Molecular Geometry and Bonding Theories

The bonds between 'atomic' species in molecules are characterized by bond distances and bond strengths.

The *angle* between three atoms is a very important molecular characteristic. Such angles are responsible for the 3D geometry of the molecule.

These geometrical considerations dictates that the molecules have *definite sizes and shapes*.

Thus molecules are 3-dimensional structures.

The three dimensional arrangement of atoms in a molecule is referred to as the molecular geometry.

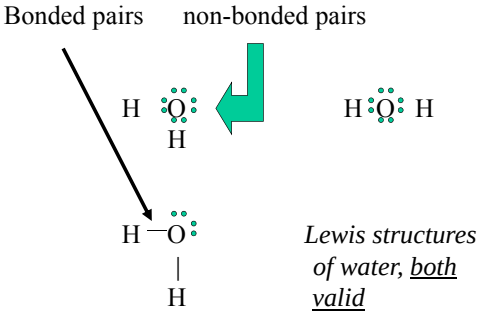
Determination of the geometry essentially boils down to the determination of the geometry of the bond *orientations* at the 'central' atom(s) in a molecule, in the 3-dimensions. Central atom – any non terminal atom in a molecule.

Thus, the first step is to find the electron 'clouds' around the 'central atom'.

Next, write the Lewis structure for the molecule.

Lewis structure simply indicates how many electron clouds/domains are associated with each atom, and the 'type' (single/double/triple /nonbonding) of the electron cloud.

Lewis structures provide electron distribution information (bonded -single, double, triple & non-bonded) - but not the geometry.



Electron pairs between/on atoms = electron clouds

Valence Shell Electron Pair Repulsion Theory VSEPR

Bonding involves electrons of the valence shells.

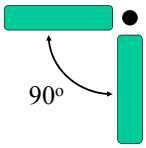
Electron pairs (clouds/domains) are negatively charged and are located on atoms.

Like charges repel, and repulsions inherently increase the energy of a 'system', in this case the molecule.

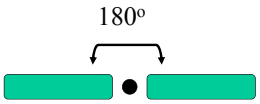
All systems tend toward a stable (low energy) state.

Repulsions cannot be eliminated, but could be *reduced* (the next best thing) by *minimizing the repulsions*.

Repulsions between electron clouds are *minimized* when the *angle between the clouds are at their optimum possible value*.



Two electron cloud case



linear
lowest repulsion
most stable

The most stable orientation of the electron pairs (i.e. least repulsive set-up) dictates the angle between the electron pairs (bond angle), that are located on the (central) atoms.

Consideration of the valence shell electron pair orientations allows the determination electron pair geometry in space and therefore the bond geometry around the central atom.

Definition:

Molecular geometry is the geometry the nuclei (atoms) of a molecule in the 3-D space. The electron domains/clouds on central atom(s) determine it.

Strategy of finding molecular geometry:

Lewis structure → # electron clouds *on central atoms* → lowest energy electron cloud orientation *on central atoms* → molecular geometry.

Electron Cloud (Electron Domains)

A single/double/triple/non-bonded electrons on "atom(s)" is considered an electron cloud/domain.

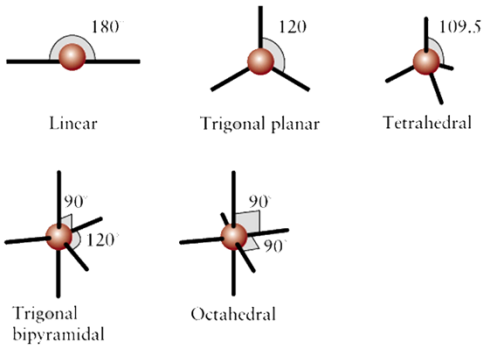
Geometry of Central Atoms with Electron Clouds

Electron-pair geometry (epg):

One of the five primary geometries (all clouds).

Molecular geometry:

Describes the arrangement of the atoms present (bonding 'clouds').



Predicting a VSEPR Structure

1. Draw the Lewis structure (see Ch. 8).
2. Determine the steric number (SN) = # clouds/domains on the 'central atom'.

   SN = (number of atoms bonded to central atom) + (number of lone pairs on central atom)
3. Use the SN to determine the geometry around the central atom.
4. Optimal molecular structure determined by the number of lone pairs and bonding 'pairs' of electrons.

The number of electron 'clouds' around the central atom range from two to six.

Our primary focus; on molecules of type AB_nE_m.

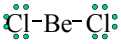
A = central atom
B = peripheral atom
E = non bonded electron pairs on A atom

Example HCl
diatomic AB and A_2 types

Always linear, regardless of the number of lone pairs on central atom.

All di-atomics - linear.

Example: $BeCl_2$ AB_2 type



180°

Cl-Be-Cl

SN=2

2 electron clouds @ central atom

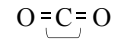
∠Cl Be Cl = 180°

electron (bonding pair) cloud geometry=*linear*

molecular geometry = *linear*

Example: CO_2 AB_2 type

SN=2



180°

2 electron clouds @ central atom
(two bonds in each cloud !)

electron 'pair' (cloud) geometry= *linear*

molecular geometry = *linear*

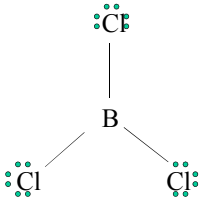
Ball and stick model

2 clouds on CA - linear

Ball and Stick Models
does not show the lone pairs

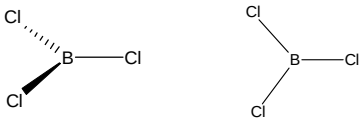
BF_3 AB_3 type

BCl_3

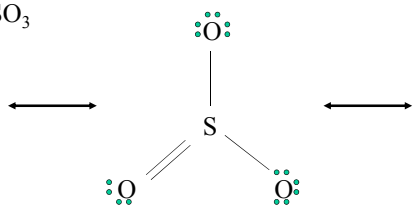


SN=3

3 clouds on CA; ∠Cl B Cl = 120°
epg: trigonal planar
molecular geometry: trigonal planar

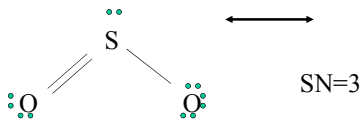


SO_3



3 clouds on CA; only central atom's electron pairs needed. Resonance makes all bonds equivalent.
epg: trigonal planar ∠OSO ≈ 120°
molecular geometry: trigonal planar

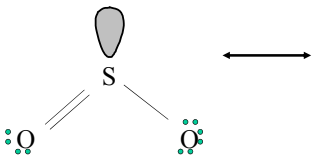
SO_2 AB_2E type



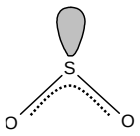
SN=3

3 clouds on CA. Electron clouds non-equivalent.
epg: trigonal planar
molecular geometry: bent

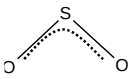
SO_2



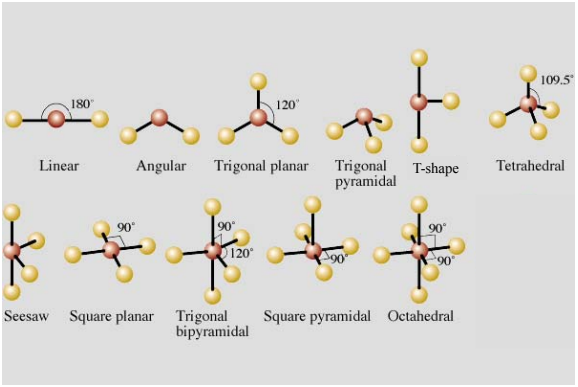
3 clouds on CA; Electron clouds non-equivalent
epg: trigonal planar ∠ OSO ≈ 120°
molecular geometry: bent/angular

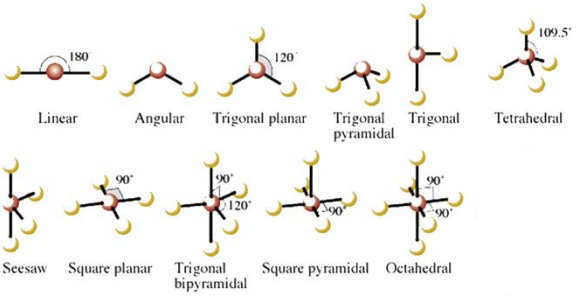


Electron cloud geometry

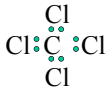


Molecular geometry



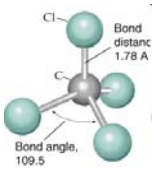


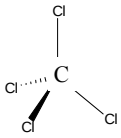
CCl_4 AB_4 type



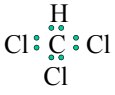
SN=4

4 clouds on CA; only central atom's electron pairs needed. Equivalent bonds. Perfectly symmetric.
epg: tetrahedral $\angle$ Cl C Cl = 109.5^{O}
molecular geometry: tetrahedral





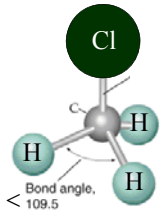
$CHCl_3$ AB_4 type



SN=4

4 clouds on CA; All bonds (clouds) non-equivalent.
epg: tetrahedral
molecular geometry: tetrahedral

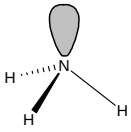
CH_3Cl



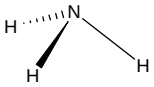
NH_3 AB_3E type

SN=4

4 clouds on CA; electron pairs non-equivalent.
epg: tetrahedral
molecular geometry: trigonal pyramid



Electron cloud geometry



Molecular geometry

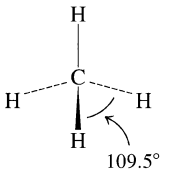
H_2O AB_2E_2 type

SN=4

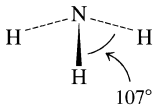
4 clouds on CA; electron pairs non-equivalent.
epg: tetrahedral
molecular geometry: bent

Electron Pair Repulsions

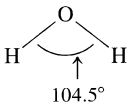
- Electron Pair Repulsion Order:
  - Lone pair—Lone pair = greatest repulsion.
  - Lone pair—Bonding pair is next.
  - Bonding pair—Bonding pair = least repulsion.
    - » Double bonds exert more repulsion than single bonds.
- Bond angles around central atom decrease as repulsive forces increase.



Tetrahedral



Trigonal pyramid

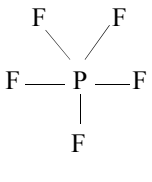


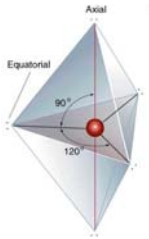
Bent

NOTE THE LONE PAIRS and bond angles

Note: Bond angles decrease as number of lone pairs increases.

PF_5 AB_5 type

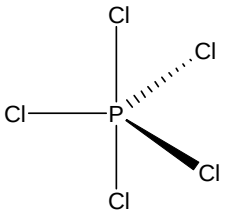




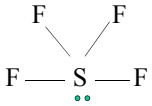
SN=5

5 clouds on CA; All bonds equivalent.
epg: trigonal bipyramid
molecular geometry: trigonal bipyramid

PF_5

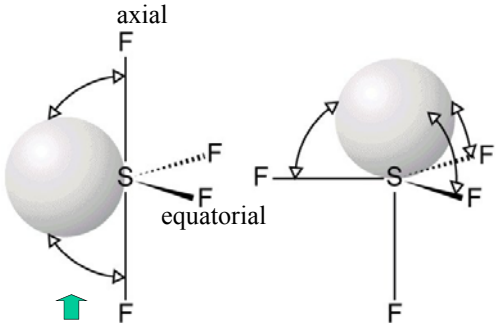


SF_4 AB_4E type



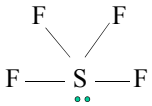
SN=5

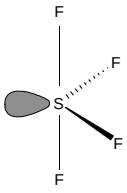
5 clouds on CA; electron pairs non-equivalent.
epg: trigonal bipyramid



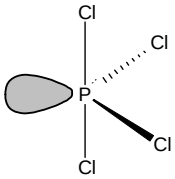
Less strong repulsions
more stable - l-p on axial position preferred

SF_4

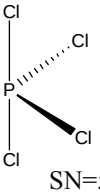




5 clouds on CA; electron pairs non-equivalent.
Place lone pair at equatorial position.
electron pair geometry: trigonal bipyramid
molecular geometry: seesaw



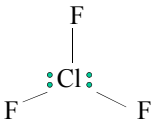
Electron pair geometry

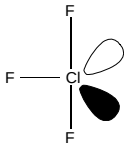


SN=5

Molecular geometry

ClF_3 AB_3E_2 type

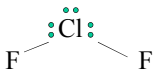


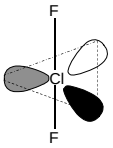


SN=5

5 clouds on CA; electron pairs non-equivalent.
epg: trigonal bipyramid
molecular geometry: T-shaped *

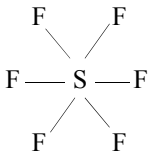
ClF_2^- AB_2E_3 type

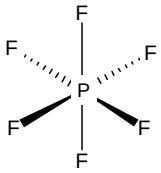




5 clouds on CA; electron pairs non-equivalent.
epg: trigonal bipyramid
molecular geometry: linear, bonds axial *

SF_6 AB_6 type

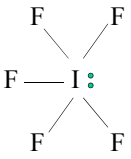




SN=6

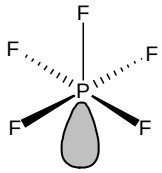
6 clouds on CA; All bonds equivalent.
epg: octahedral
molecular geometry: octahedral *

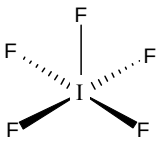
IF_5 AB_5E type



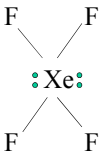
SN=6

6 clouds on CA; electron pairs non-equivalent.
epg: octahedral
molecular geometry: square pyramid *



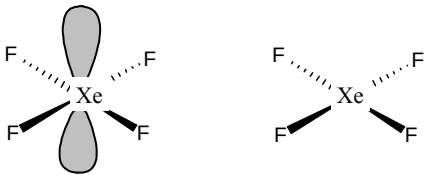


XeF_4 AB_4E_2 type



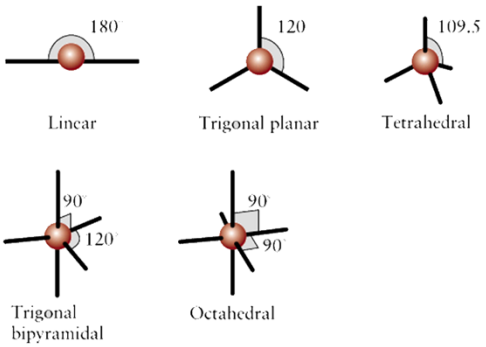
SN=6

6 clouds on CA; electron pairs non-equivalent.
epg: octahedral
molecular geometry: square planar *

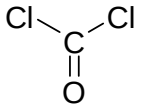


The *electron pair structure* is determined by the bonded and non-bonded 'pairs' of electrons.

The name of the molecular *structure type*, however, *disregards* the *lone pair* electrons.

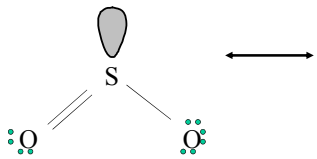


Distortions from 'ideal' geometries,



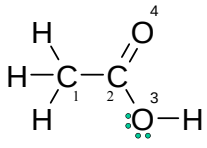
C=O is a double bond (carries more electrons).
Repulsions between C=O and C-Cl larger than C-Cl and C-Cl.
$\angle$ Cl C O > 120^{O}, $\angle$ Cl C Cl < 120^{O}.

SO_2



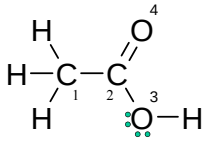
3 clouds on CA; Electron clouds non-equivalent
epg: trigonal planar $\angle$ OSO < 120^{O}
molecular geometry: bent

Many 'central atom' case;

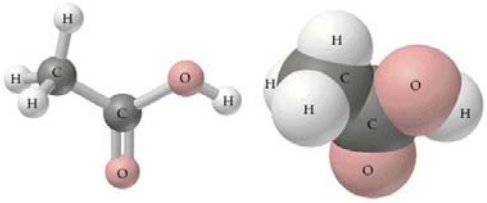


Angles are non-ideal. $\angle$ HCH
$\angle$ HC(1)C(2)
$\angle$ C(1)C(2)O(3)
$\angle$ C(2)O(3)H

Many ‘central atom’ case;

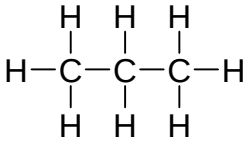


Angles are non-ideal. ∠ HCH ~109
∠ HC(1)C(2) ~109
∠ C(1)C(2)O(3) ~120
∠ C(2)O(3)H ~109

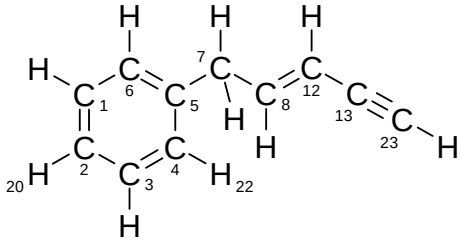


Acetic acid

Propane



*

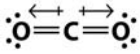


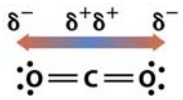
Predict approximate angles.

Polar Bonds and Polar Molecules

Requirements for Polar Molecule:

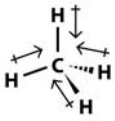
1. Molecule must contain polar bonds (i.e., covalent bond between atoms with ΔEN).
2. Orientation of polar bonds results in *charge separation* from one part of the molecule to another.

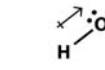




Polar bonds… but linear shape results dipole moments cancelling - nonpolar!

Bond Dipole:
- Separation of charge within a covalent bond.





Dipole of each bond

Polar Molecule:
- Vectors of bond dipoles sum > zero.

Nonpolar

Dipole of molecule

Polar!

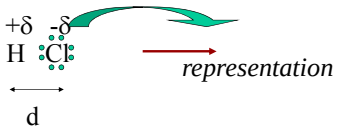
Dipole Moment

Unequal sharing of covalent bond electrons partially shift the electrons to the more en atom.

The partial shift enriches the electron content on the high en atom making a partial negative charge on it (-δ).

The low en atom acquires a +δ charge.

Result: *polar bond*.



The entity with a separation of charges by a length is referred to as a dipole.

Dipole moment $\mu = d\delta$

Measures the polarity; extent of separation of + and − charge centers in a molecule.

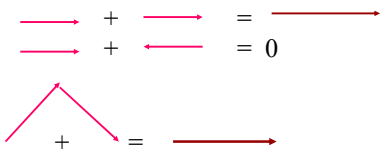
(Units = *debyes* (D); 1 D = 3.34×10^{-30} coul·m)

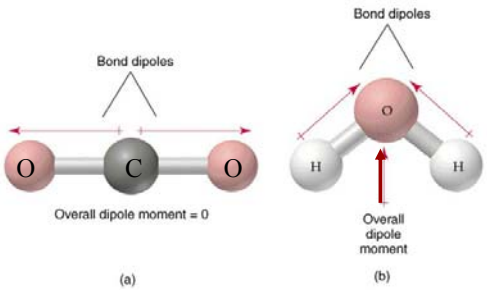
For *polyatomics*, the center of the - δs and the center of the + δs must be considered to determine the dipole moment.

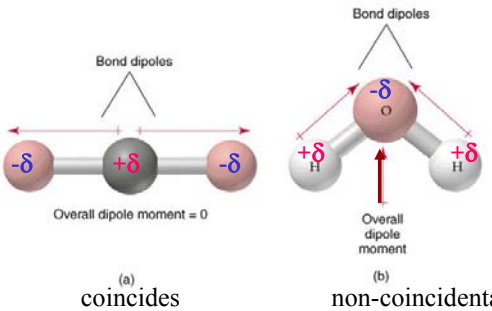
If the charge centers coincide, d = 0, making the molecular μ = 0.

Thus the geometry of the molecule is a very important factor that would determine μ.

To determine the *molecular dipole moment*, first find the bond dipole moments, then add them vectorially.



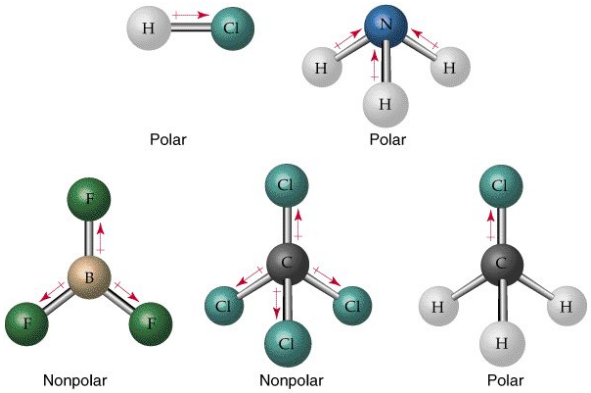




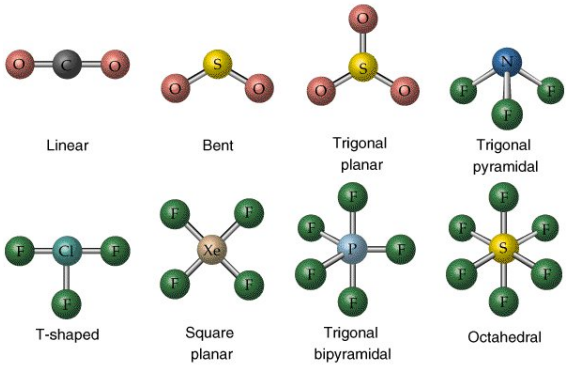
coincides non-coincidental

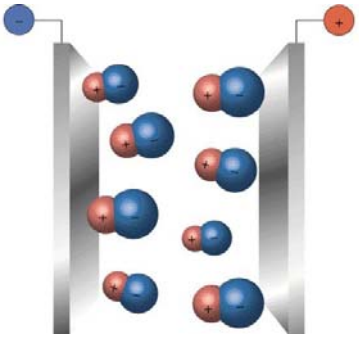
charge centers

What would be the dipole moment of water if ∠HOH = 180°?

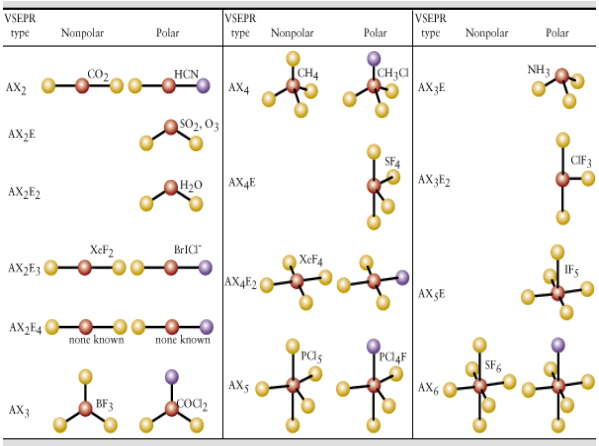


Predict the molecular dipole moments (polarity);





when placed in an electric field, polar molecules align along the field.



Matter exist as solids liquids and gases.

Under a set of conditions (T,P) all matter do exist in one of the above forms.

In solids “entities/particles” are strongly attracted to their immediate neighbors whereas in liquids they are less attracted and in gas phase they are least attracted to one another.

The degree of such attractions are manifested in their melting and boiling points and volatility.