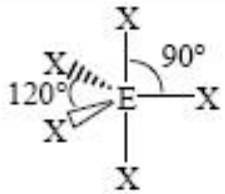
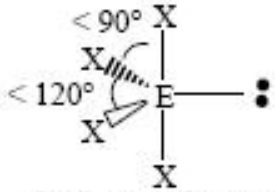
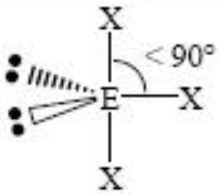
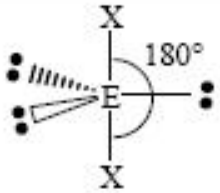
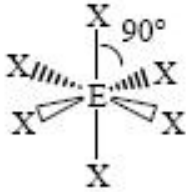
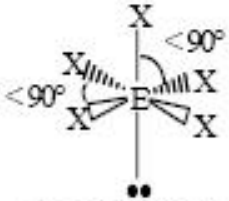
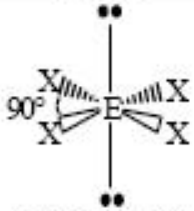
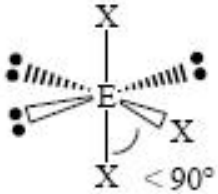
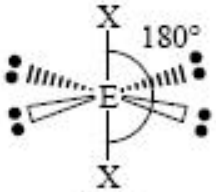
- Q: The molecules below take **<u>sp^3d</u>** hybrid (i.e. the electron pairs are in the trigonal bipyramid shape), please draw their molecular shapes.
  - (a) PCl_5; (b) SF_4; (c) ClF_3; (d) XeF_2.
- Solution:





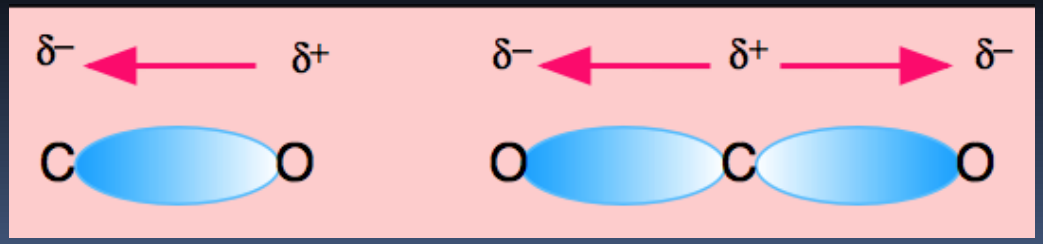
PCl_5 (trigonal bipyramid) SF_4 (sawhorse) ClF_3 (T-shaped) XeF_2 (linear)

VSEPR Geometries

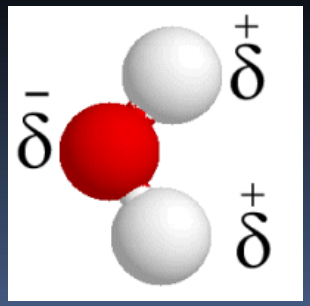
Steric No.	Basic Geometry 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	 Linear				
3	 Trigonal Planar	 Bent or Angular			
4	 Tetrahedral	 Trigonal Pyramid	 Bent or Angular		
5	 Trigonal Bipyramid	 Sawhorse or Seesaw	 T-shape	 Linear	
6	 Octahedral	 Square Pyramid	 Square Planar	 T-shape	 Linear

Molecule's Polarity

- Polar molecule and Nonpolar molecule
  - Sum of all dipoles in a molecule
  - Diatomic molecules: H_2, O_2, N_2, HCl
  - Polyatomic molecules: H_2O (V-shaped), CO_2 (linear), C_2H_4 (planar), C_2H_3Br (planar), C_2H_2 (linear), HCN (linear), CCl_4 (tetrahedron).



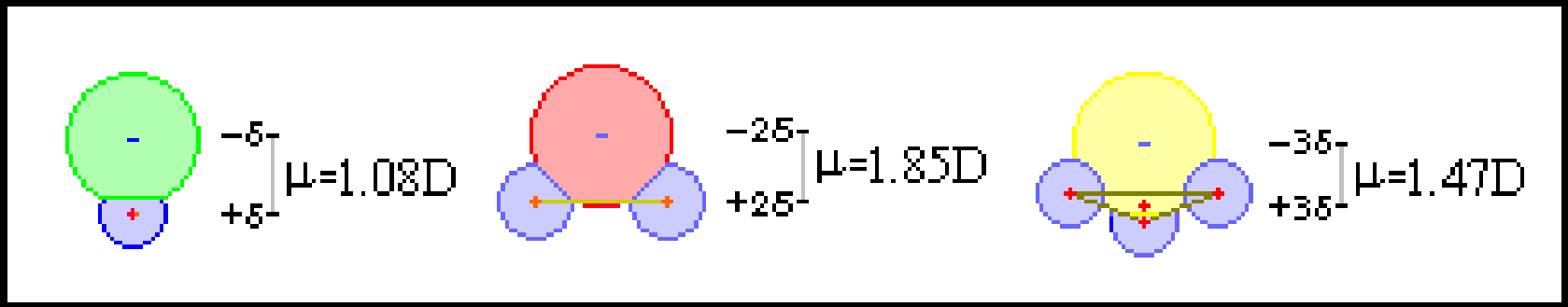
CO_2 (linear shape, nonpolar)



H_2O (V-shape, polar)

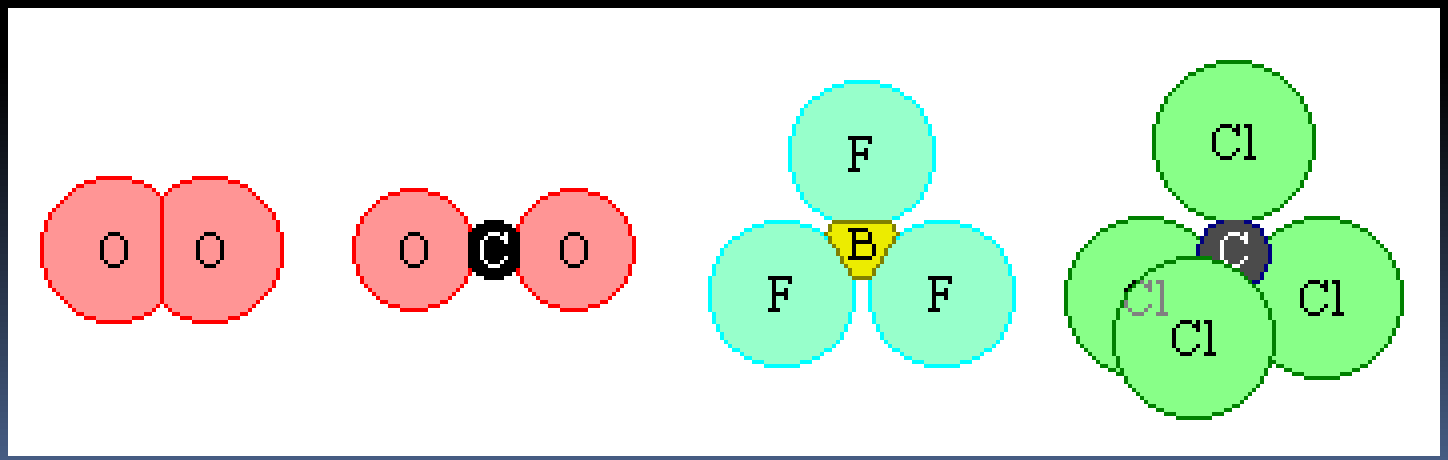
Polarity of Polyatomic Molecules

Polar Molecules



HCl **H_2O** **NH_3**

Nonpolar Molecules



O_2 **CO_2** **BF_3** **CCl_4**