Chemical Bond

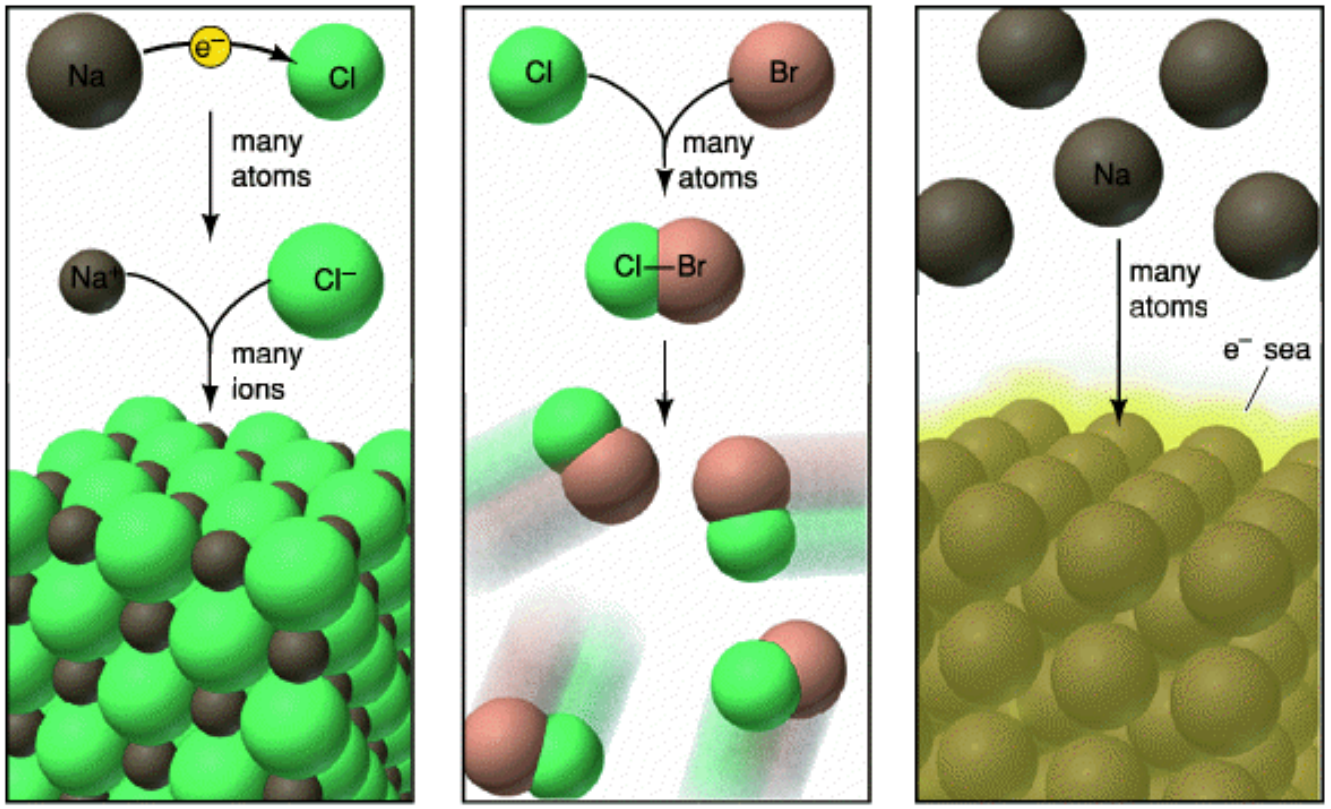
Reason for bonding between atoms = a **lower total energy** of bound atoms than the sum of energies of sepatated atoms

Mechanism of bond formation = sharing, transfer, and redistribution of **valence electrons**

- Model of **localized** electron **pairs** (Lewis, VB, VSEPR, hybridization)
- Model of **delocalized** electrons (MO)

Chemical Bond

Ionic Covalent Metallic



A Ionic bonding **B** Covalent bonding **C** Metallic bonding

Types of Chemical Bond

Covalent = sharing of electrons (e pairs, 1e H_2^+) by several atoms (2, 3, 4....), three-center-two-electron bonds

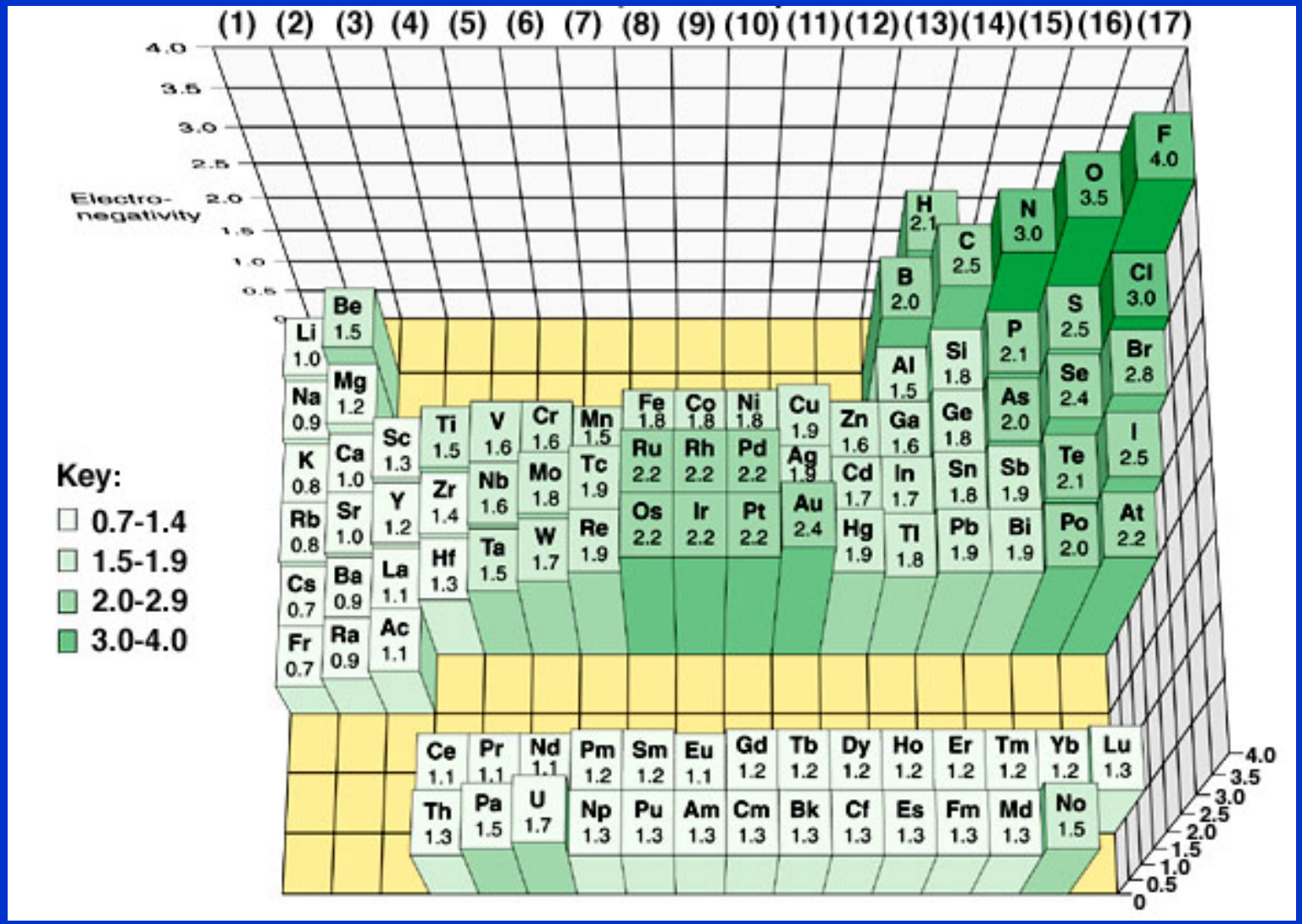
Metallic = sharing of electrons among many atoms, band theory

Ionic = transfer of electrons, formation of ions, Coulombic attractive forces between oppositely charged ions

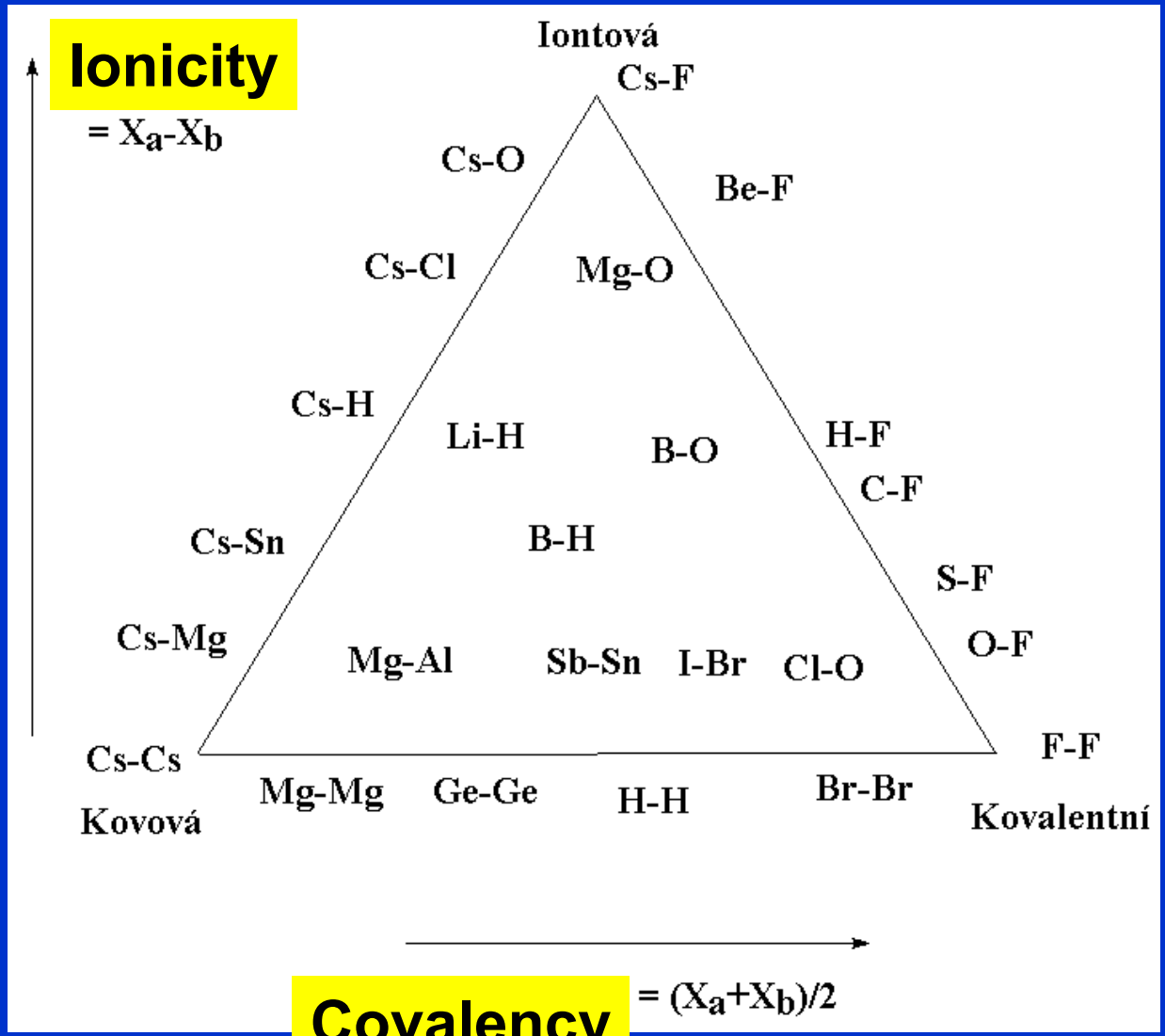
Van der Waals = Coulombic attractive forces between temporary charges (dipoles)

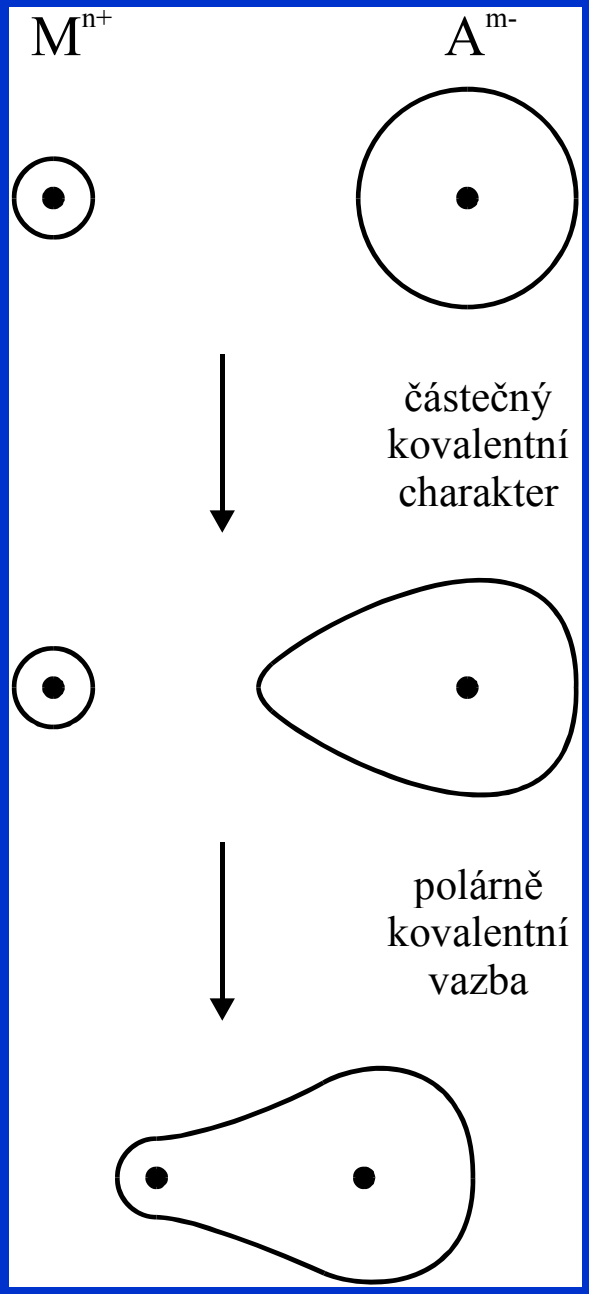
Topological = mechanical joining of molecules (rotaxenes, catenanes, carcerands)

Pauling's Electronegativities



Van Arkel Triangle



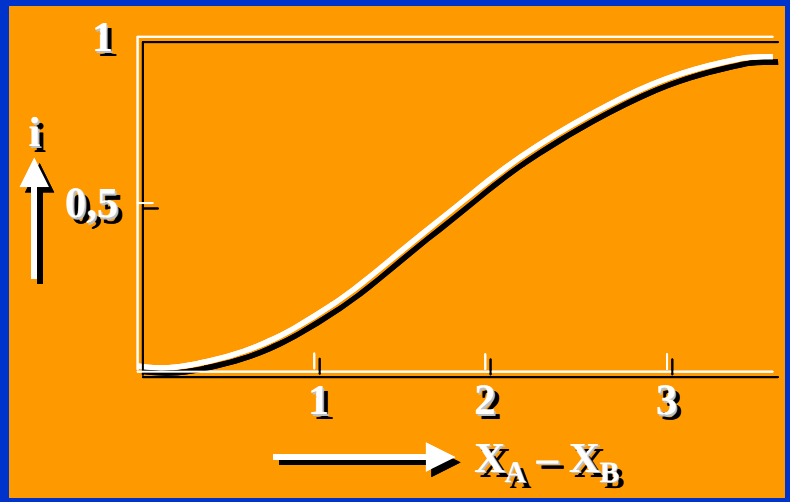


Smooth transition between ionic and covalent extremes

$\Delta\chi = (\chi_A - \chi_B)$

Bond Ionicity

$i = 1 - \exp[-0.21(\chi_A - \chi_B)^2]$



ionic

covalent

Ionic and Covalent Bond

LiCl > NaCl > KCl > RbCl > CsCl

Covalency incr.

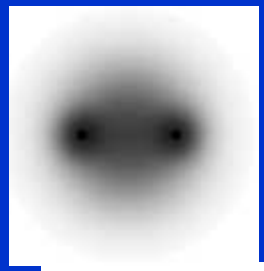
NaI > NaBr > NaCl > NaF

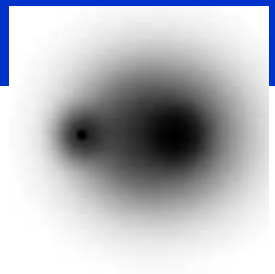
Covalency incr.

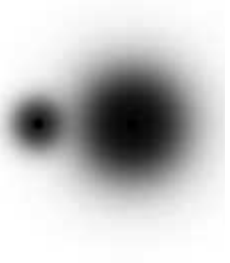
AlN > MgO > NaF

Ionicity incr.

Ionic and Covalent Bond



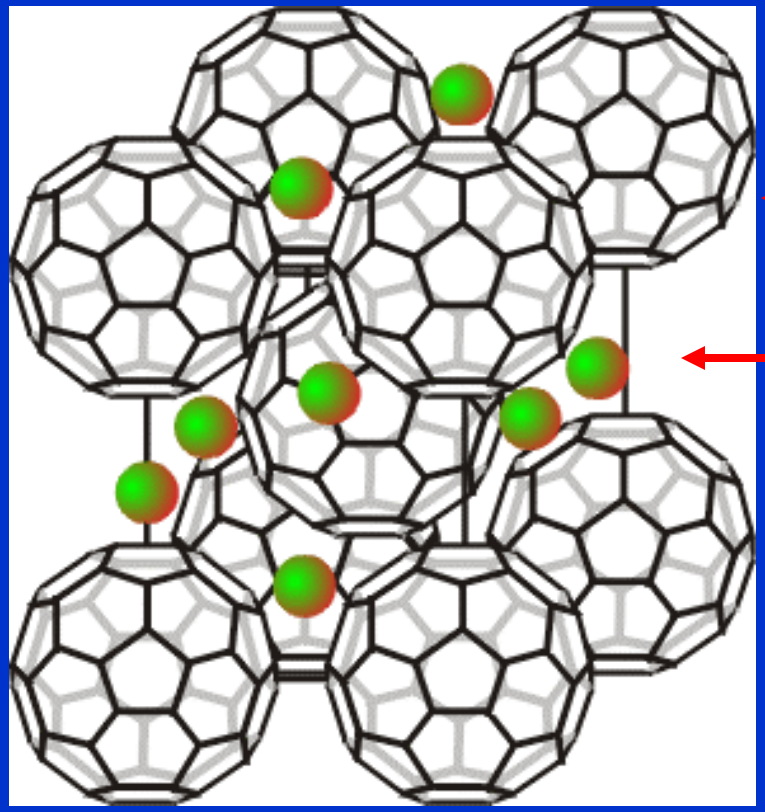




$$\Delta\chi = (\chi_A - \chi_B)$$

Ionic and Covalent Bond

K_3C_{60}

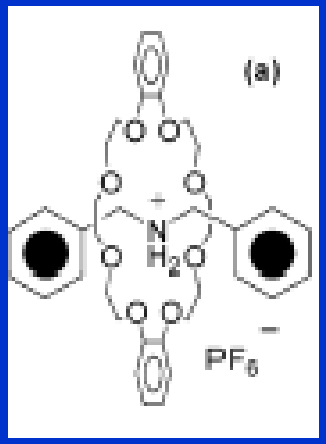


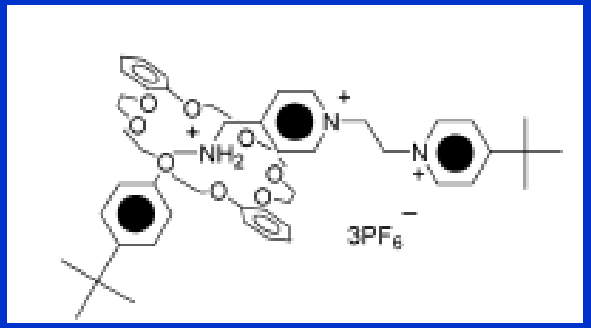
Covalent

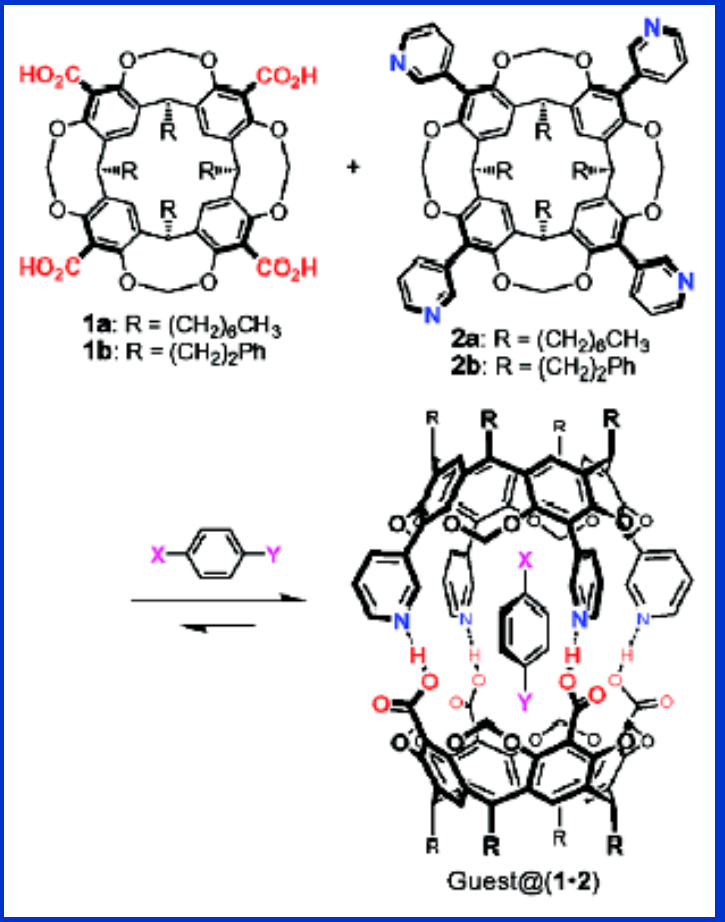
Ionic

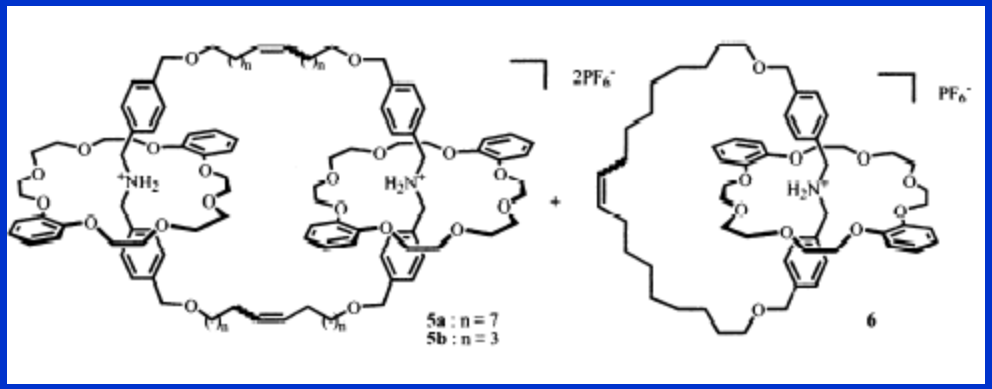
K^+ and $(C_{60})^{3-}$

Topological Bond
rotaxenes, catenanes, carcerands





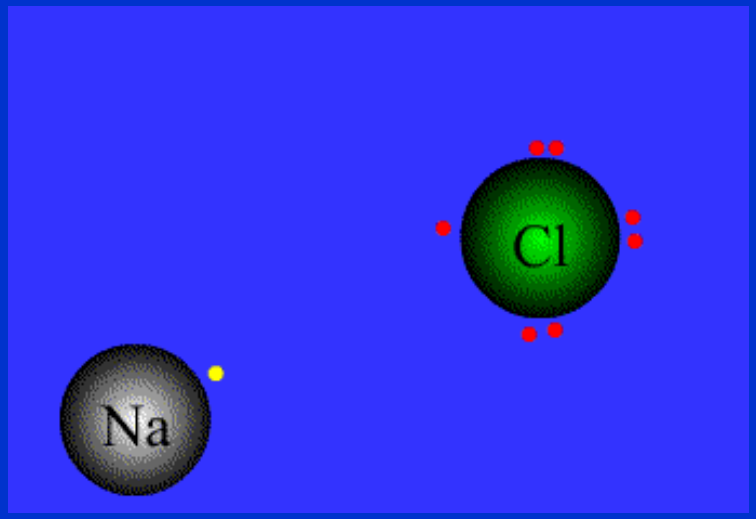




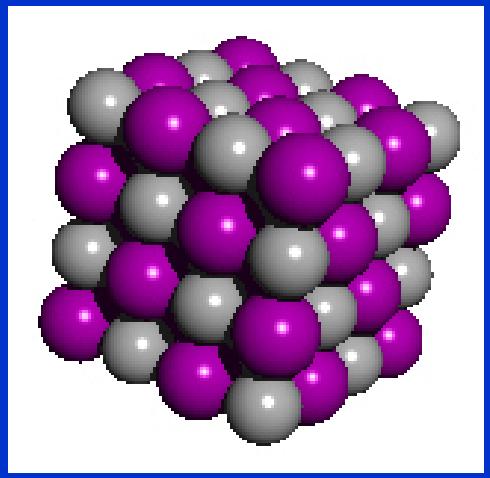
Ionic Bond

$Na(s) + ½\ Cl_2(g) \rightarrow NaCl(s)$ **$\Delta H^0_f = -410.9\ kJ\ mol^{-1}$**

exothermic reaction heat



Octet formation for both Na^+ and Cl^-



- There is no NaCl molecule
- NaCl is a formula unit
- Infinite lattice of ordered cations and anions

Lattice Energy, L

Lattice Energy = energy released upon formation of one mole of solid from ions in the gas phase

Coulombic attractive force b/w 2 ions

$$F = \frac{1}{4\pi\varepsilon_0}\frac{Z_+ Z_- e^2}{r^2}$$

Z = ion charges
r = distance

Lattice Energy L [kJ mol^{-1}]
Coulombic attractive and repulsive forces in 1 mole of ions

$$L = N_A M \frac{Z_+ Z_- e^2}{4\pi\varepsilon_0 r}$$

M = Madelung constant
Accounts for lattice geometry
(NaCl, CsCl, CaF_2, ZnS,....)

Lattice Energies of Alkali Metal Halides

L [kJ mol^{-1}]	F	Cl	Br	I
Li	1037	862	785	729
Na	918	788	719	670
K	817	718	656	615
Rb	784	694	634	596
Cs	729	672	603	568

$$L = N_A M \frac{Z_+ Z_- e^2}{4\pi\varepsilon_0 r} \approx k \frac{Z_+ Z_-}{r}$$

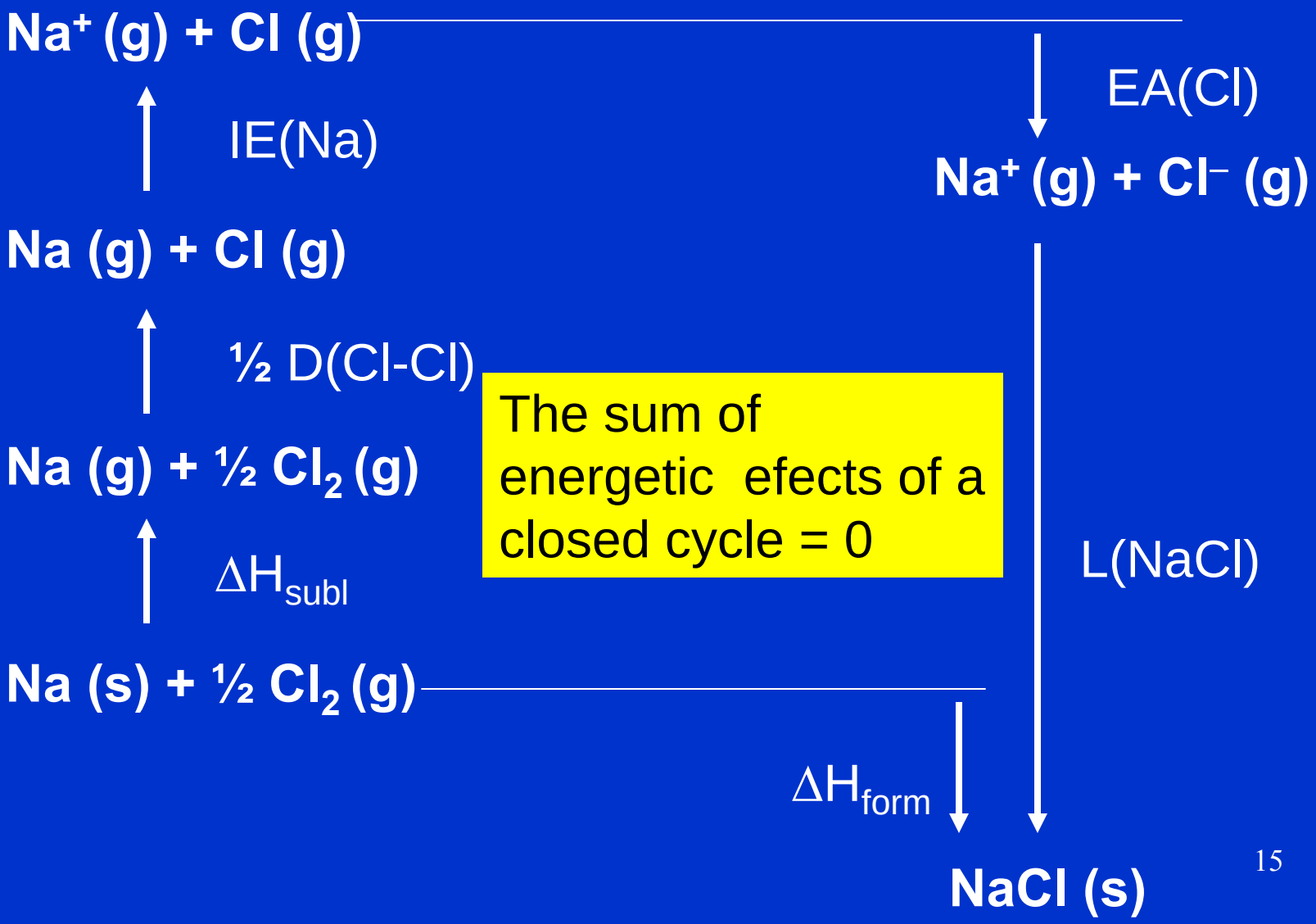
Lattice Energy and Physical Properties

	L [kJ mol^{-1}]	T_m [^{0}C]		L [kJ mol^{-1}]	T_m [^{0}C]
NaF	913	996	KF	808	857
NaCl	778	801	KCl	703	770
NaBr	737	747	KBr	674	742
NaI	695	660	KI	636	682

$$L \approx k \frac{Z_+ Z_-}{r}$$

	L [kJ mol^{-1}]	T_m [^{0}C]	Mohs
$MgCl_2$	2326	714	-
MgO	3920	2642	6.0
CaO	3513	2570	4.5
SrO	3283	2430	3.5
BaO	3114	1925	3.3
ScN	7547	-	-

Born–Haber Cycle

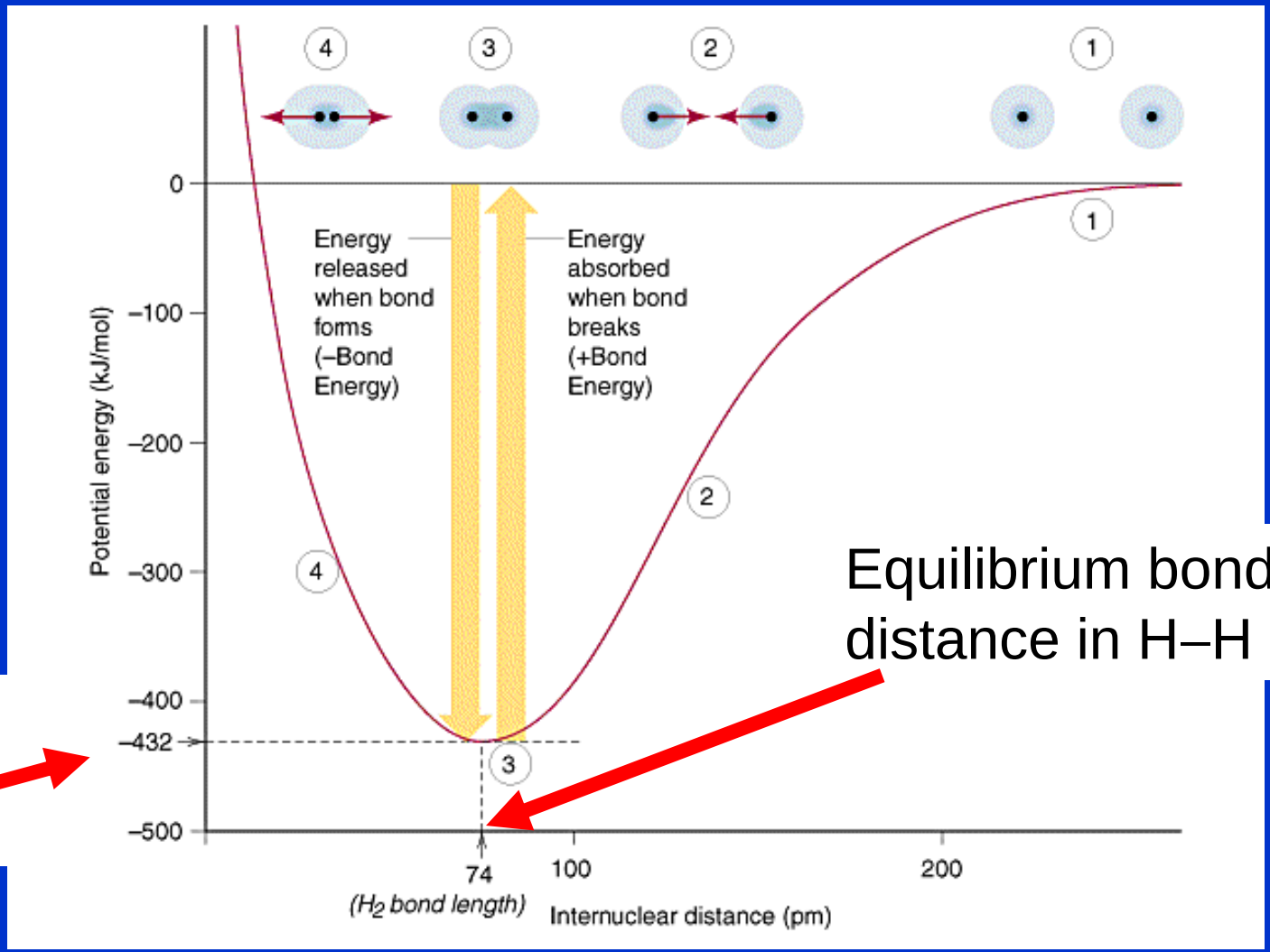


Born–Haber Cycle

$Na(s) \rightarrow Na(g)$	$\Delta H_{subl} = 107.3$ kJ mol^{-1}
$\frac{1}{2}\ Cl_2(g) \rightarrow Cl(g)$	$\frac{1}{2}$ D(Cl-Cl) = 122 kJ mol^{-1}
$Na(g) \rightarrow Na^+(g) + e^-$	IE(Na) = 496 kJ mol^{-1}
$Cl(g) + e^- \rightarrow Cl^-(g)$	EA(Cl) = –349 kJ mol^{-1}
$Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$	L(NaCl) = –778 kJ mol^{-1}
$Na\ (s) + \frac{1}{2}\ Cl_2\ (g) \rightarrow NaCl(s)$	ΔH_{form} = –401.7 kJ mol^{-1}

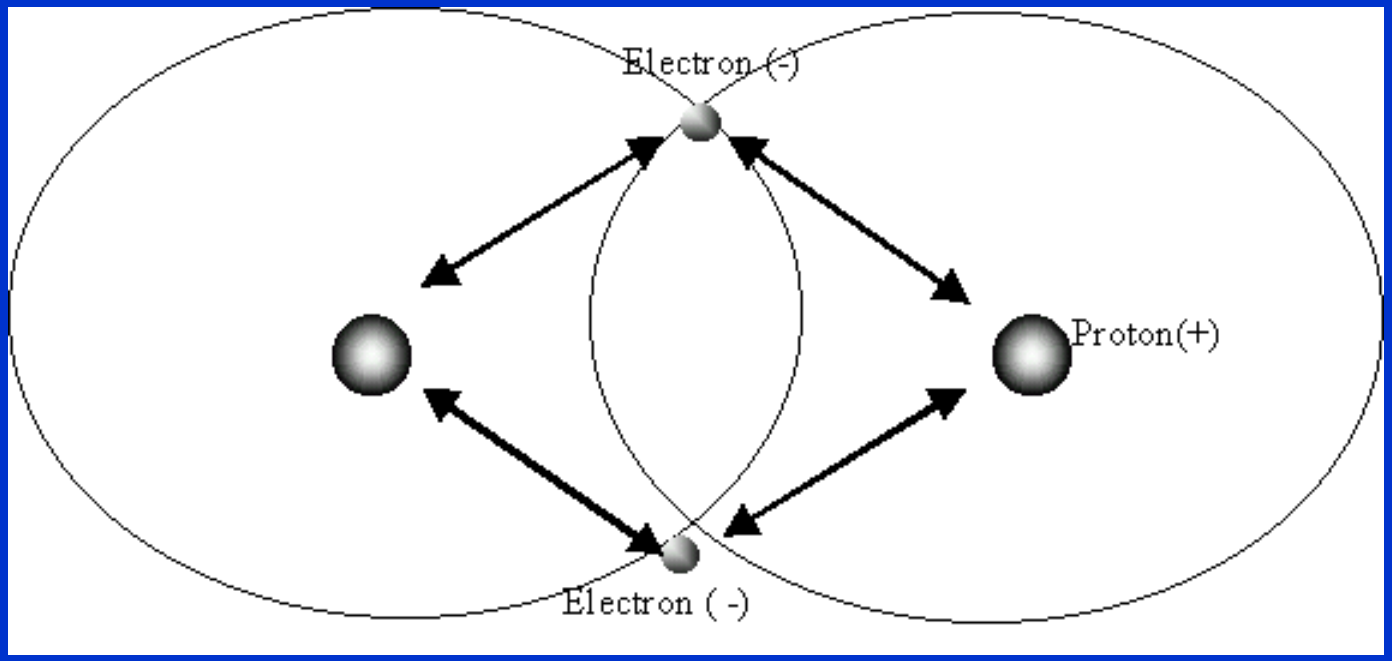
Covalent Bond

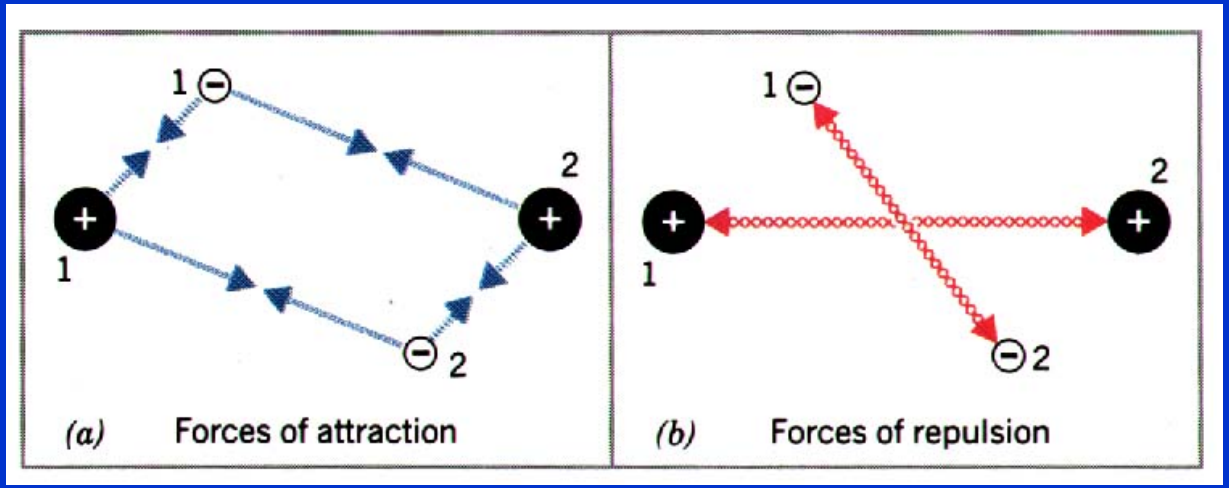
Covalent Bond in H_2

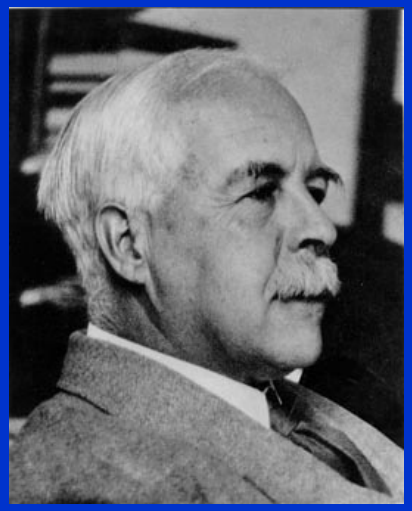


Bonding energy H–H

Equilibrium bonding distance in H–H


Electron (-)
Proton(+)
Electron (-)

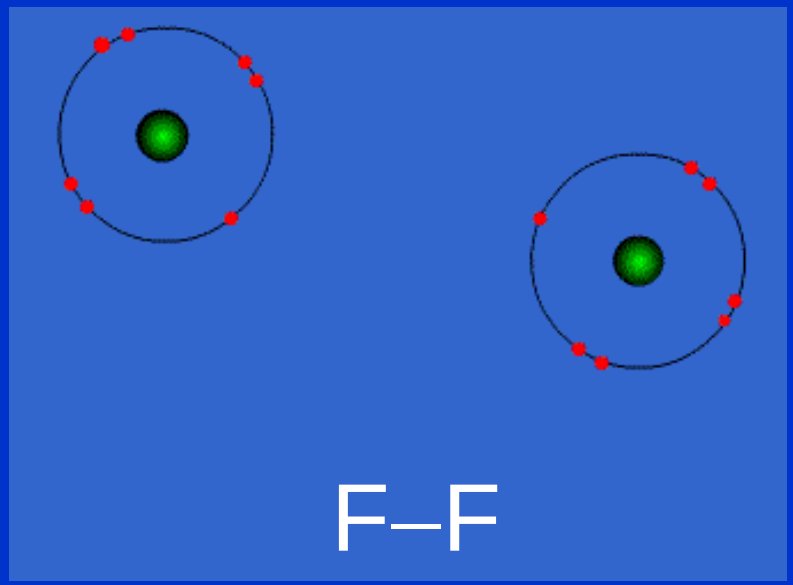

1
2
1
2
(a) Forces of attraction
1
2
1
2
(b) Forces of repulsion

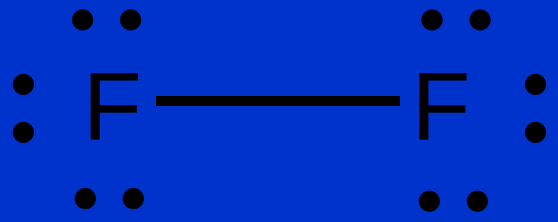


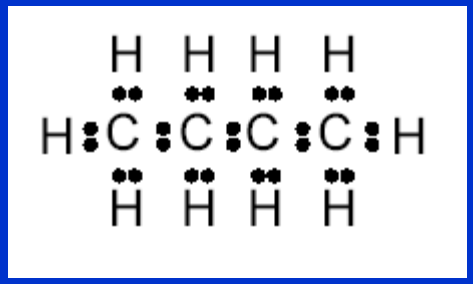
Gilbert N. Lewis
(1875-1946)

Covalent Bond

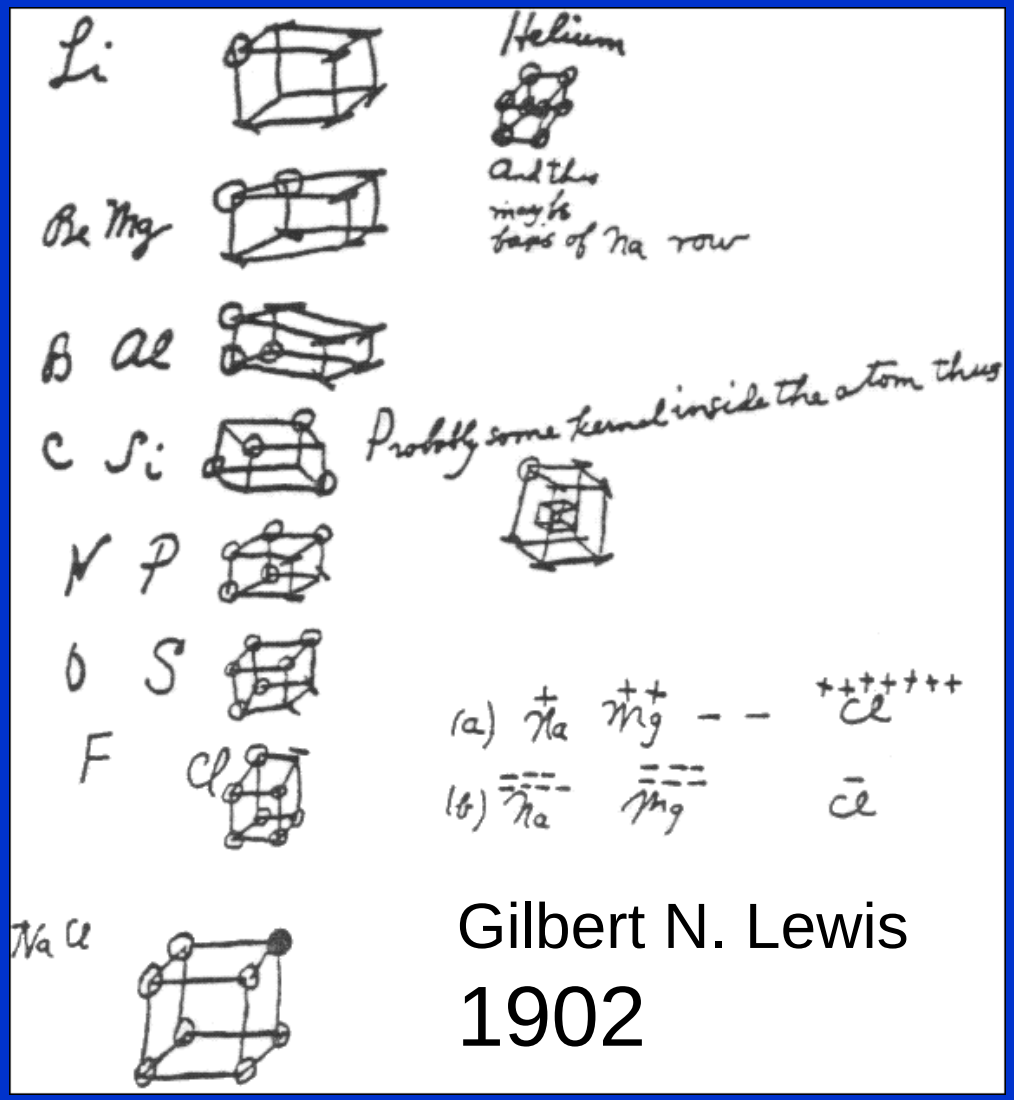
Atoms share electron pairs to attain electronic octet in their valence shell





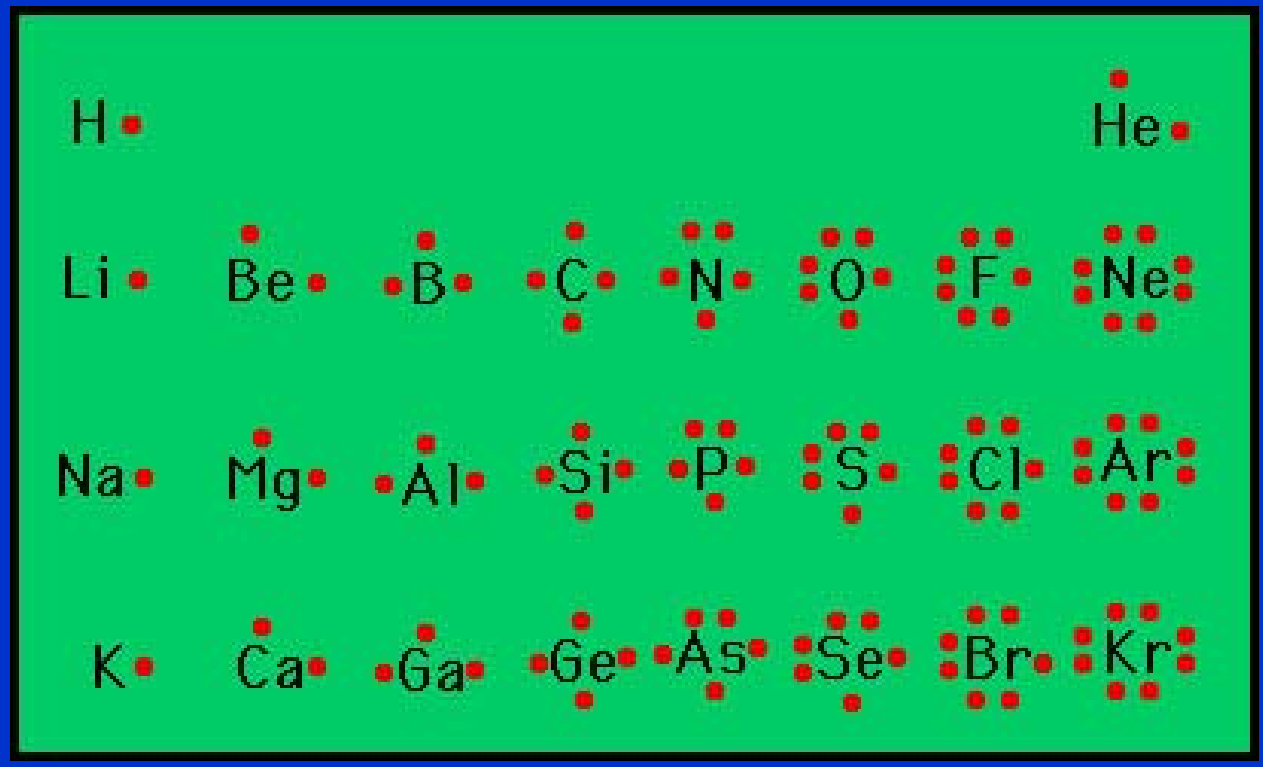


Octet Rule

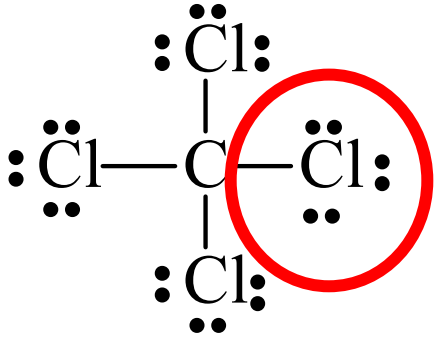


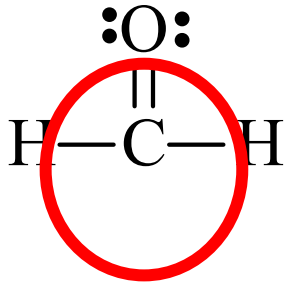
He	$1s^2$
Ne	$[He]\ 2s^2\ 2p^6$
Ar	$[Ne]\ 3s^2\ 3p^6$
Kr	$[Ar]\ 3d^{10}\ 4s^2\ 4p^6$
Xe	$[Kr]\ 4d^{10}\ 5s^2\ 5p^6$
Rn	$[Xe]\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^6$

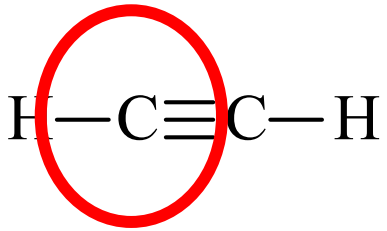
Lewis Structures

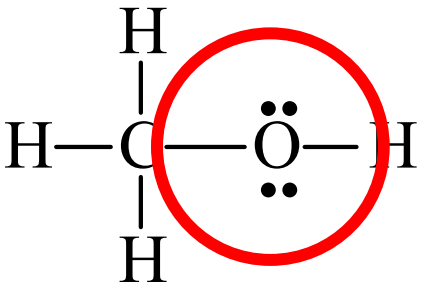


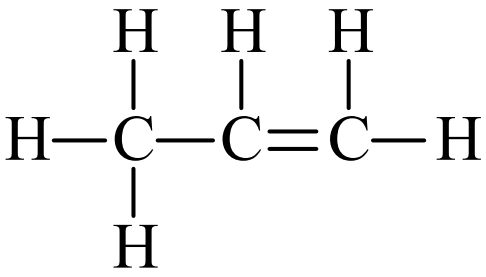
Lewis Structures - Octets

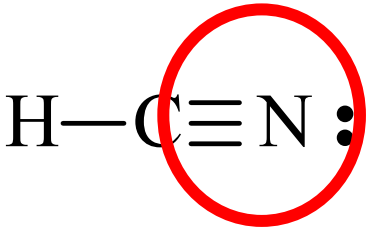








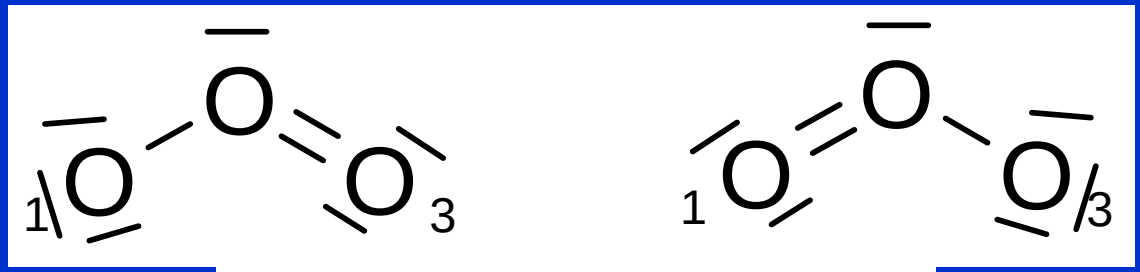


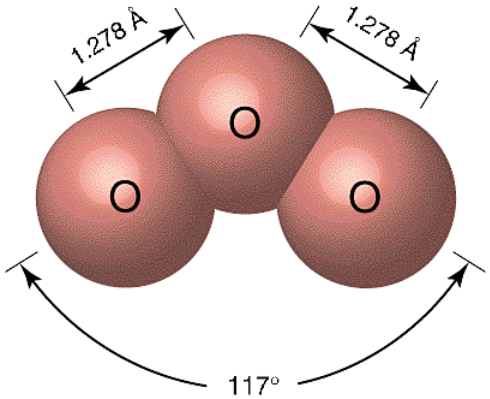


Lewis Resonance Structures

Positions of nuclei are unchanged, move electron pairs

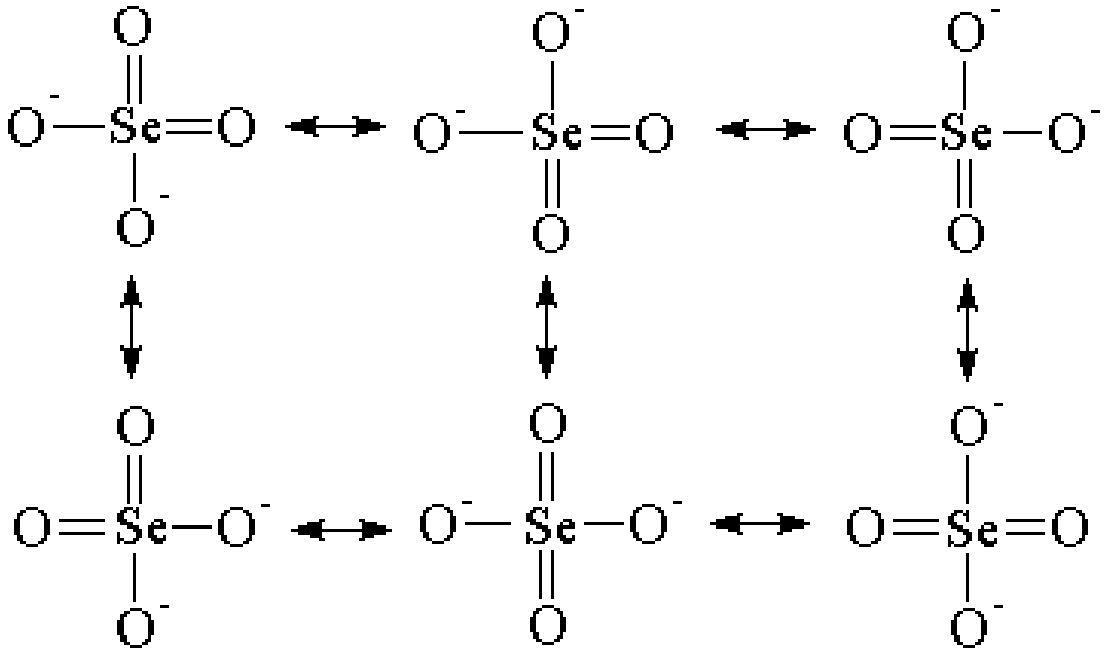
Bonding situation is described by superposition of all resonance structures

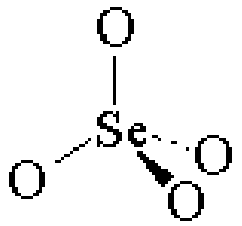




Bond order = 1.5

Lewis Resonance Structures





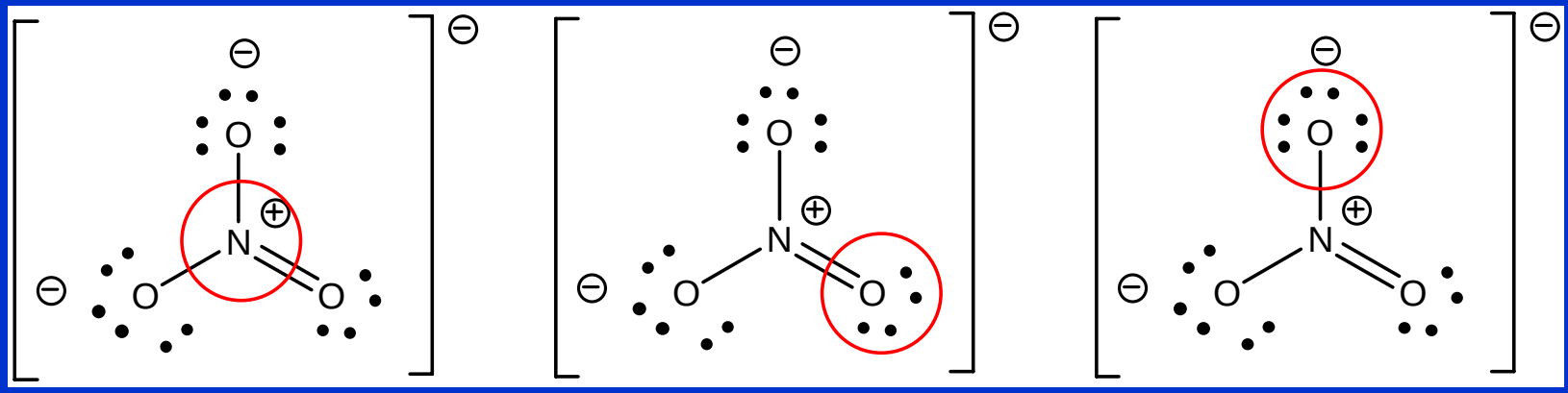
Bond order = 1.5

Charge on O = -0,5

Formal Charge

Oxidation Number = all e moved to more electronegative atom
Formal oxidation number for balancing redox equations
Not a real charge on an atomu

Formal Charge = difference between number of valence electrons on a free atom and valence electrons assigned to an atom in a molecule: free e pairs count full, bonding pairs halved between atoms



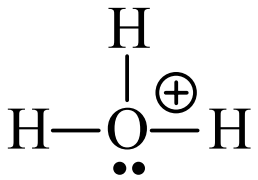
Formal Charge

Atoms strive to attain minimal formal charge, zero at the best

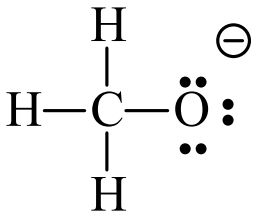
Negative formal charge is placed on **the most electronegative** atom

Sum of formal charges in a molecule (ion) equals **total charge** on a given molecule

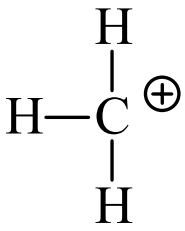
Formal Charge



O: 6 - 5 = +1

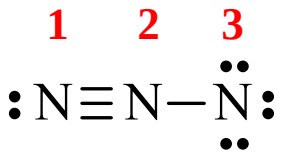


C: 4 - 4 = 0
O: 6 - 7 = -1

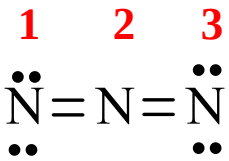


C: 4 - 3 = +1

C: 4 - 5 = -1
O: 6 - 5 = +1

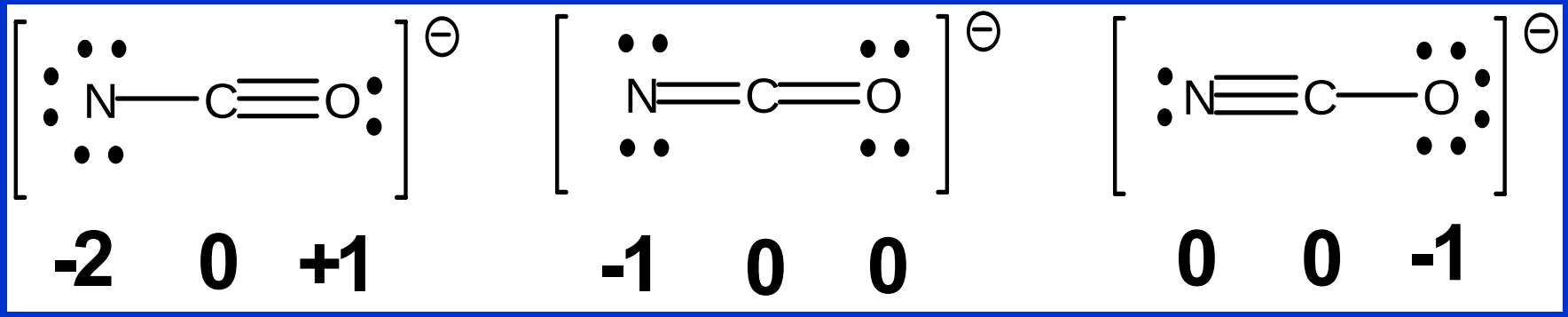


N_1: 5 - 5 = 0
N_2: 5 - 4 = +1
N_3: 5 - 7 = -2



N_1: 5 - 6 = -1
N_2: 5 - 4 = +1
N_3: 5 - 6 = -1

Formal Charge

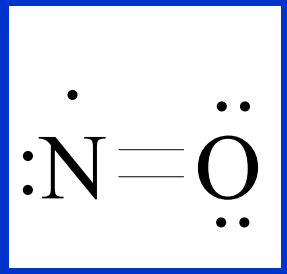


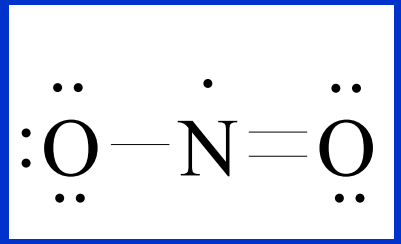
Formal charges too big

THE BEST FORMULA

Negative charge resides on a less electronegative atom

Molecules with Unpaired Electrons

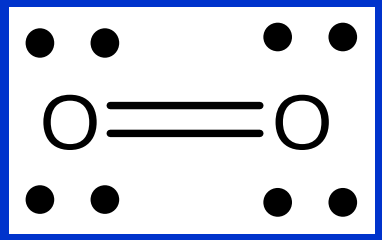




Dimerisation NO_2·

$2\ NO_2\ (g) \rightleftarrows N_2O_4\ (g)\quad K_c = 210$

?



O_2

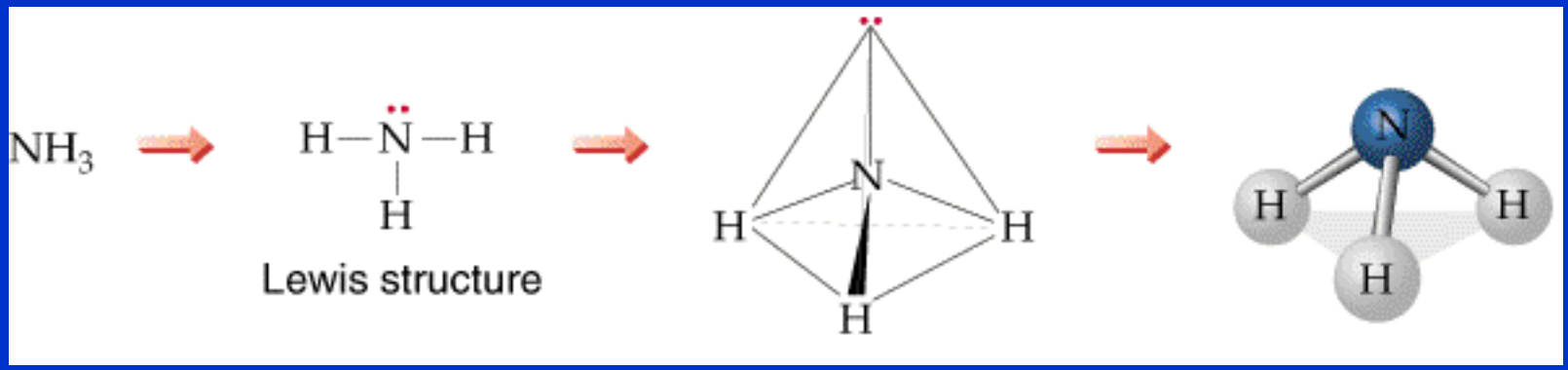
Paramagnetic molecule = Unpaired electrons

= Lewis structures insufficiently describe real situation → delocalized e

VSEPR Model

VSEPR = valence shell electron repulsion

Empirical set of rules to predict shapes of coordination sphere of atoms and thus the molecular shape (also ions and molecular fragments) for main group elements and transition metals with electron configuration d^0 or d^{10}.



VSEPR Model

Molecule = central atom + ligands + free electron pairs

Ligands = atoms or groups

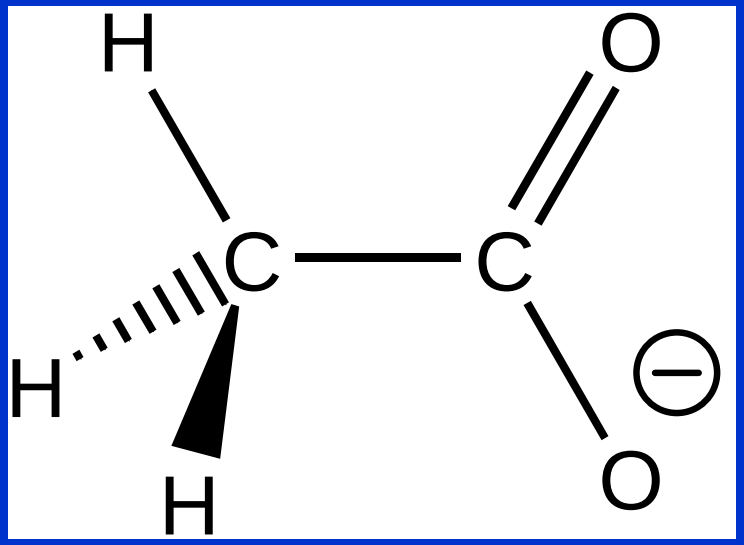
Ligands have usually higher electronegativity than the central atom (except H or metals)

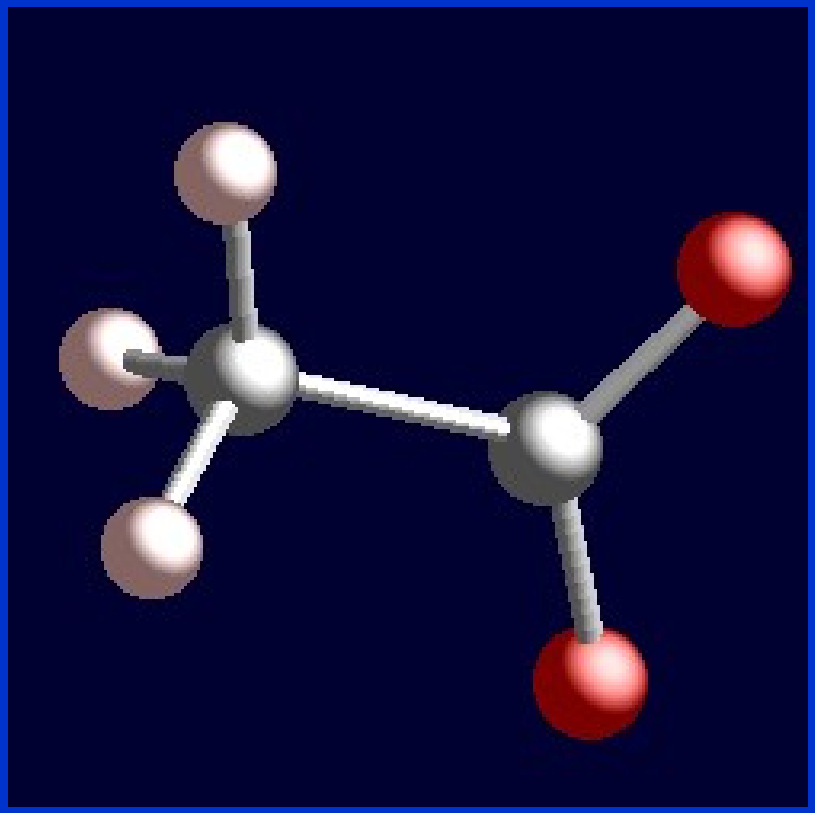
Valence electrons are arranged in pairs:

- Bonding electron pairs
- Free electron pairs (nonbonding)

Central Atom vs. Ligand

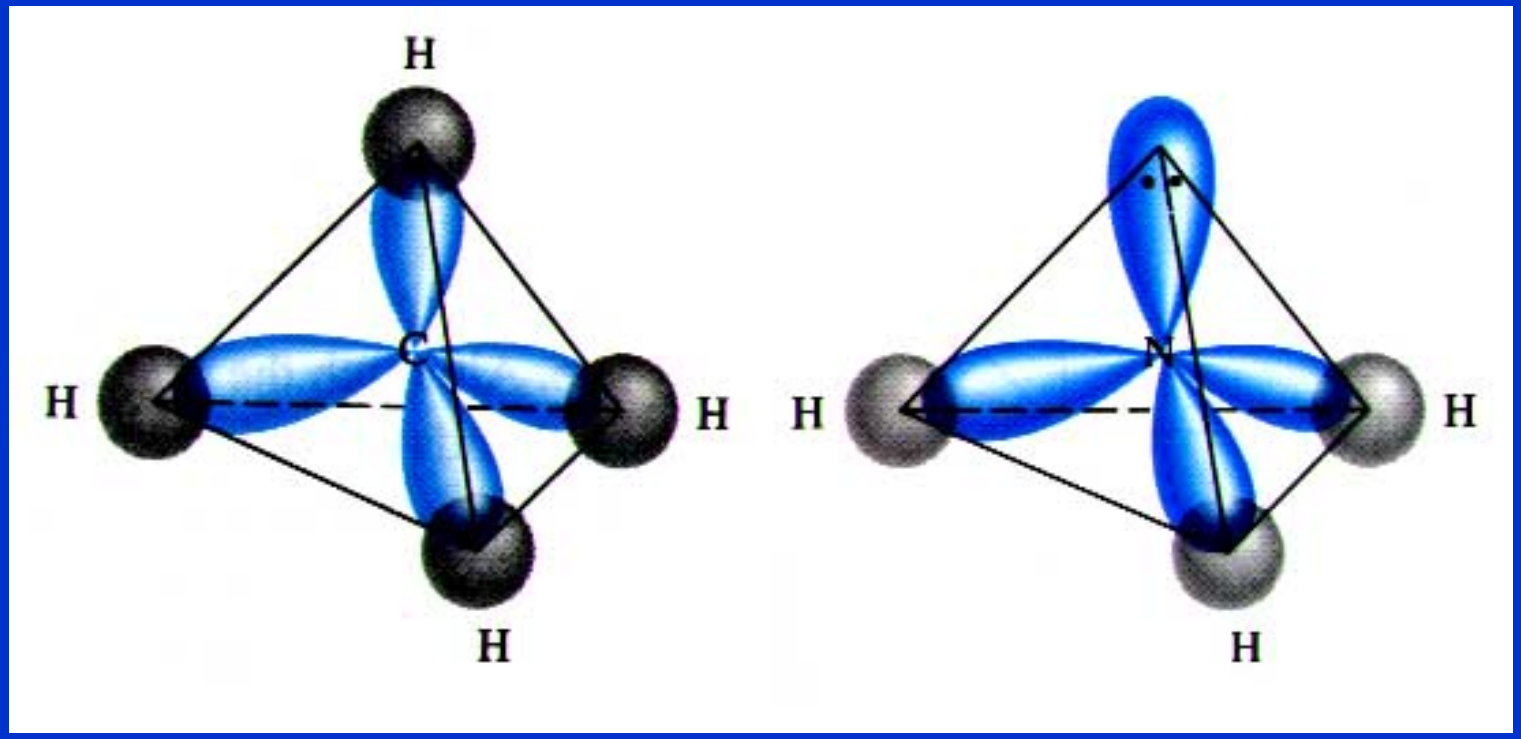
CH_3COO^-





VSEPR Model

Basic shape of coordination sphere of an atom is given by the number of occupied **domains**
= number of bonds (disregarding multiplicity)
+ number of free electron pairs



VSEPR Model

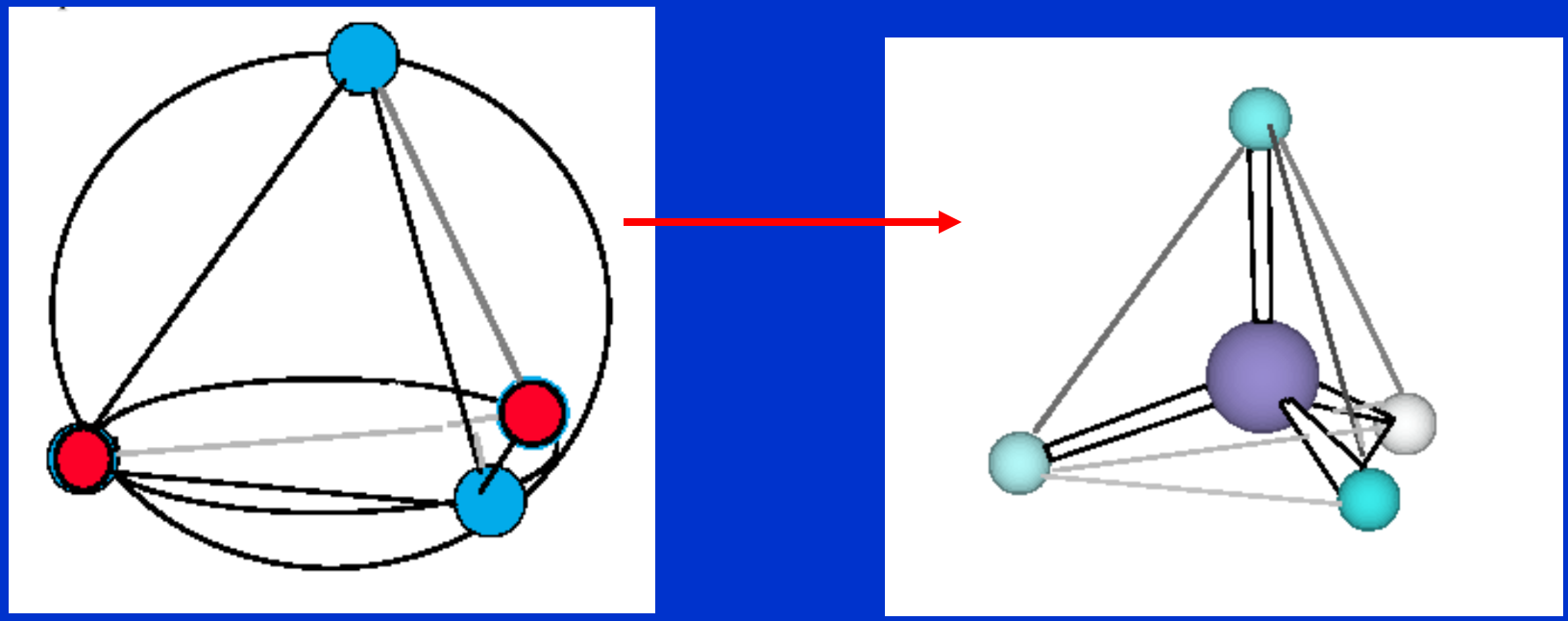
Each electron pair occupies part of space around the central atom and excludes (repels) other electrons
= Pauli exclusion principle

Electron pairs arrange themselves around the central atom **so that they are as far as possible from each other** to minimize repulsion

Free electron pairs occupy **larger** space around the central atom than **bonding** electron pairs

FREE > BONDING

Tetrahedral Molecule of Methane CH_4



Place 4 points on a sphere, so that their distances are maximum $\rightarrow$ tetrahedron

VSEPR Model

Free electron pairs and bonding electron pairs arrange around the central atom to minimize total energy by minimizing repulsion :

Central atom	+ 2 ligands	linear
Central atom	+ 3 ligands	equilateral triangle
Central atom	+ 4 ligands	tetrahedron
Central atom	+ 5 ligands	trigonal bipyramidal or square pyramidal
Central atom	+ 6 ligands	octahedral
Central atom	+ 7 ligands	pentagonal bipyramidal

VSEPR

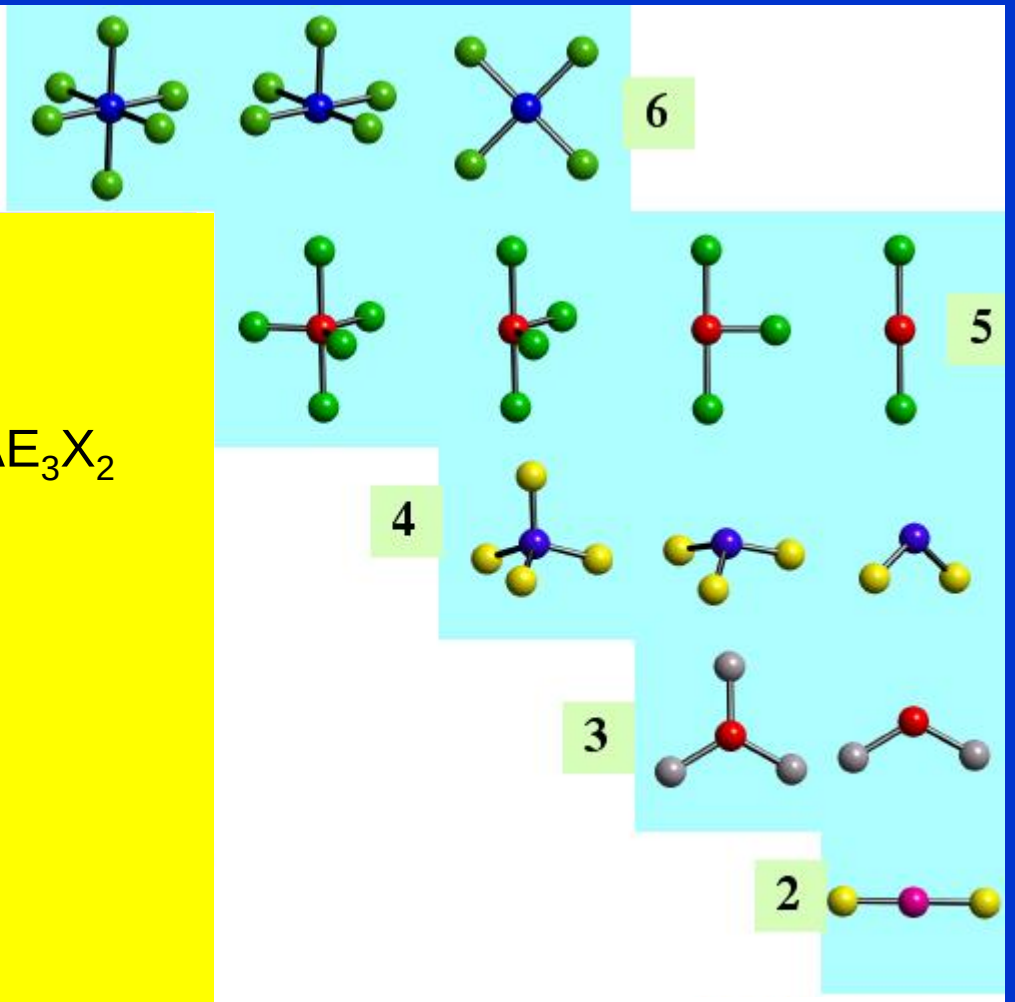
AX_6 AEX_5 AE_2X_4

AX_5 AEX_4 AE_2X_3 AE_3X_2

AX_4 AEX_3 AE_2X_2

AX_3 AEX_2

AX_2



VSEPR Model

Final molecular shape = **positions of nuclei**
(disregard the free electron pairs)

The volume of space around the central atom occupied by electron pairs decreases:

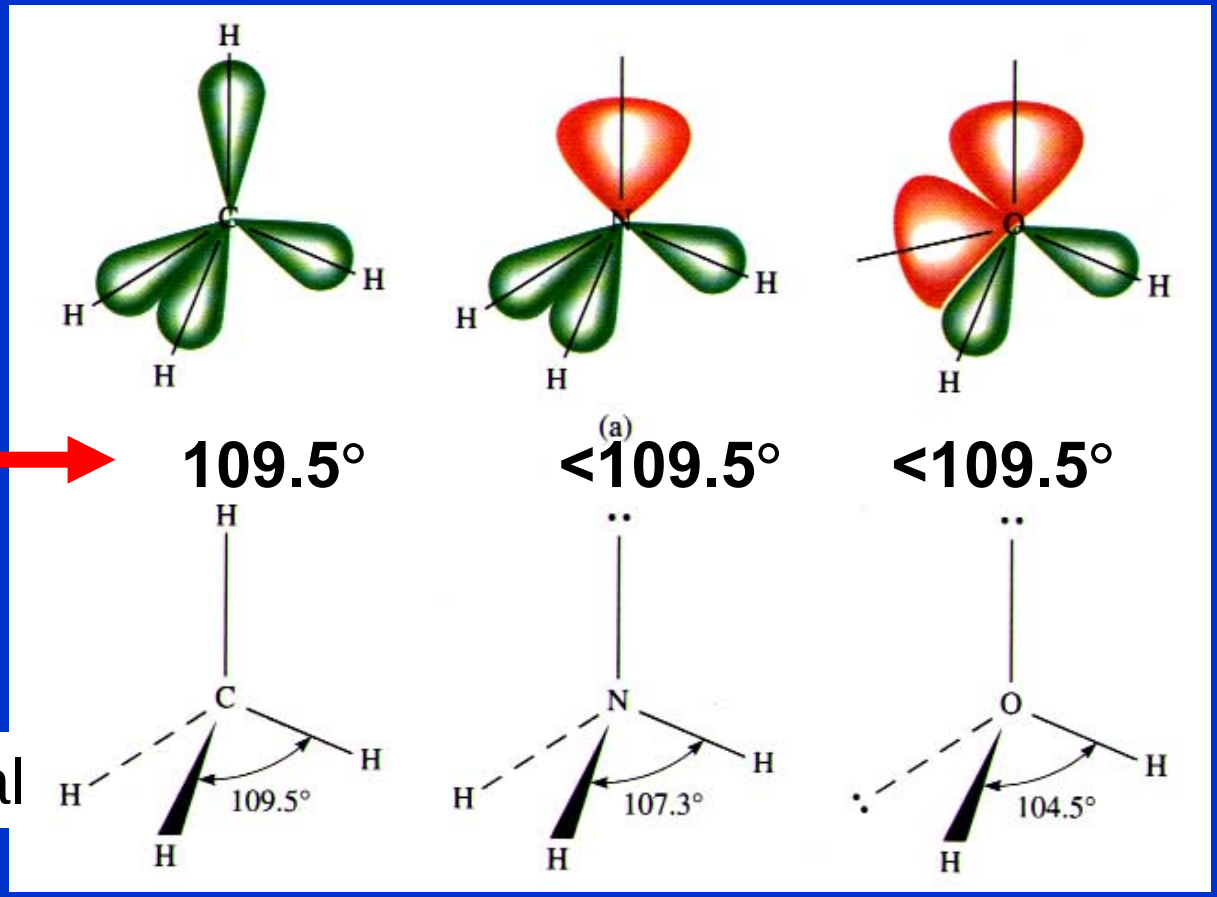
triple > double > single bond

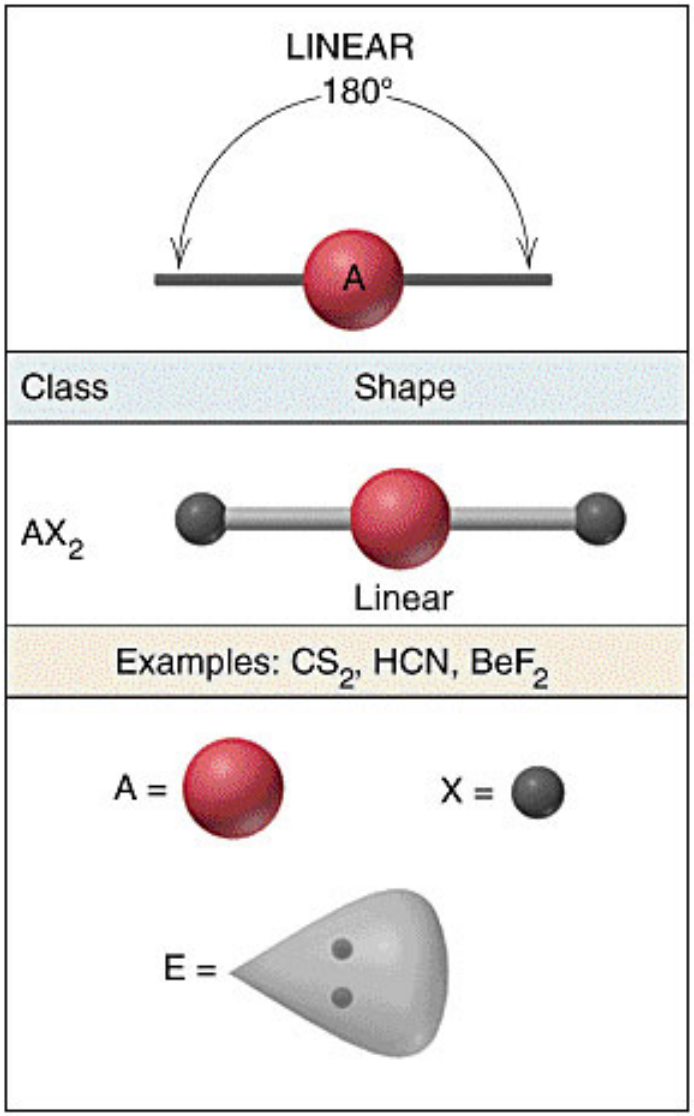
Repulsion among electron pairs decreases:

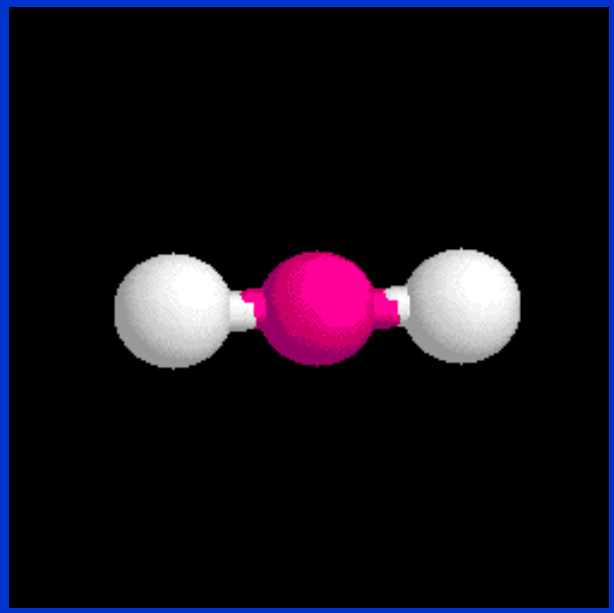
free - free > free - bonding > bonding - bonding

Deformation of Bond Angles

VSEPR model predicts deformation of bond angles from ideal values – but not an actual value

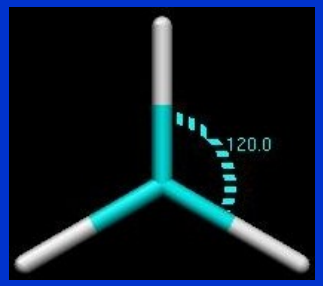


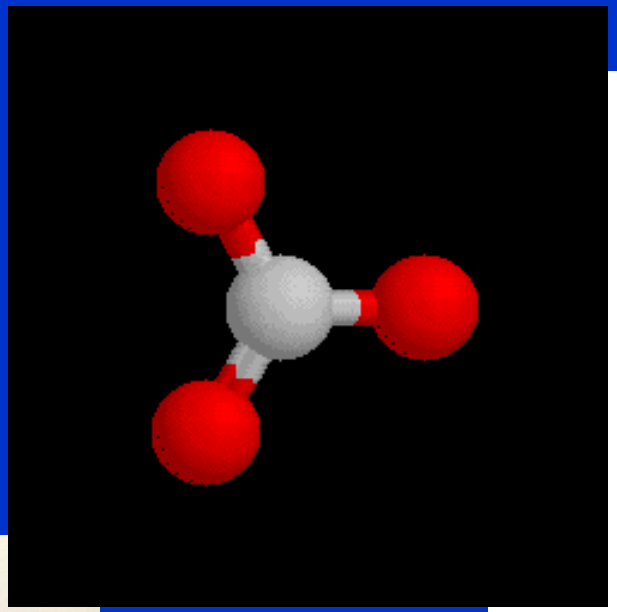




AX_2

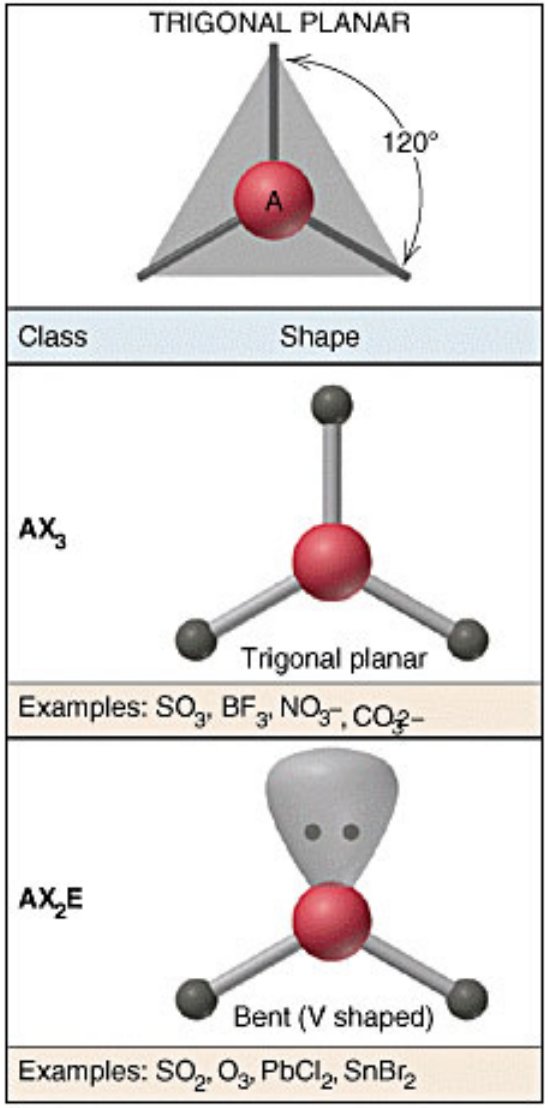
Bond Angle = 180°



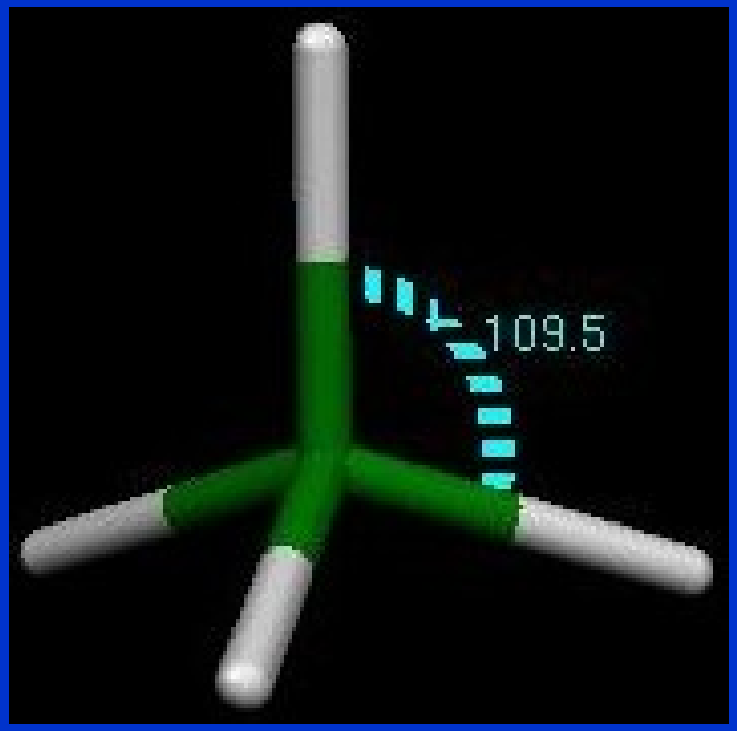


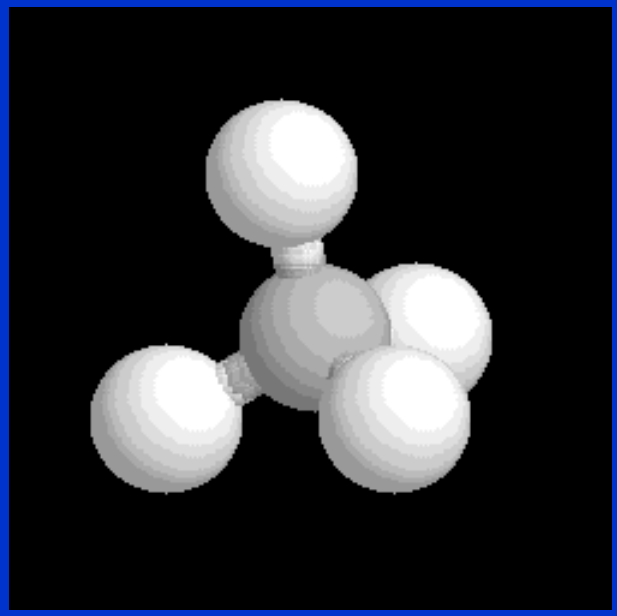
AX_3 : Bond Angle = 120°

AEX_2 : Bond Angle < 120°



Tetrahedral Bond Angle

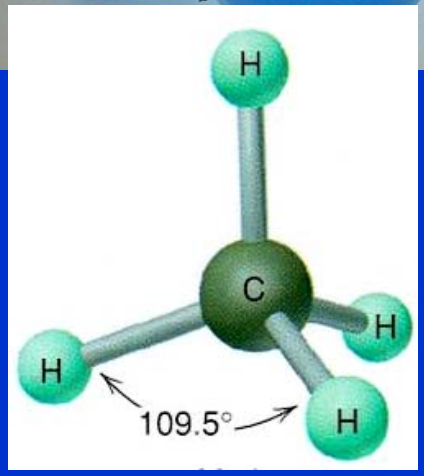




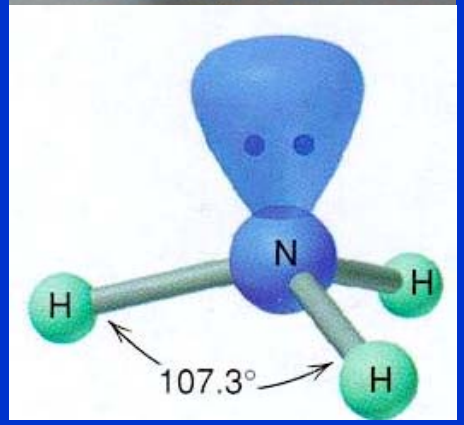
AX_4

Tetrahedral Bond Angle = 109.5°

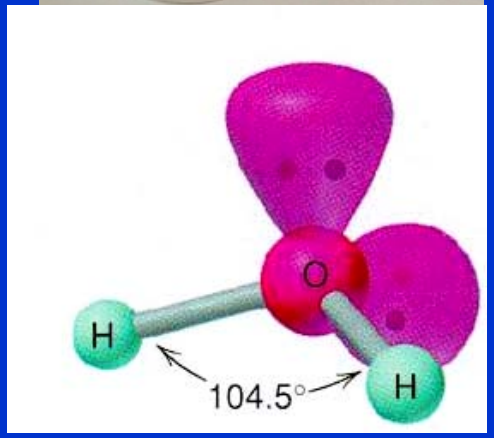
Deformation of Bond Angles



Tetrahedral



Trigonal pyramidal



Bent

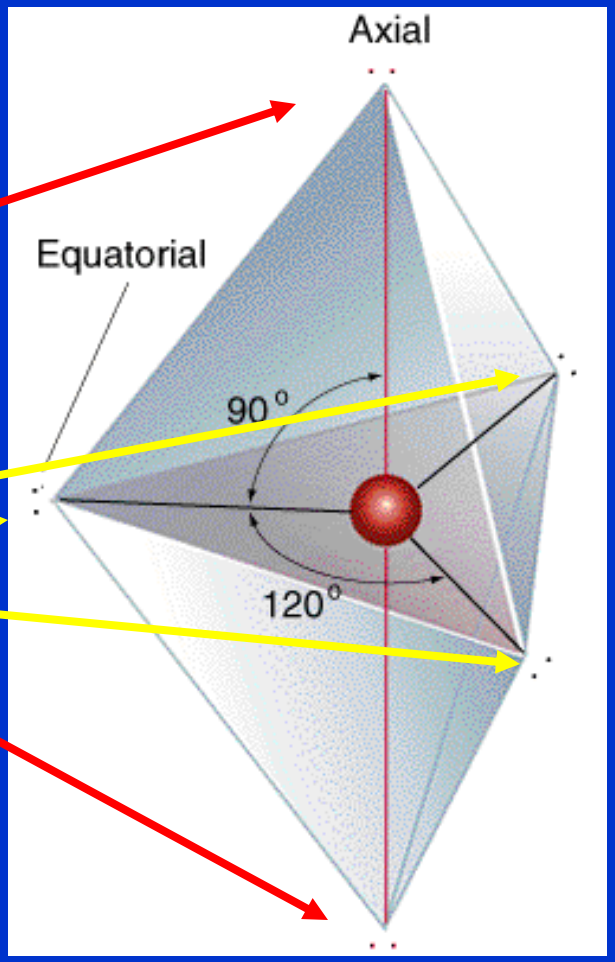
Trigonal Bipyramid

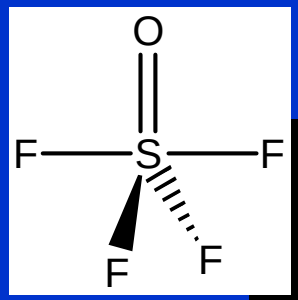
TBP has 2 different types of vertices = 2 chemically different types of substituents or positions

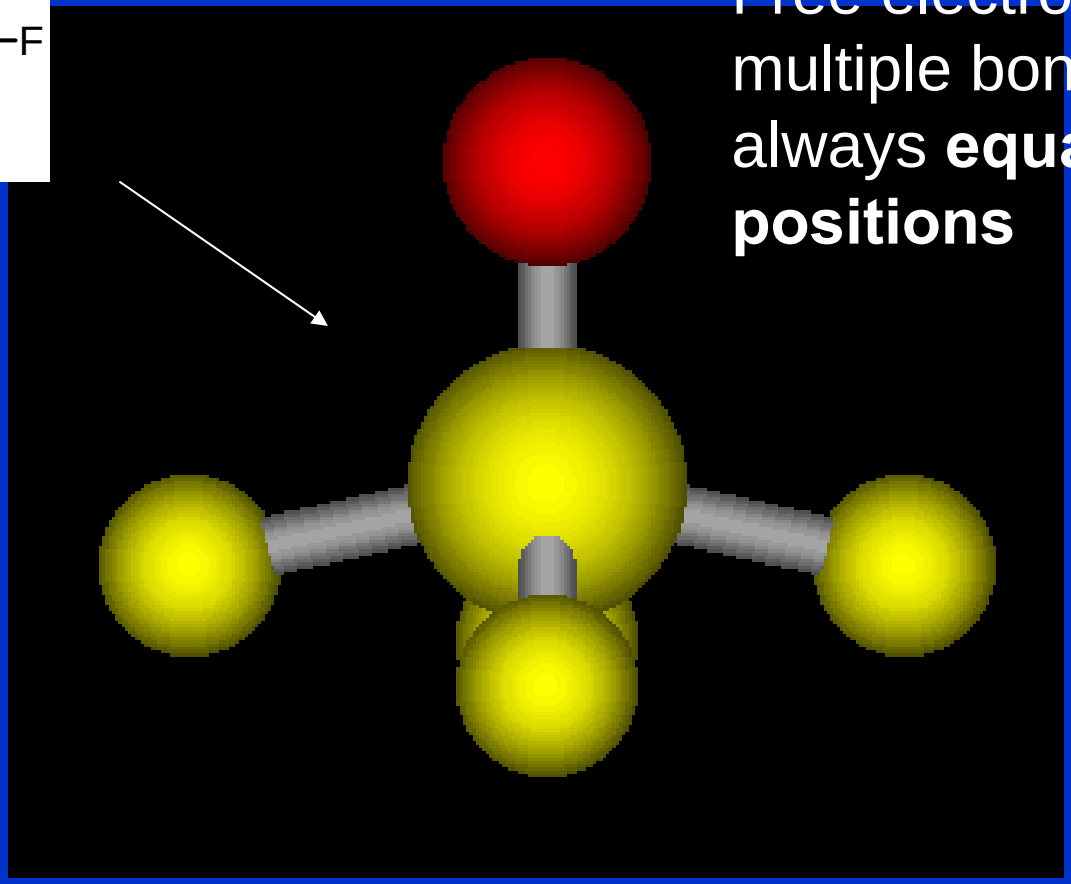
2 axial

3 equatorial

Free electron pairs and multiple bonds occupy always equatorial positions

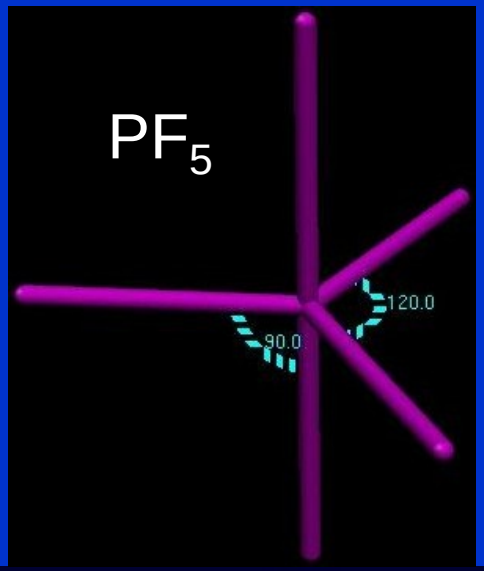


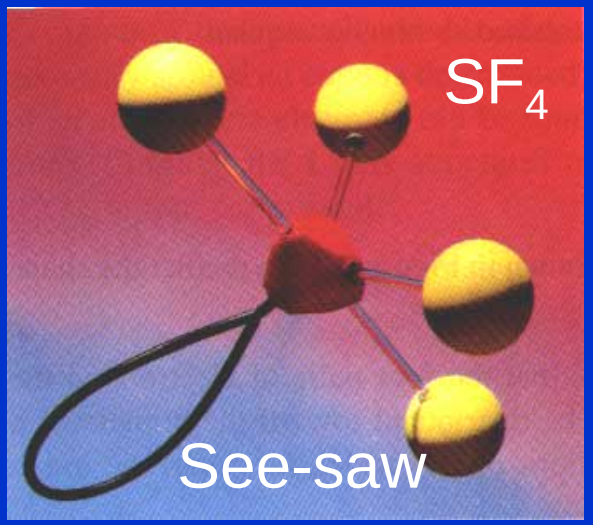




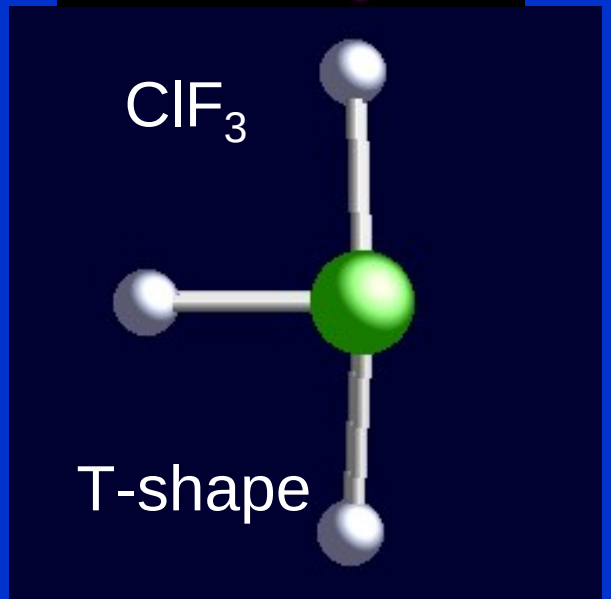
Free electron pairs and multiple bonds occupy always **equatorial positions**

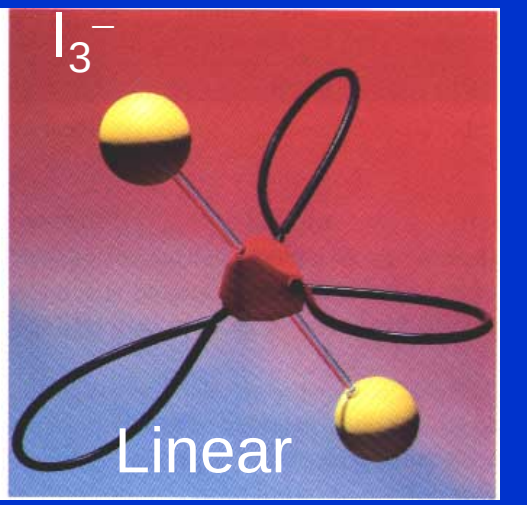
Trigonal Bipyramidal



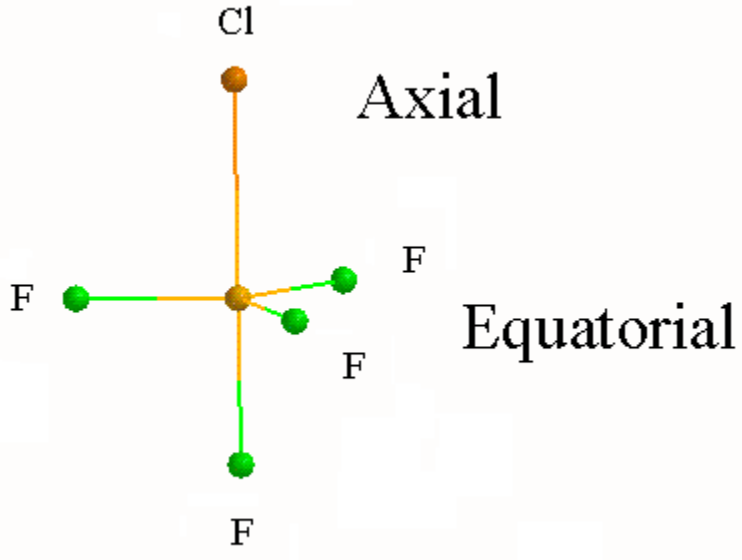


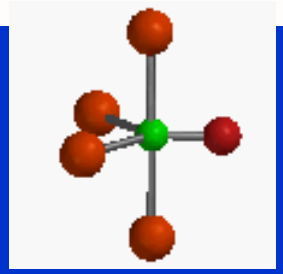
Molecular shape is given by positions of nuclei

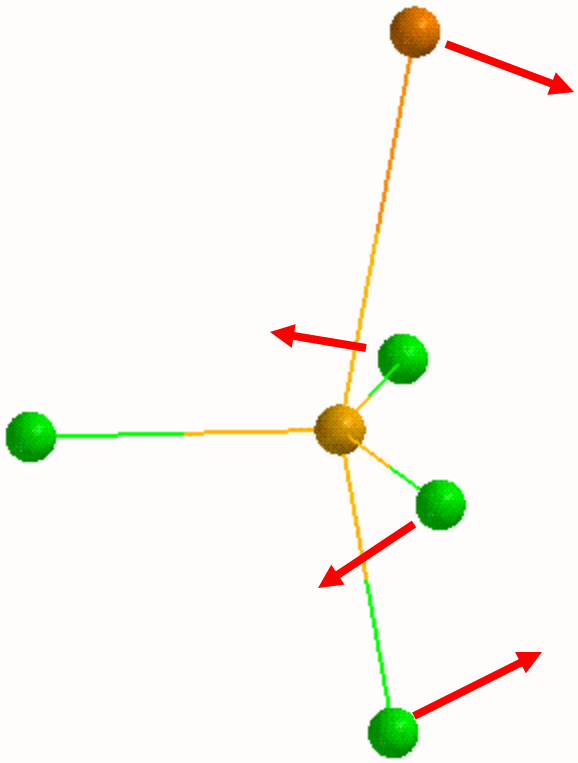




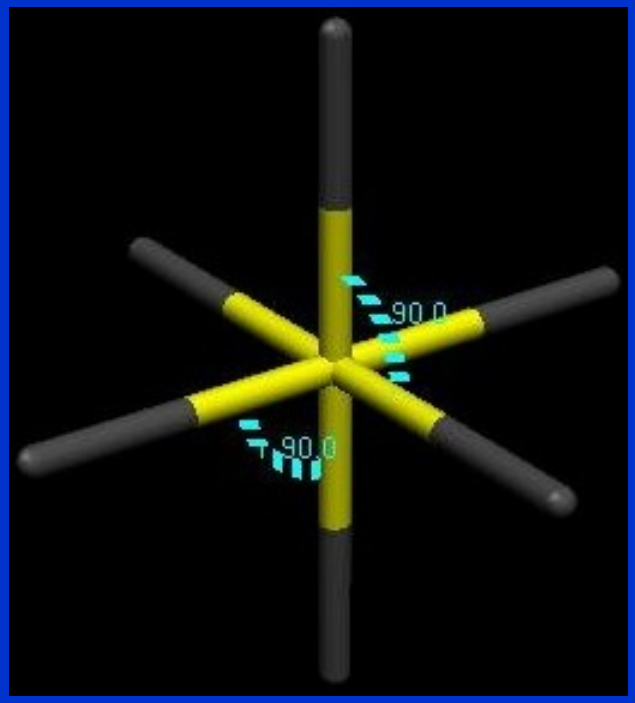
Trigonal Bipyramidal (TBP) and Square Pyramidal (SP)

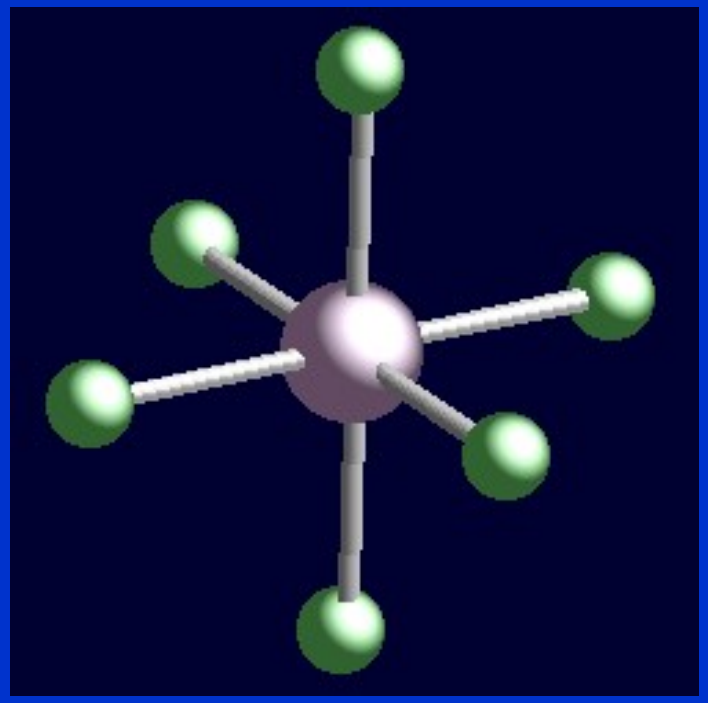






Octahedron

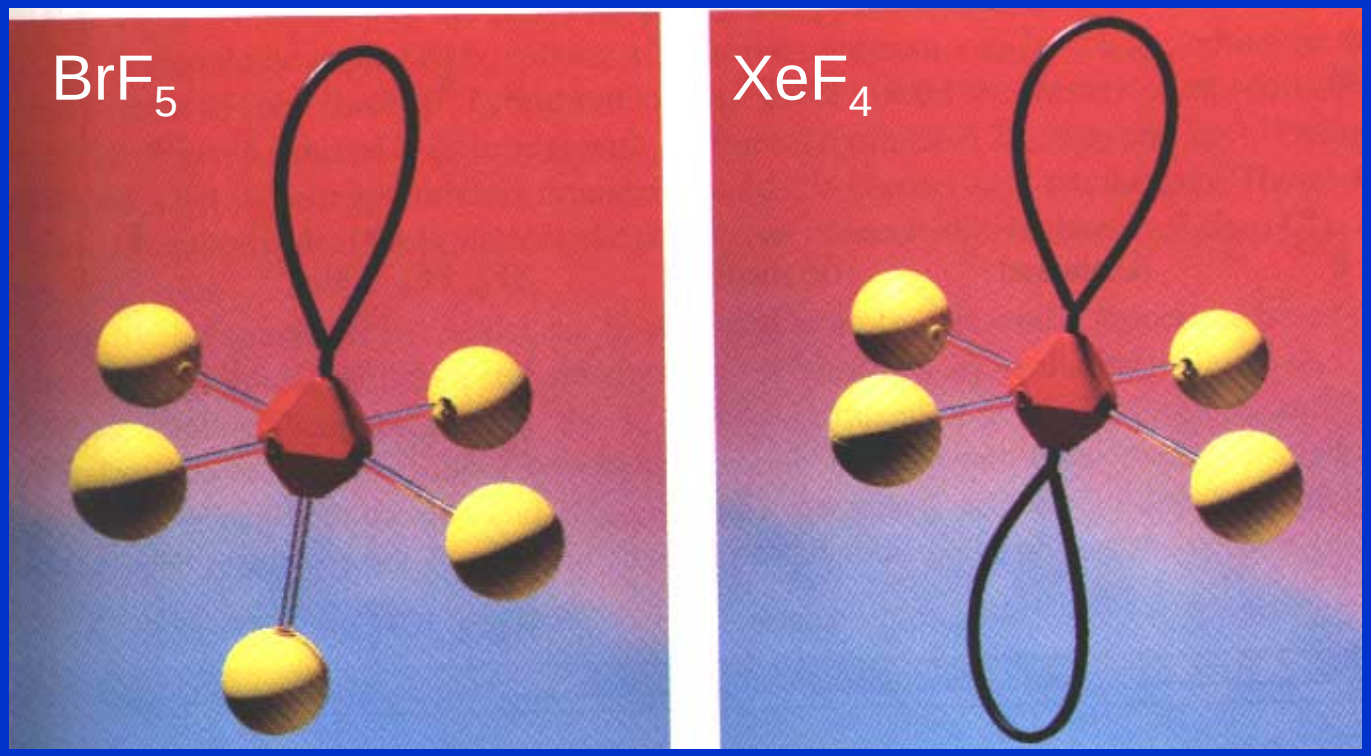




AX_6

Bond angles in octahedron = 90°

Octahedron



Square pyramidal

Square planar