화학 General Chemistry
034.020-005

2018 Spring Semester

Tue/Thr 9:30~10:45
Building 028-302

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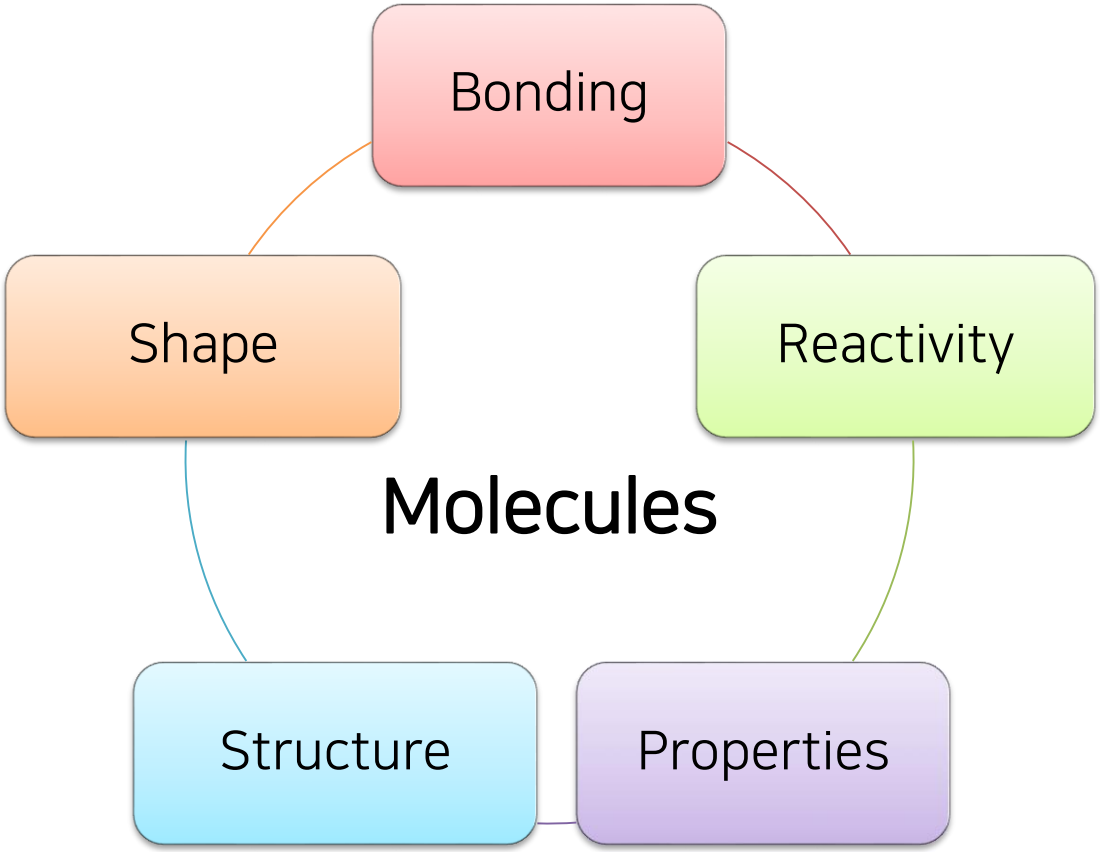
Chapter 1. Atom (electrons; atomic orbitals)

Chapter 2. Chemical Bondings (ionic vs covalent bonding)

Chapter 3. Molecular Structures and Shapes

Lecture 3. Structure and Shape of Molecules



1) VSEPR (Valence Shell Electron Pair Repulsion) model
2) VB (Valance Bond) theory
3) MO (Molecular Orbital) theory

1) Valance Shell Electron Pair Repulsion (VSEPR)

Lewis structure shows the linkages and lone pairs 2-dimensionally.

VSEPR model suggests the **3D arrangement** of atoms and shape of molecules

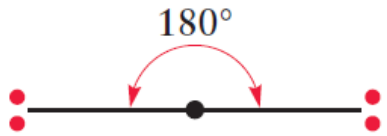
1. Only the positions of atoms are considered to identify the molecular shape.
2. Treat multiple bond as a single region with high electron density.
3. Minimize repulsions between lone pair (LP) – LP (1), bonding pair (BP) – LP (2), or BP – BP (3). Arrange them as far as possible.

Valence Shell Electron Pair Repulsion:
The structure around a given atom is determined *principally* by minimizing electron pair repulsions.

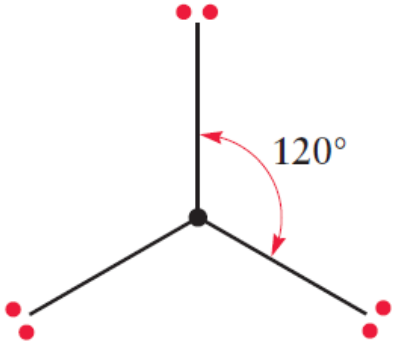
3.1. VSEPR Model

Steric Number of the central atom

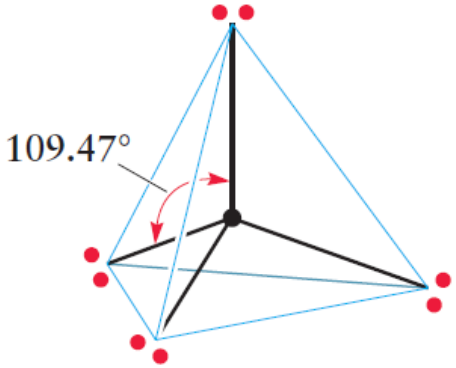
SN = # of atoms bonded to c.a.
+ # of lone pairs on c.a.



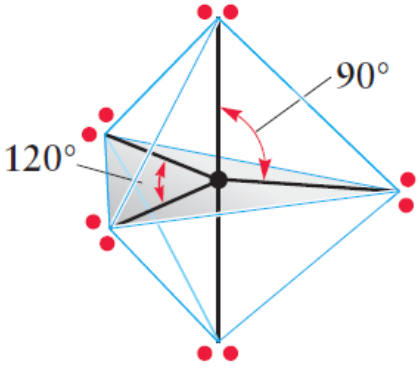
2: Linear



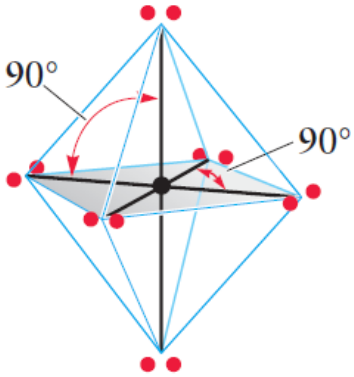
3: Trigonal planar



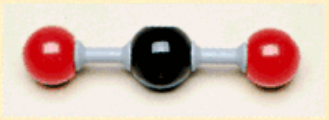
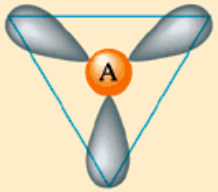
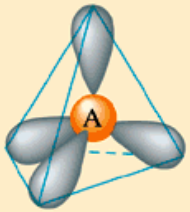
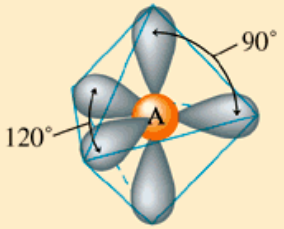
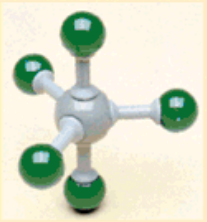
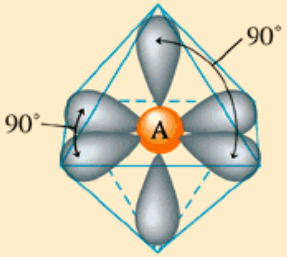
4: Tetrahedral

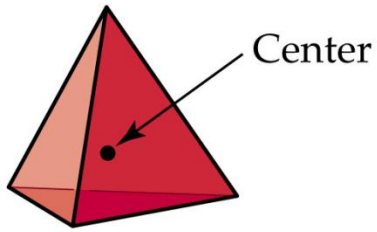


5: Trigonal bipyramidal

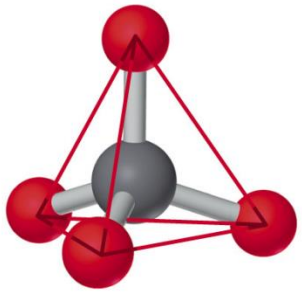


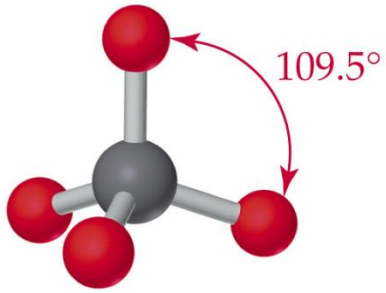
6: Octahedral

Number of Electron Pairs	Arrangement of Electron Pairs		Example
2	Linear		
3	Trigonal planar		
4	Tetrahedral		
5	Trigonal bipyramidal		
6	Octahedral		

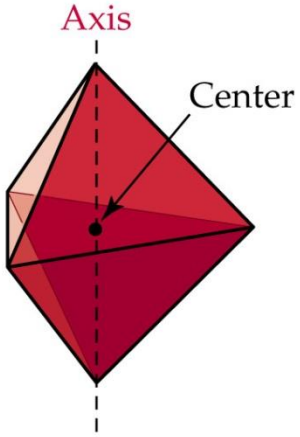


A regular tetrahedron

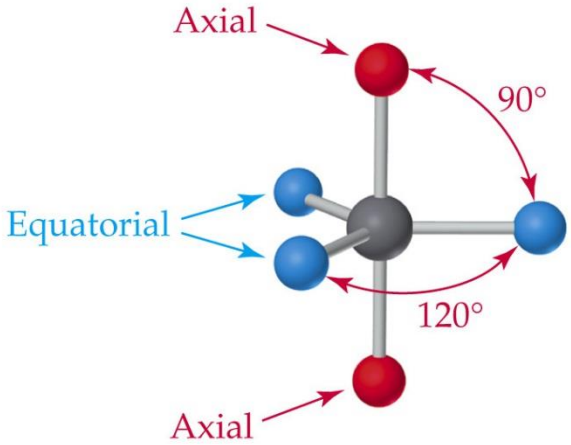




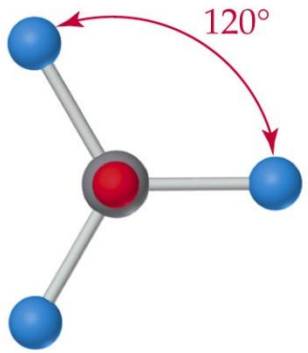
A tetrahedral molecule



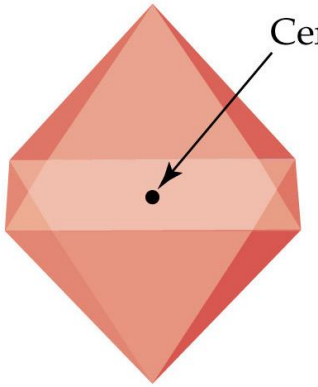
A trigonal bipyramid

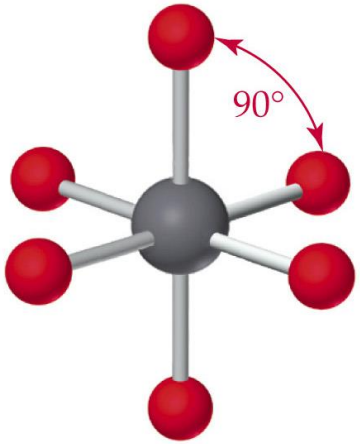


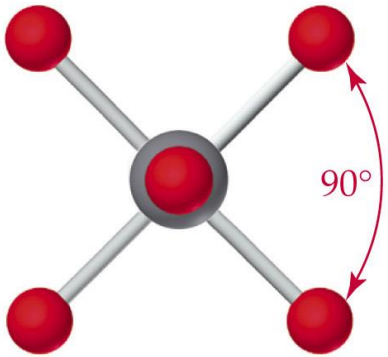
Side view



Top view

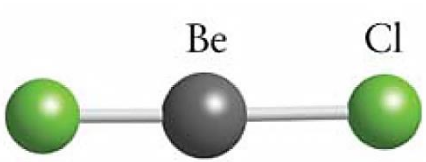






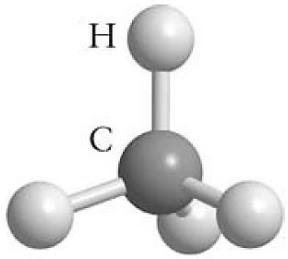
Examples

$BeCl_2$



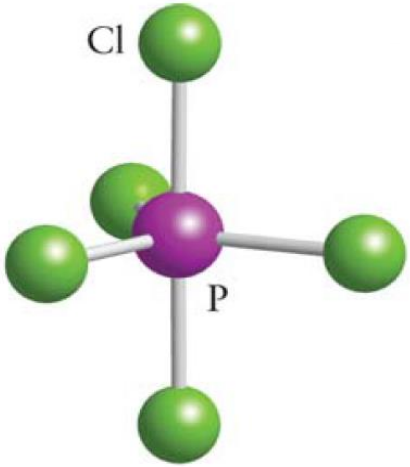
linear

CH_4



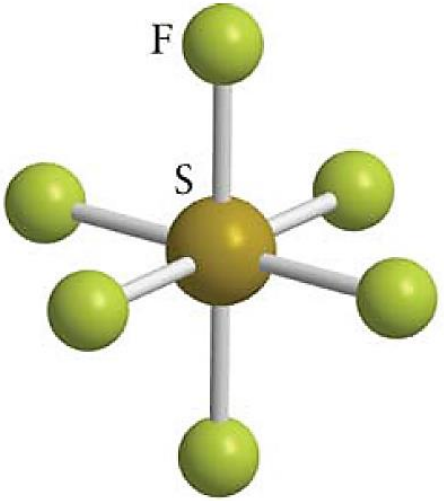
tetrahedral

PCl_5



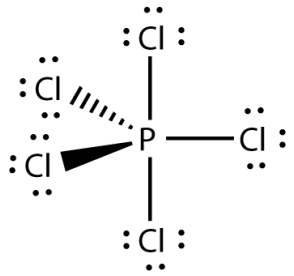
Trigonal bipyramidal

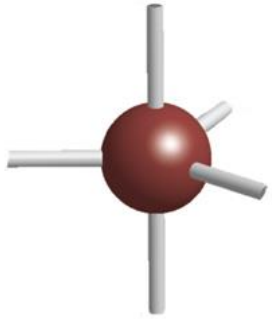
SF_6



octahedral

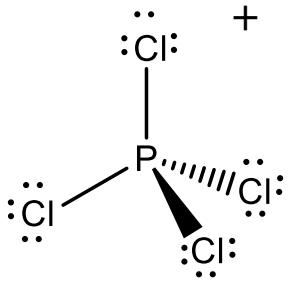
PCl_5 (5+5x(7)=40 valence electrons)

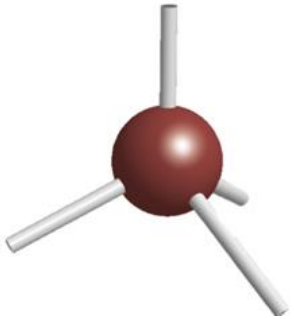




5-electron pairs
→ trigonal bipyramid

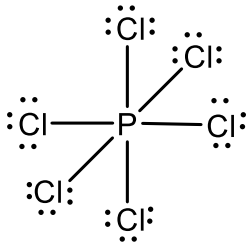
PCl_4^+ (5+4(7)-1=32 valence electrons)
4-electron pairs

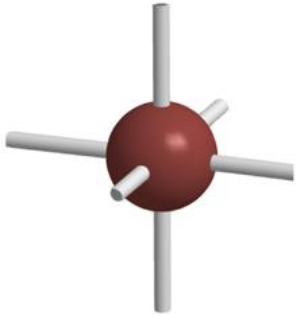




→ tetrahedron

PCl_6^- (5+6(7)+1=48 valence electrons),
6-electron pairs

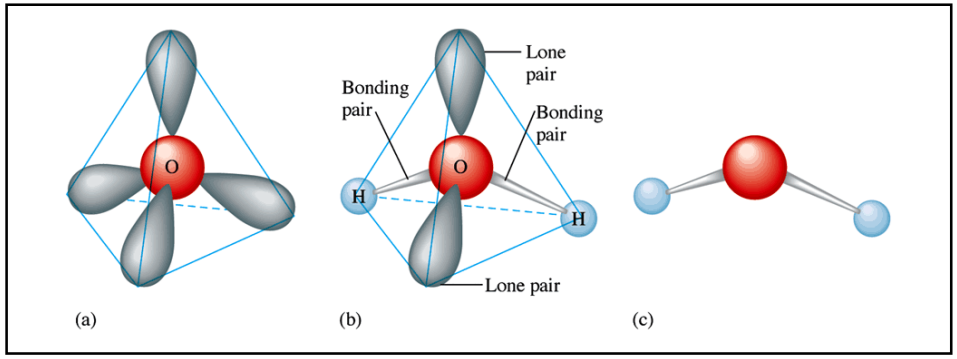


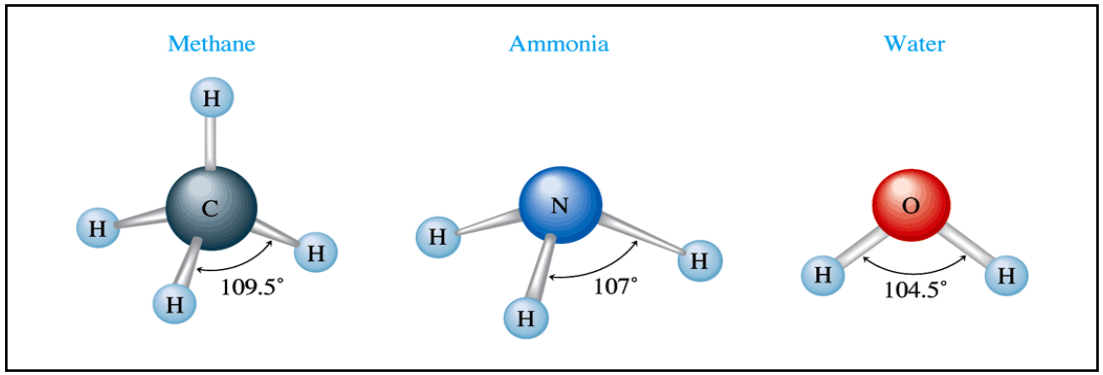


→ octahedral

3.2. VSEPR Model for Lone Pairs on the Central Atom

H-Ö-H 4-electron pairs (including lone pairs)





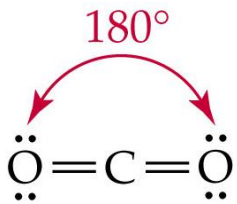
Lone pair against lone pair

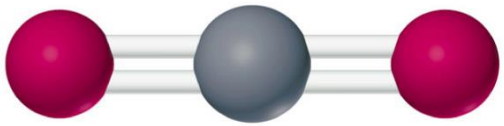
Lone pair against bonding pair

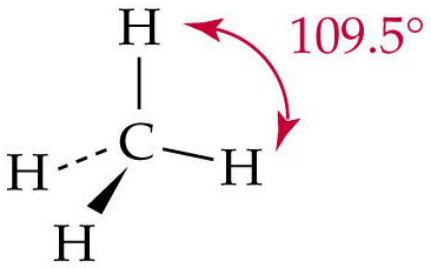
Bonding pair against bonding pair

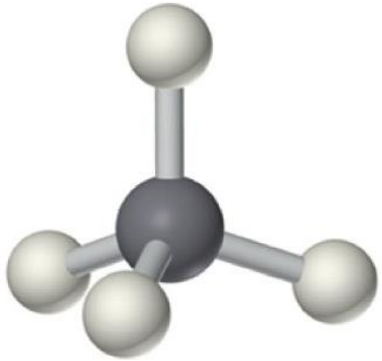
Stronger repulsion

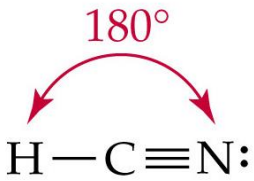
SN = 2, 3, and 4

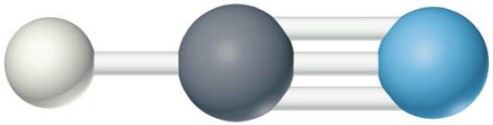


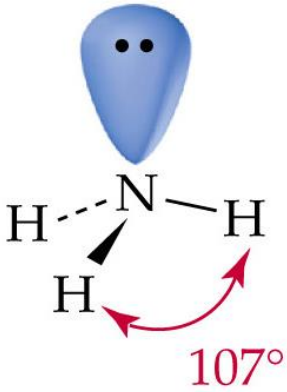


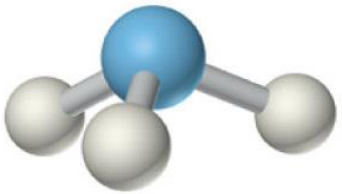


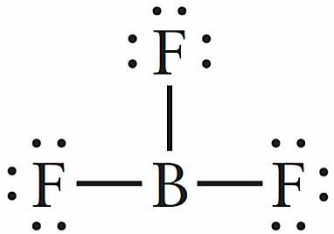


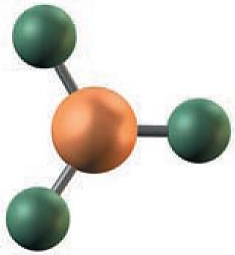


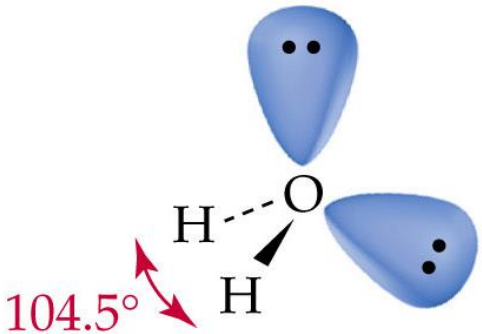




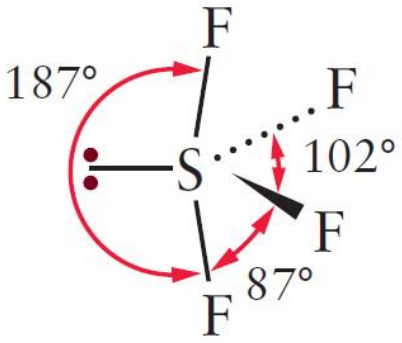






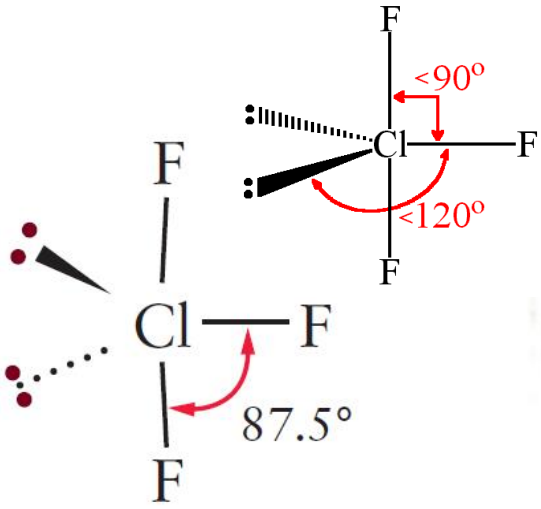


SN = 5



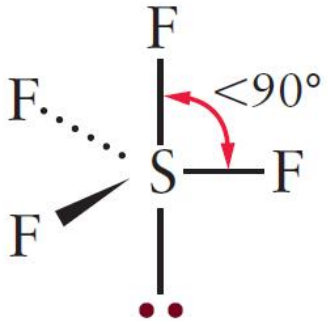
(b) SF_4

Seesaw
(low-energy, favored)



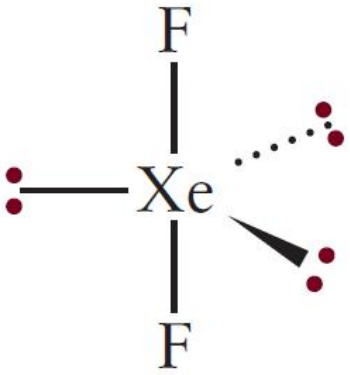
(d) ClF_3

Distorted T



(c) SF_4

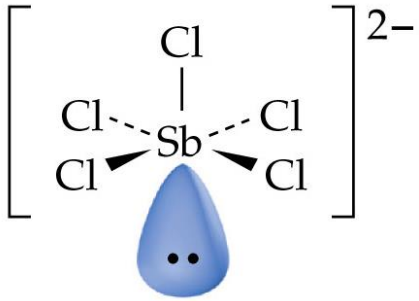
Distorted pyramid
(high-energy, not favorec

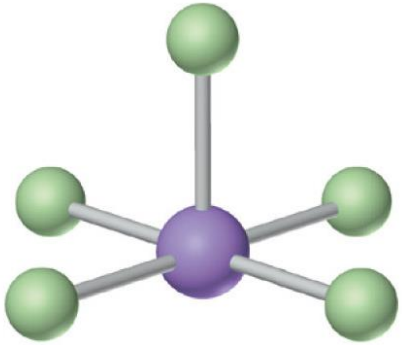


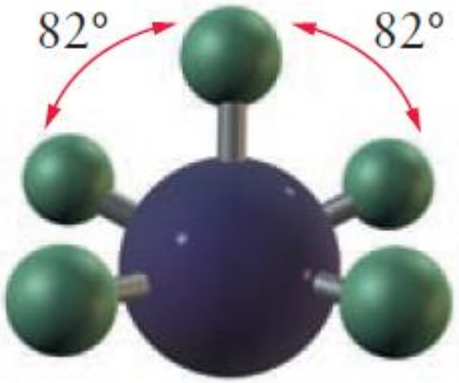
(e) XeF_2

Linear

SN = 6

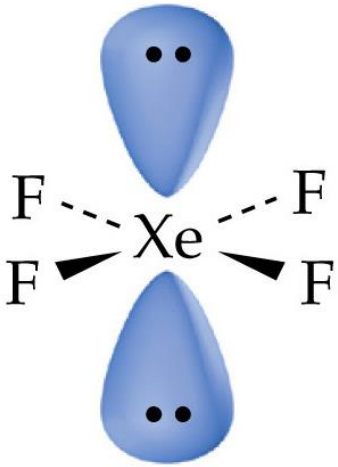


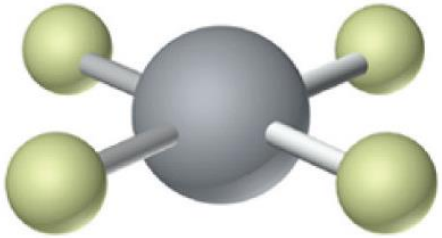




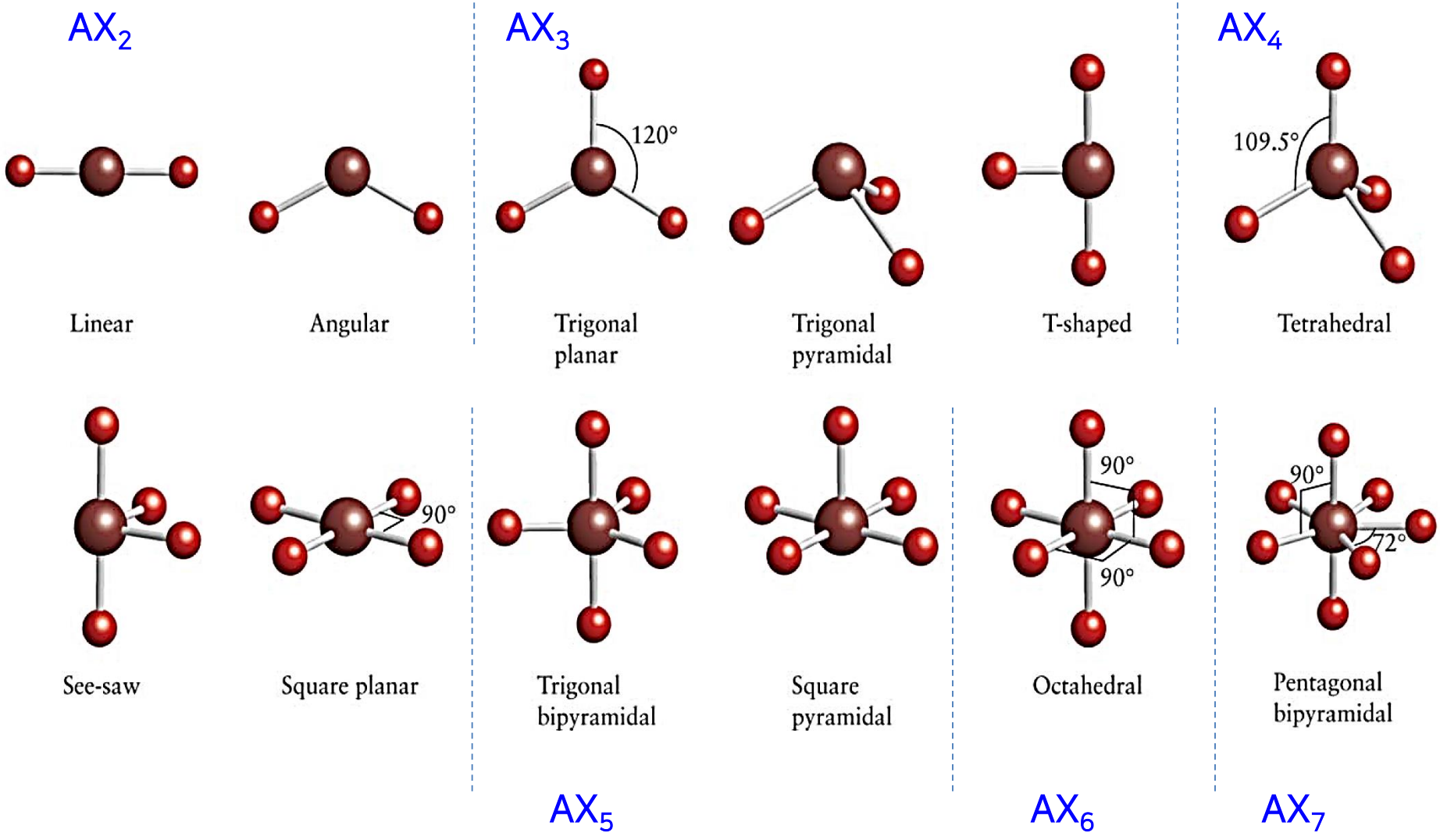
Sb: $5s^2 5p^3$

Sb^{2-}: $5s^2 5p^5$



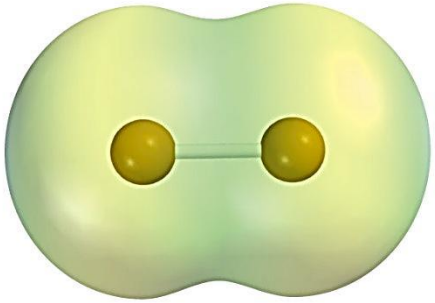


Molecular Shape is determined by the number of atoms and lone pairs (= Steric Number)



3.3. Polar Molecules

Cl:Cl A nonpolar covalent bond

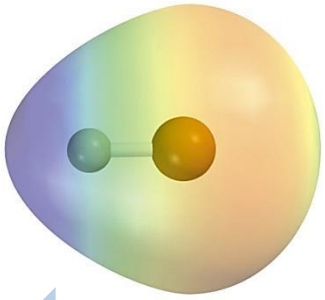


$^{\delta+}H—Cl^{\delta-}$

[H :Cl]

A polar covalent bond.

The bonding electrons are attracted more strongly by Cl than by H.



dipole

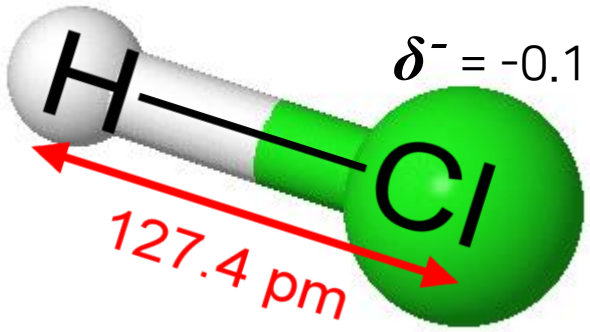
Dipole moment

$$\mu = qR$$

$$1\ \text{D} = 3.336 \times 10^{-30}\ \text{C m}$$

Partial Charge & Percent of Ionic Character

δ^+ = +0.178

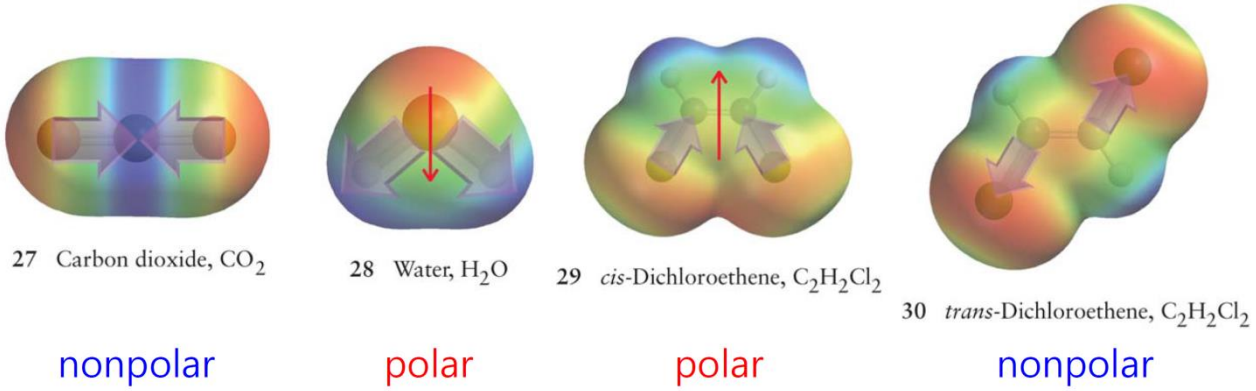


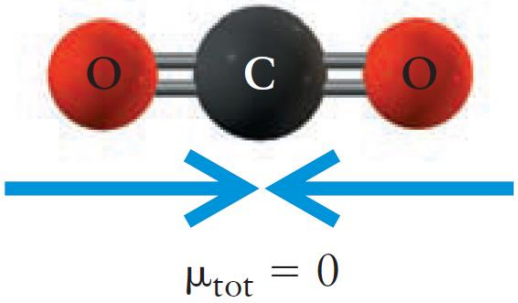
δ^- = -0.178

ts of Diatomic Molecules

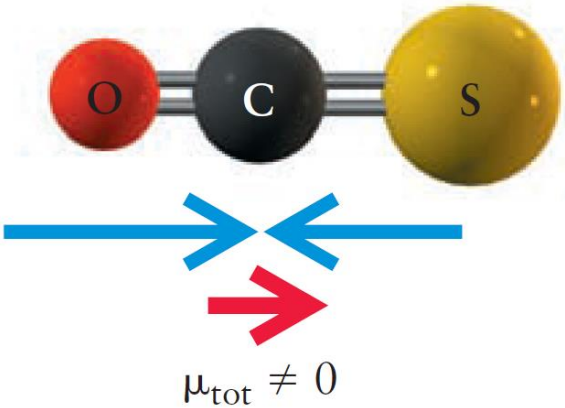
Bond Length (Å)	Dipole Moment (D)	% Ionic Character (100 δ)
0.751	0	0
1.131	0.112	2
1.154	0.159	3
1.620	0.448	6
1.632	0.888	11
1.424	0.828	12
1.284	1.109	18
0.926	1.827	41
2.347	7.884	70
2.027	7.129	73
1.604	5.882	76
2.824	10.628	78
2.365	9.001	79
2.671	10.269	82
2.176	8.593	82
1.570	6.327	84
1.931	8.156	88

Net Dipole

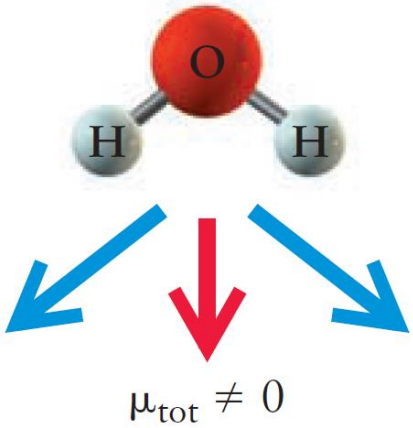




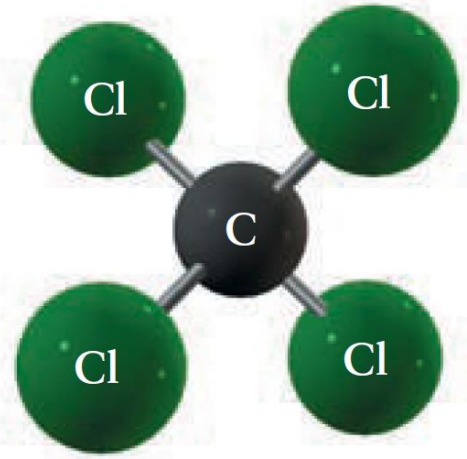
(a)

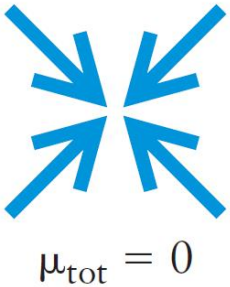


(b)



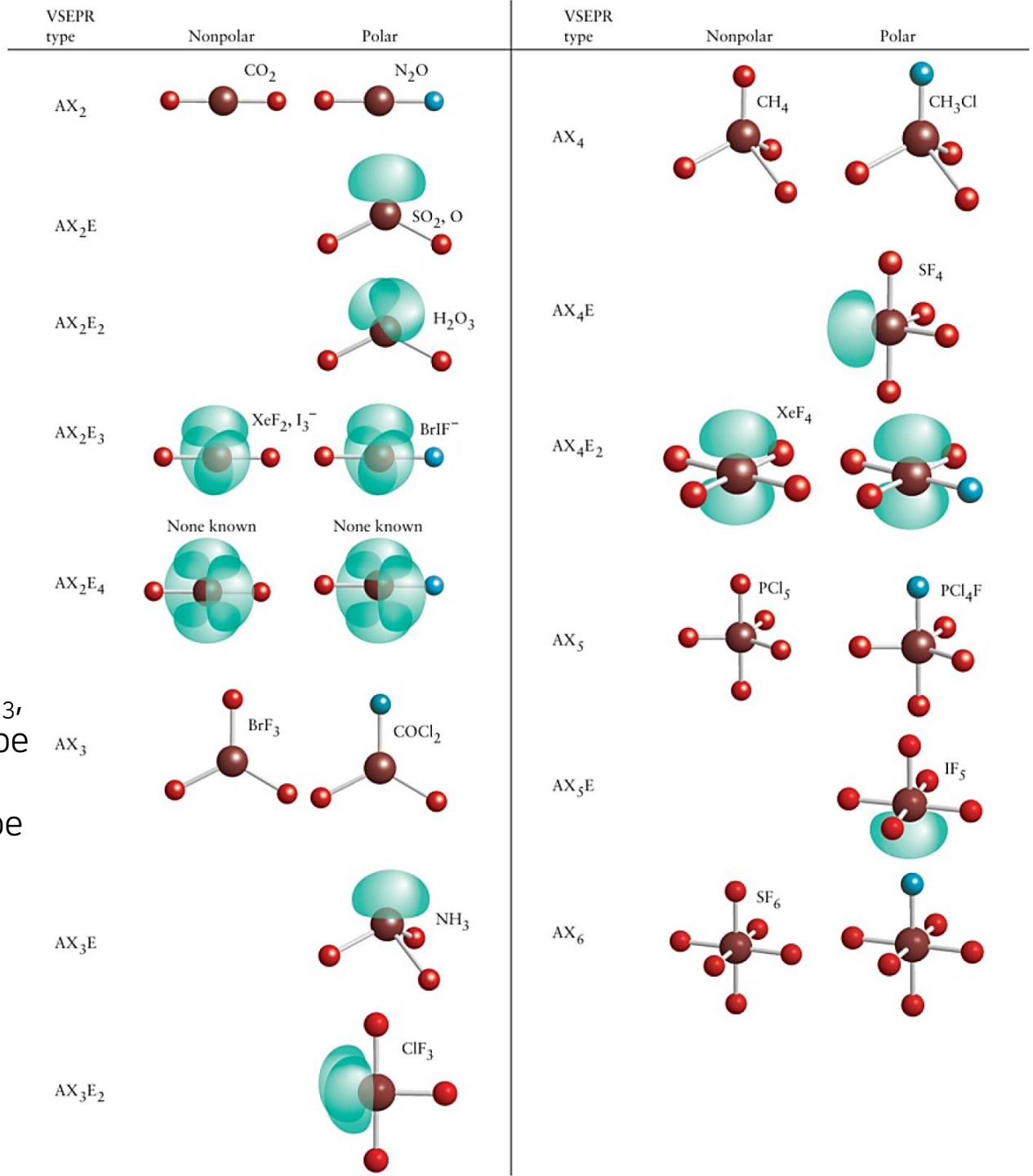
(c)





(d)

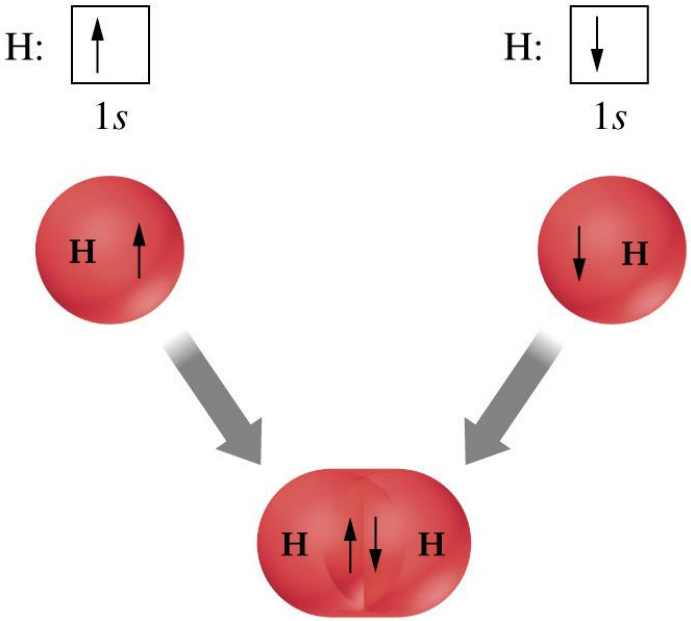
Correction)
BrF_3 is not a AX_3, but is AX_3E_2-type molecule.
BF_3 is a AX_3-type one.



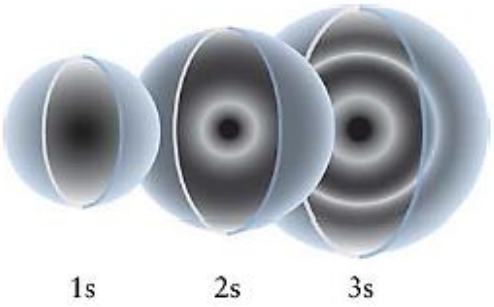
Valence Bond Theory

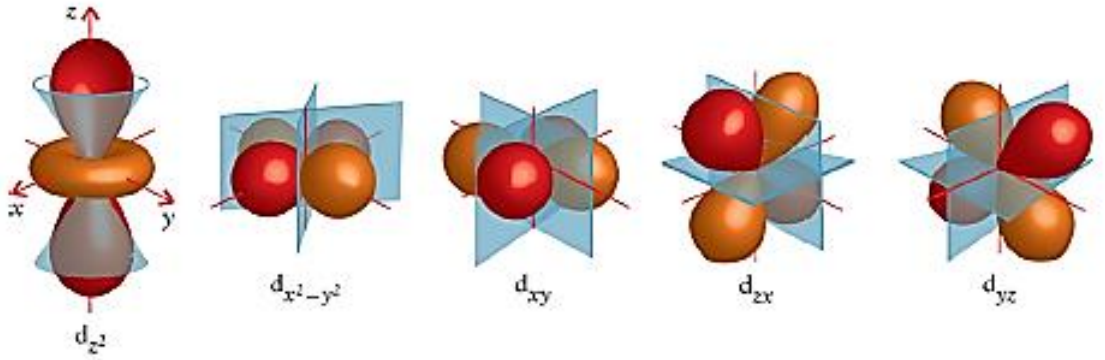
- An approximate Quantum Theory that solves problem of Lewis/VSEPR.

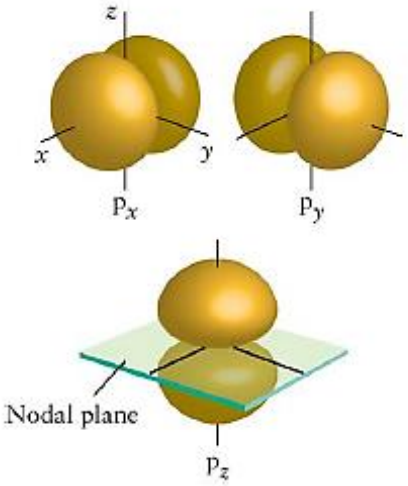
- A bond is formed by the two electrons placed in the overlapped region of atomic orbitals of two atoms.

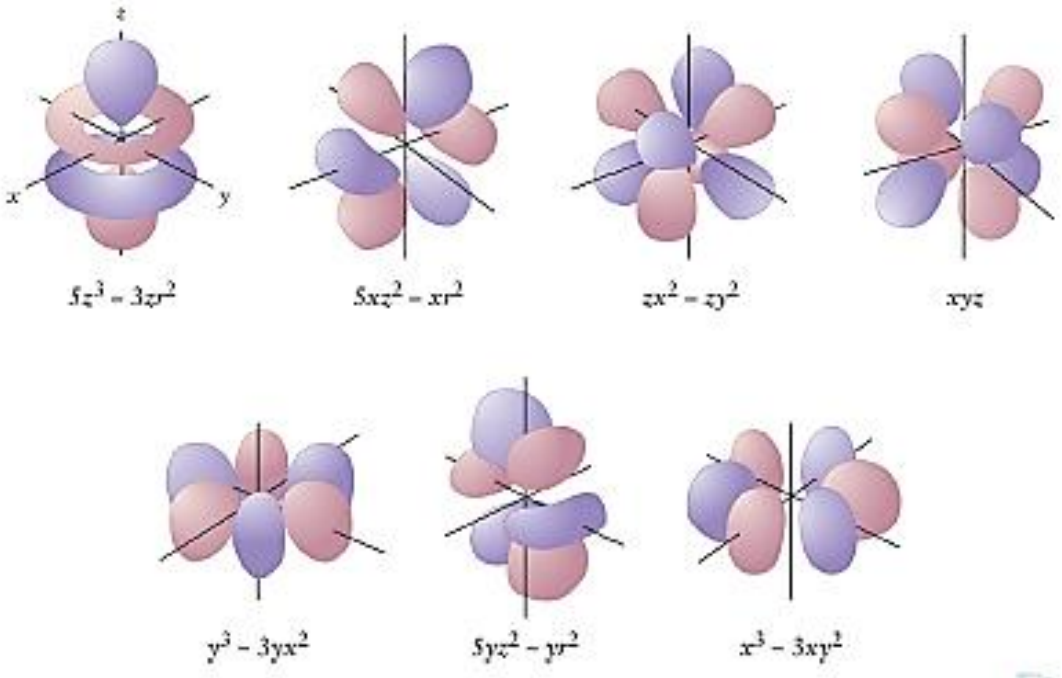


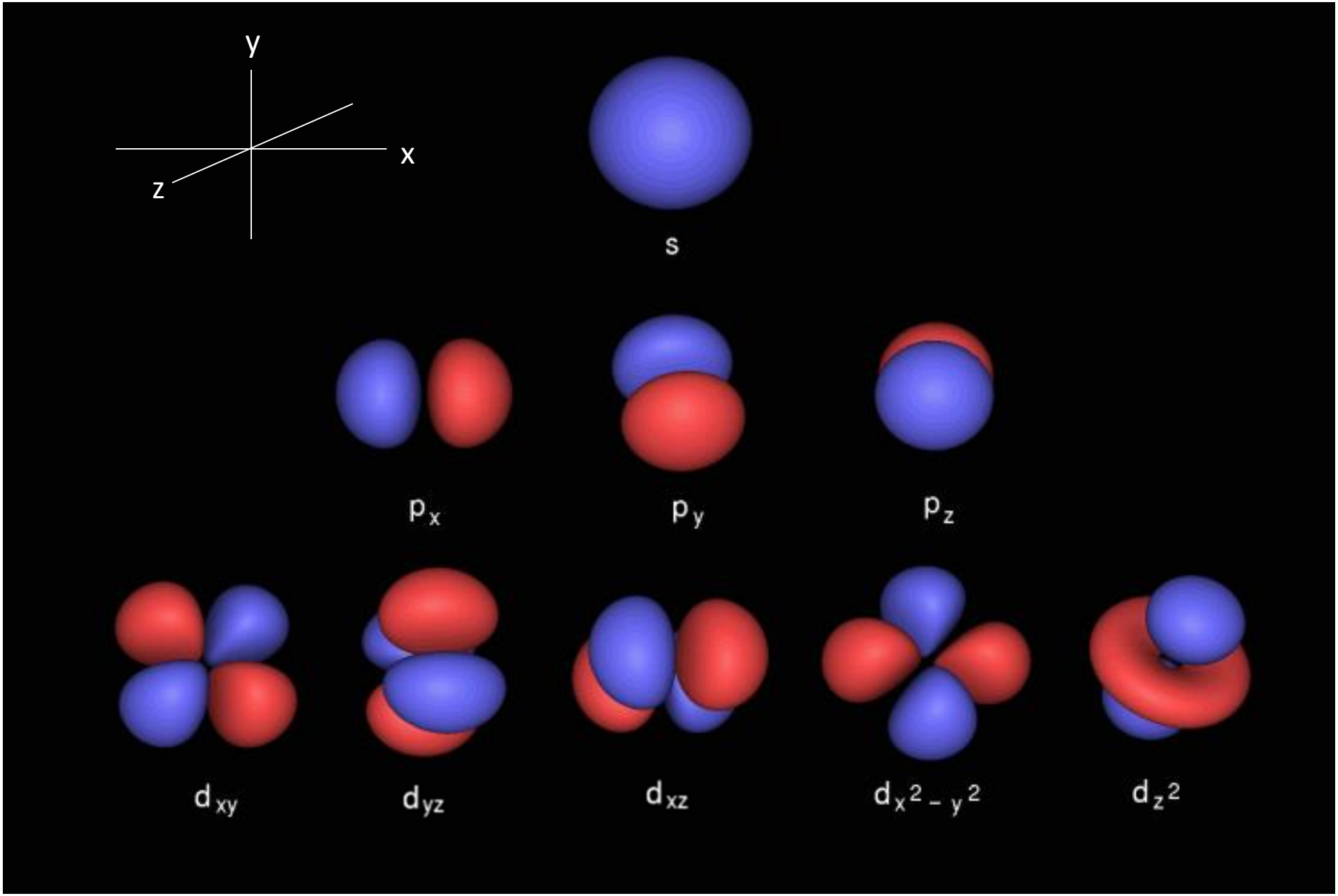
Valance Bond Theory explains covalent bonding with atomic orbitals



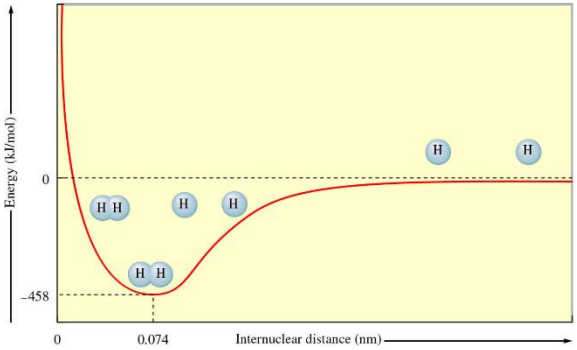


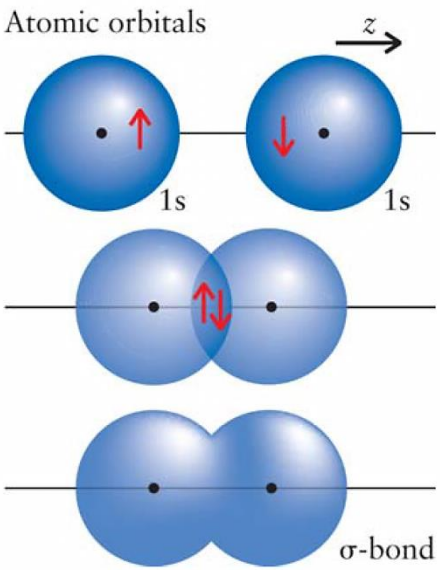





y
x
z
s
p_x
p_y
p_z
d_{xy}
d_{yz}
d_{xz}
$d_{x^2-y^2}$
d_{z^2}

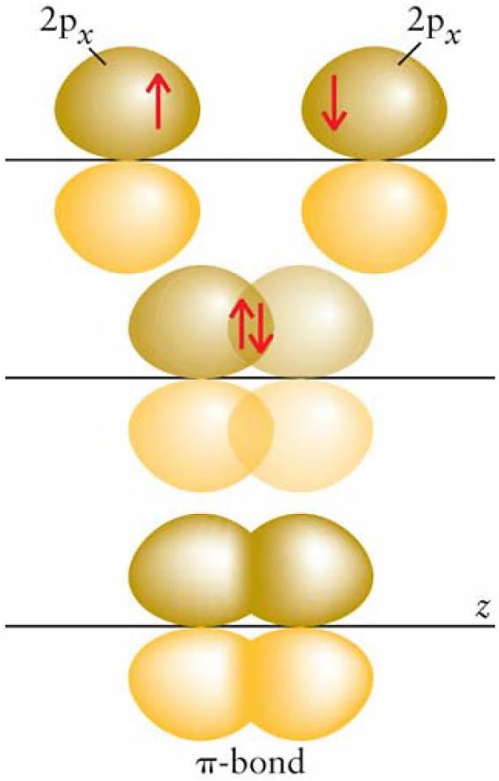
3.4. Orbital Overlap: Bonding!





σ bond:

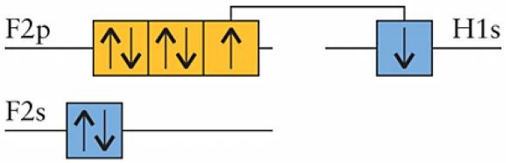
- No nodal plane including bond axis
- Cylindrical or sausage shape



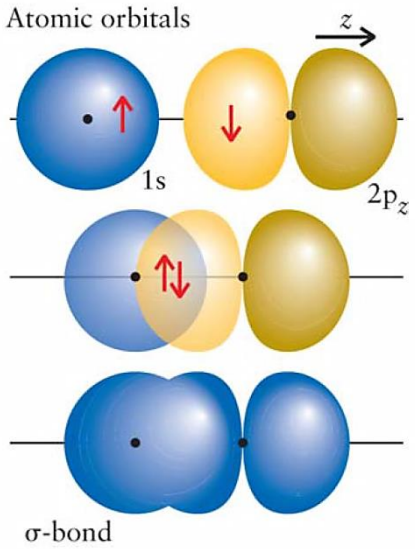
π bond

- Nodal plane including bonding axis
- lobes

Examples



33 Hydrogen fluoride, HF



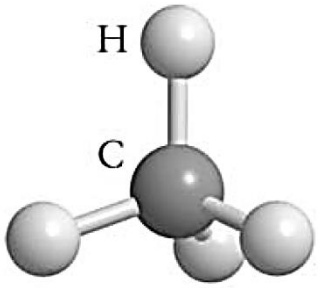
Multiple bond = one **σ** bond + the other **π** bonds

Comparison of VB and Lewis/VSEPR

- In Lewis/VSEPR theory, shapes of molecules are determined by bond-bond repulsion

- In VB, shapes are determined by the orientation of **overlapped orbitals.**

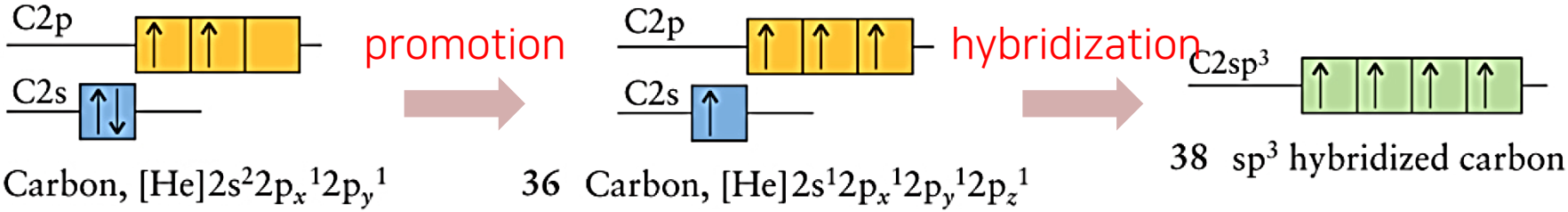
3.5. Hybridization of Orbitals



1 Methane, CH_4

all the C-H bonds are equivalent.

Electron promotion and Hybrid orbital



35 Carbon, $[He]2s^2 2p_x^1 2p_y^1$ 36 Carbon, $[He]2s^1 2p_x^1 2p_y^1 2p_z^1$ 38 sp^3 hybridized carbon

Electron promotion: electron relocation to a higher-energy orbital

Hybrid orbital: hybridizing orbitals

General Rules for Hybridization

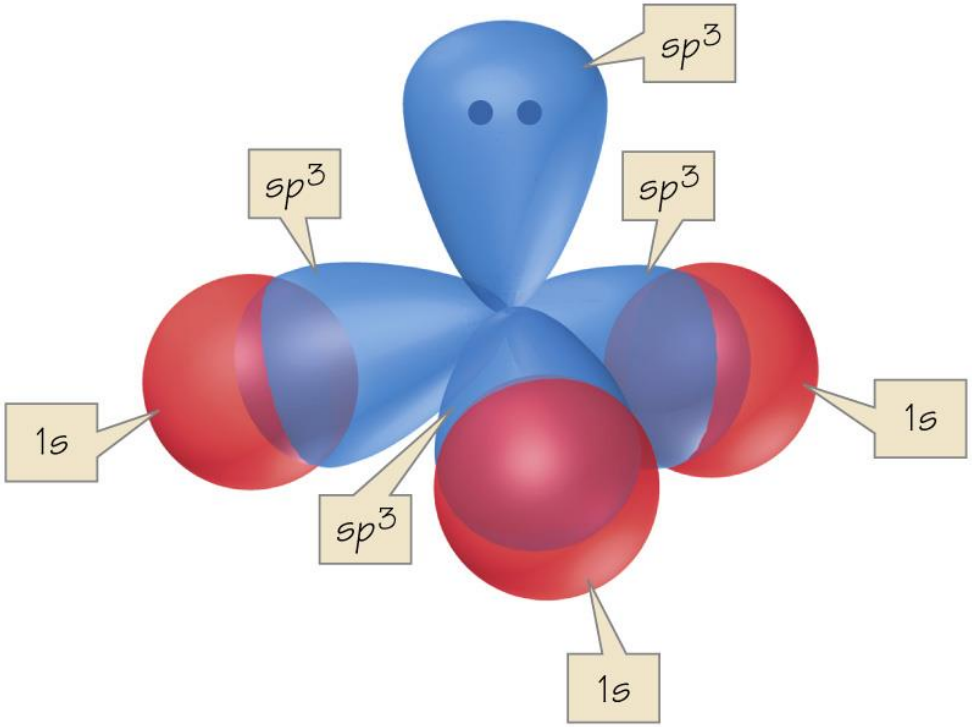
- Number of hybrid orbitals
  = number of atomic orbitals used (one s + three p orbitals = four sp^3 orbitals).

- To form covalent bonds, hybrid orbitals may overlap either with atomic or hybrid orbitals.

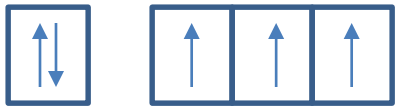
- Molecular shape is determined by the shapes and orientations of hybrid orbitals, which are different from the shapes and orientations of atomic orbitals.

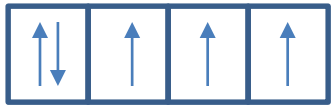
- Therefore, CH_4 is in tetrahedral shape even though the atomic orbitals of the carbon atom are perpendicular each other (90^o).

Bonding in NH_3



N: $1s^2$ $2s^2$ $2p^3$





$4sp^3$

1) sp^3 hybridization

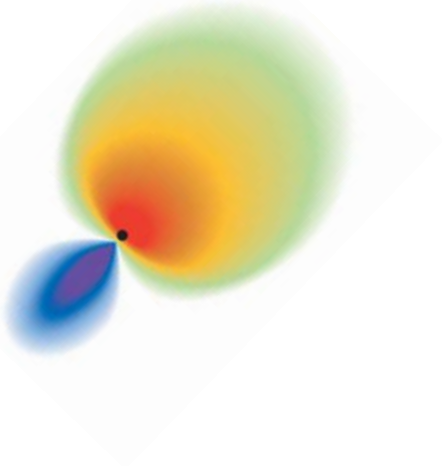
4 sp^3 hybrids

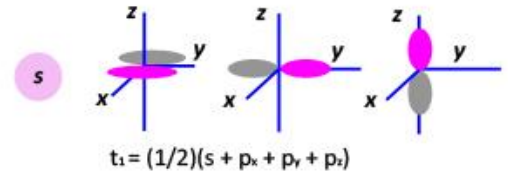
$$h_1 = \frac{1}{2}(s + px + py + p_z)$$

$$h_2 = \frac{1}{2}(s + px - p_y - p_z)$$

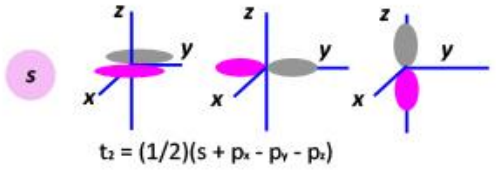
$$h_3 = \frac{1}{2}(s - p_x + p_y - p_z)$$

$$h_4 = \frac{1}{2}(s - p_x - p_y + p_z)$$

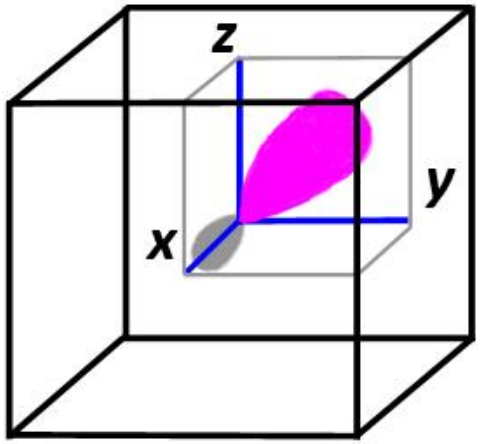


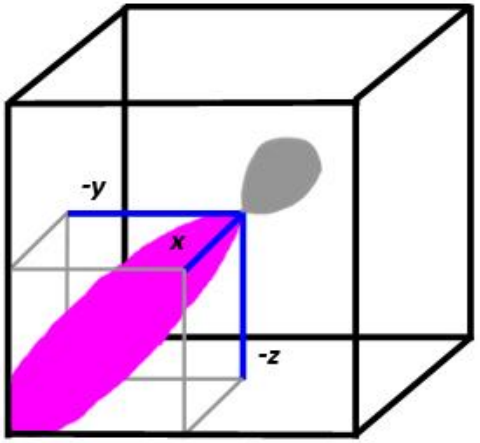


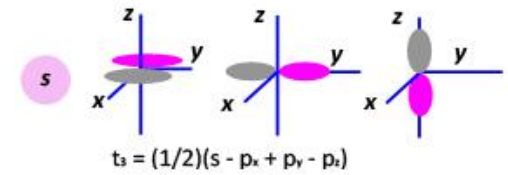
$t_1 = (1/2)(s + p_x + p_y + p_z)$



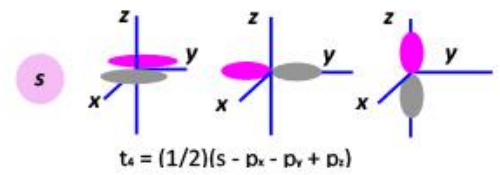
$t_2 = (1/2)(s + p_x - p_y - p_z)$



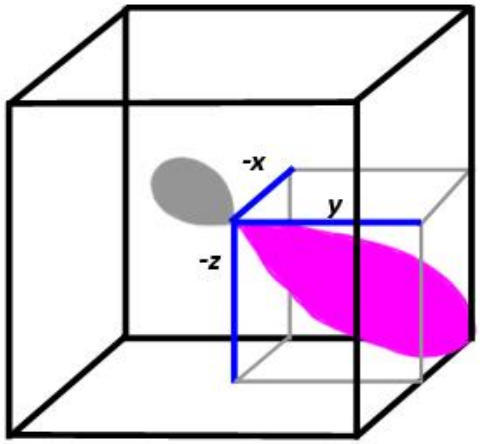


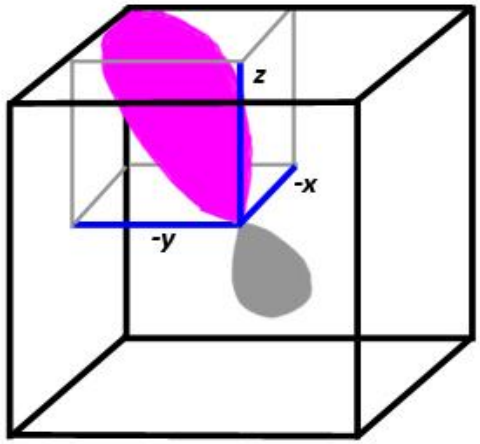


$t_3 = (1/2)(s - p_x + p_y - p_z)$



$t_4 = (1/2)(s - p_x - p_y + p_z)$





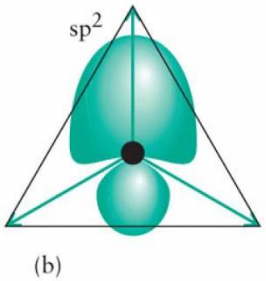
2) sp^2 & sp hybridization

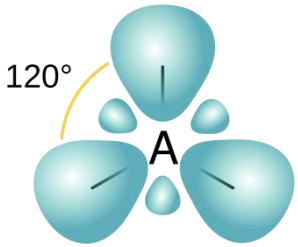
3 sp^2 hybrids

$h_1 = s + 2^{1/2} p_y$

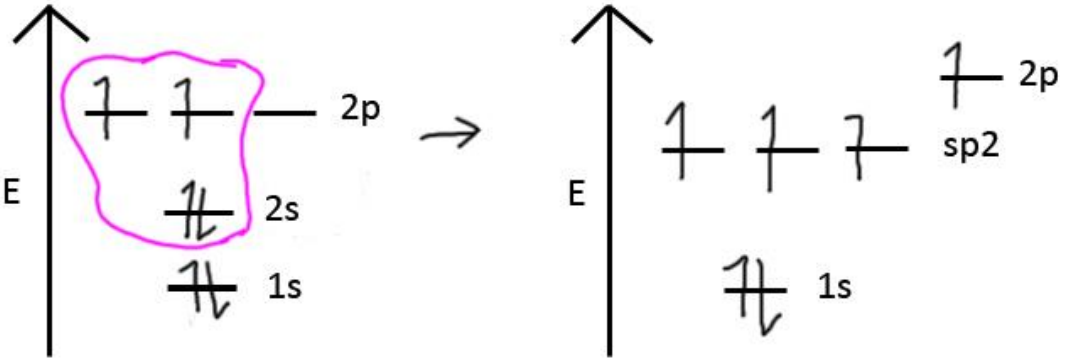
$h_2 = s + (3/2)^{1/2} p_x - (1/2)^{1/2} p_y$

$h_3 = s - (3/2)^{1/2} p_x - (1/2)^{1/2} p_y$





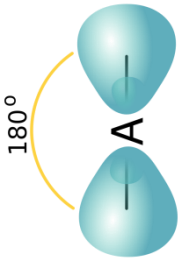
C $1s^2 2s^2 2p^2$



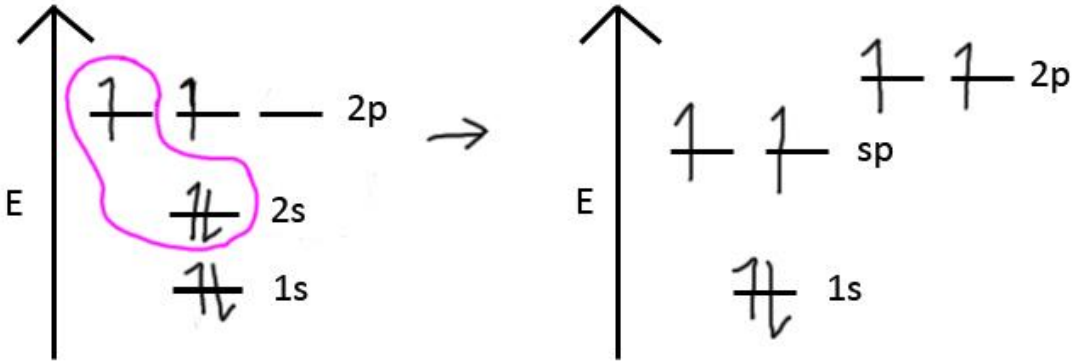
2 sp hybrids

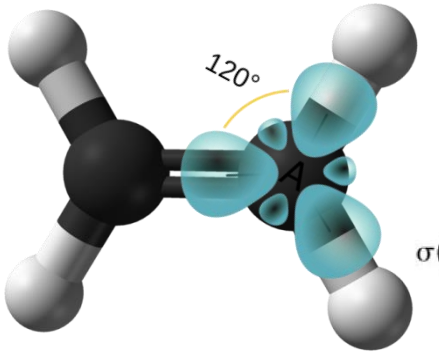
$h_1 = s + p_z$

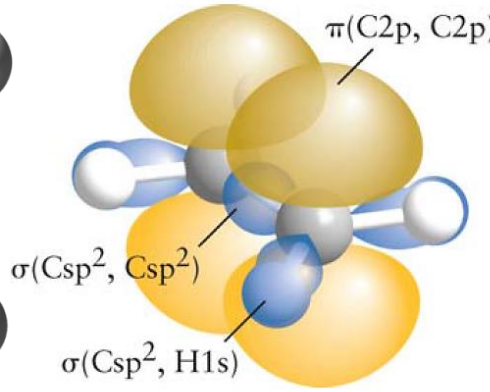
$h_2 = s - p_z$

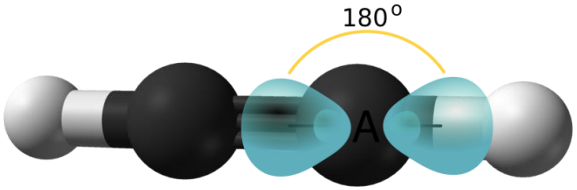


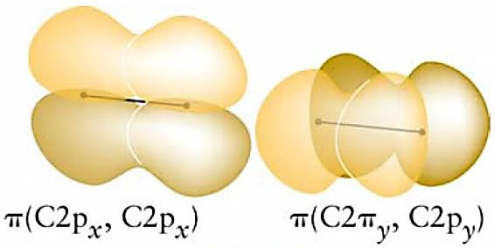
C $1s^2 2s^2 2p^2$

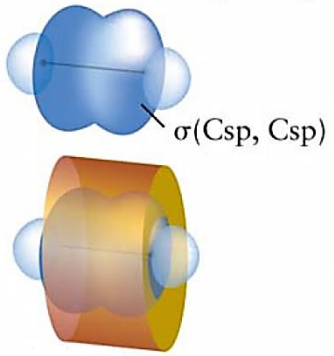


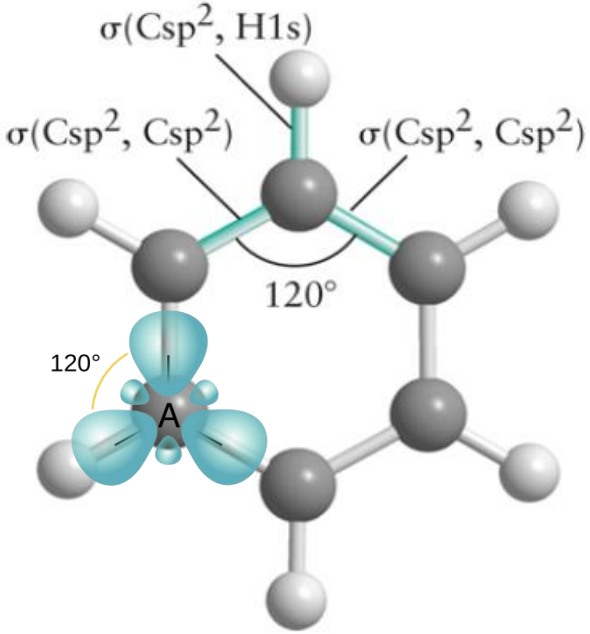

120°
A

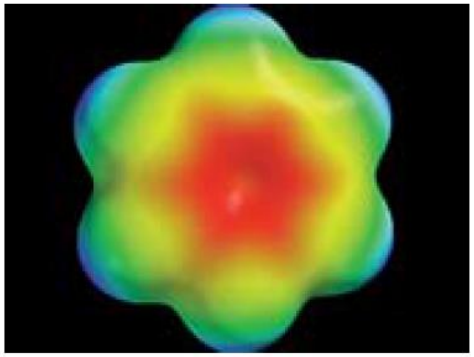

π(C2p, C2p)
σ(Csp², Csp²)
σ(Csp², H1s)


180°
A


π(C2p$_x$, C2p$_x$)
π(C2π$_y$, C2p$_y$)


σ(Csp, Csp)


σ(Csp², H1s)
σ(Csp², Csp²)
σ(Csp², Csp²)
120°
120°
A



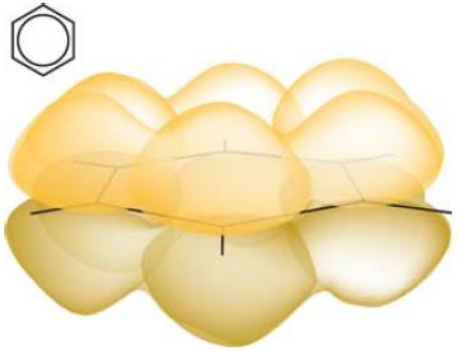
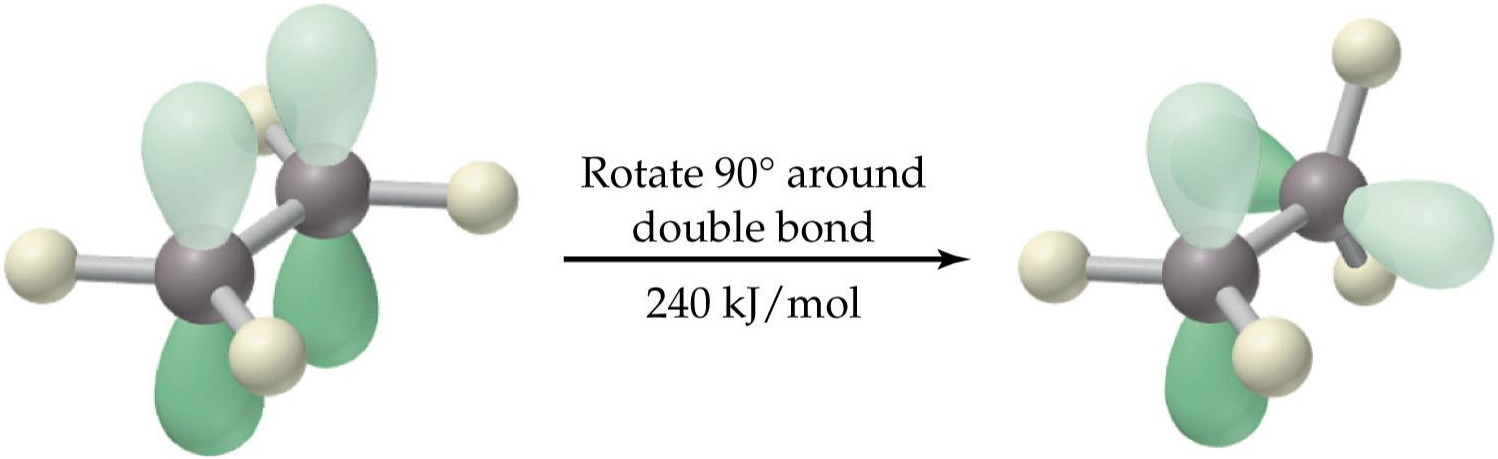


TABLE 3.5

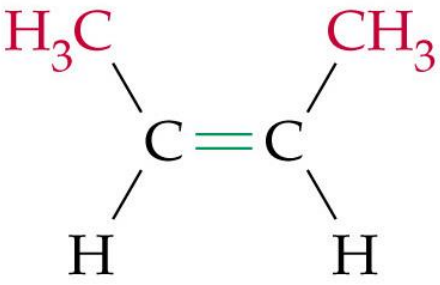
Three Types of Carbon–Carbon Bonds

Bond	Molecule	Bond Length (Å)	Bond Energy (kJ mol^{-1})
C—C	C_2H_6 (or H_3CCH_3)	1.536	345
C=C	C_2H_4 (or H_2CCH_2)	1.337	612
C≡C	C_2H_2 (or HCCH)	1.204	809

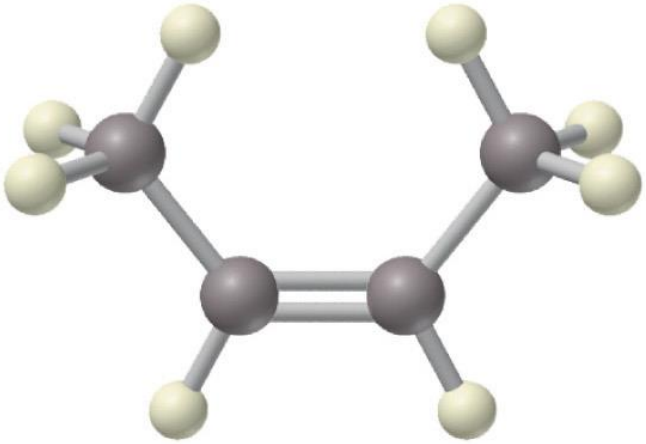


Pi bond—*p* orbital overlap

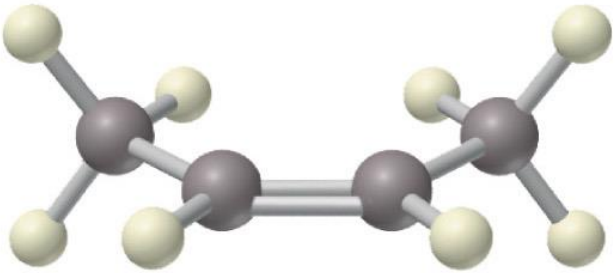
Broken bond—no *p* orbital overlap



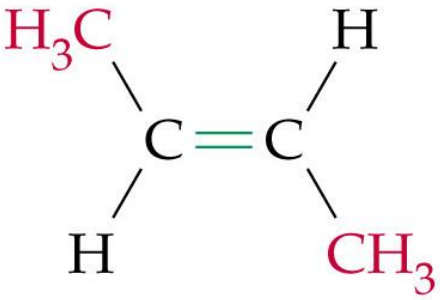
cis-2-Butene
(methyl groups on
the same side)



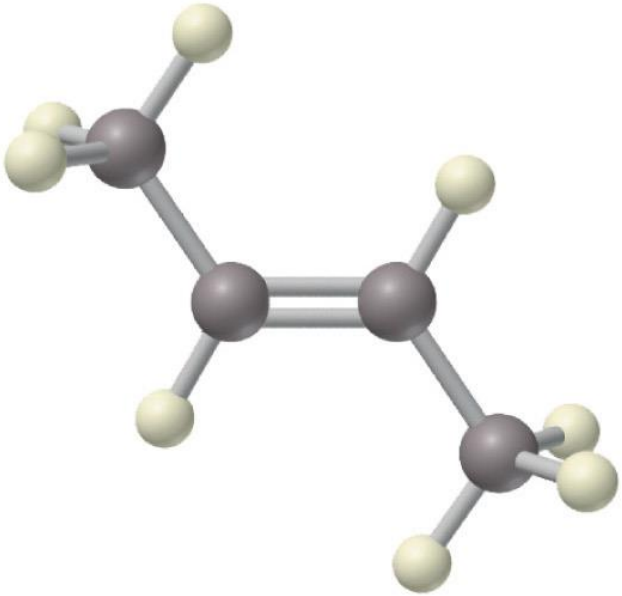
(Top view)



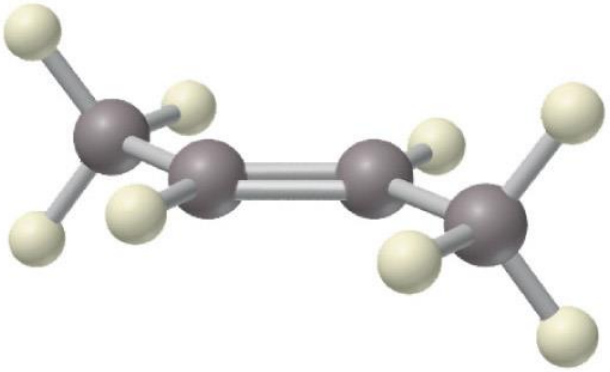
(Side view)



trans-2-Butene
(methyl groups on
opposite sides)



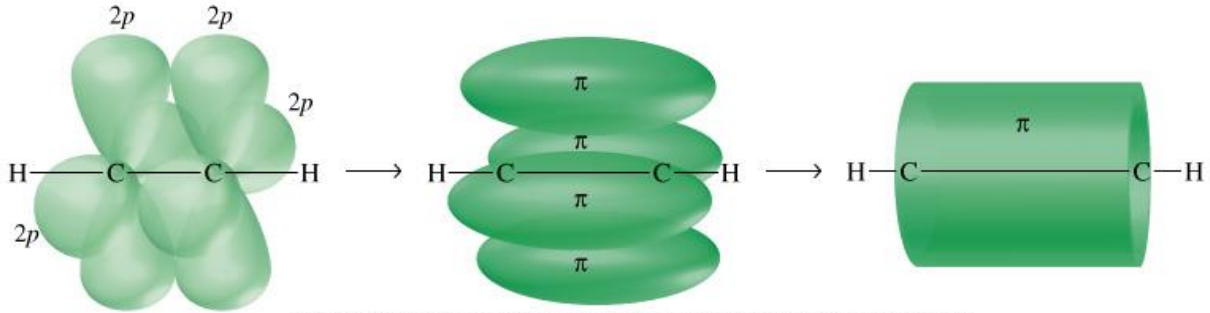
(Top view)



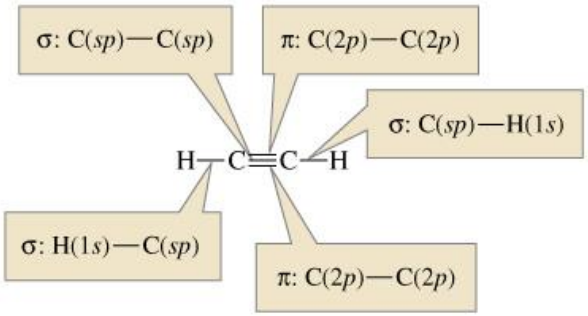
(Side view)

C_2H_2

(a) The σ-bond framework



(b) Formation of π-bonds by the overlap of half-filled 2*p* orbitals



(c) Hybridization and bonding scheme

In Lewis structure,

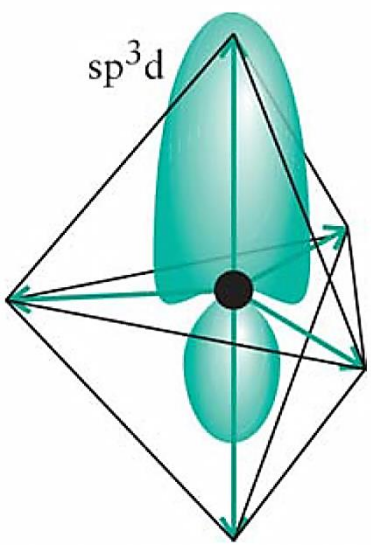
double bond == two identical single bonds

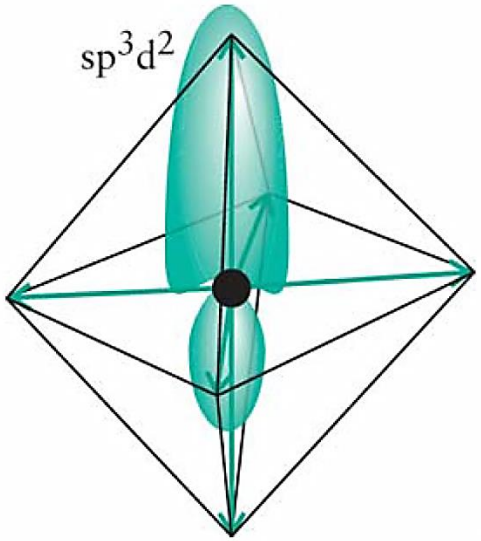
In VB theory,

double bond = sigma bond + pi bond

Triple bond = sigma bond + two pi bonds

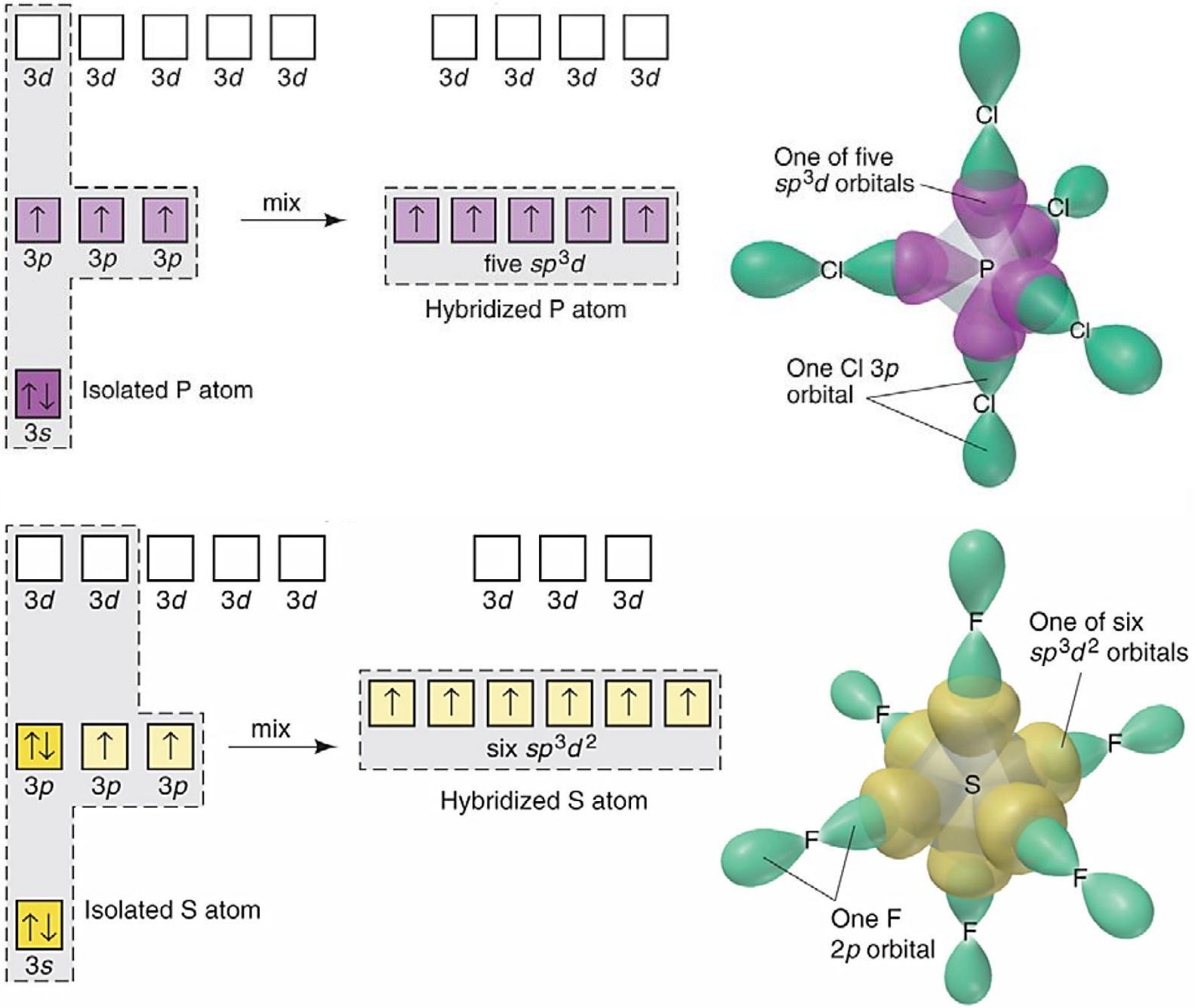
3) sp^3d & sp^3d^2 hybridization





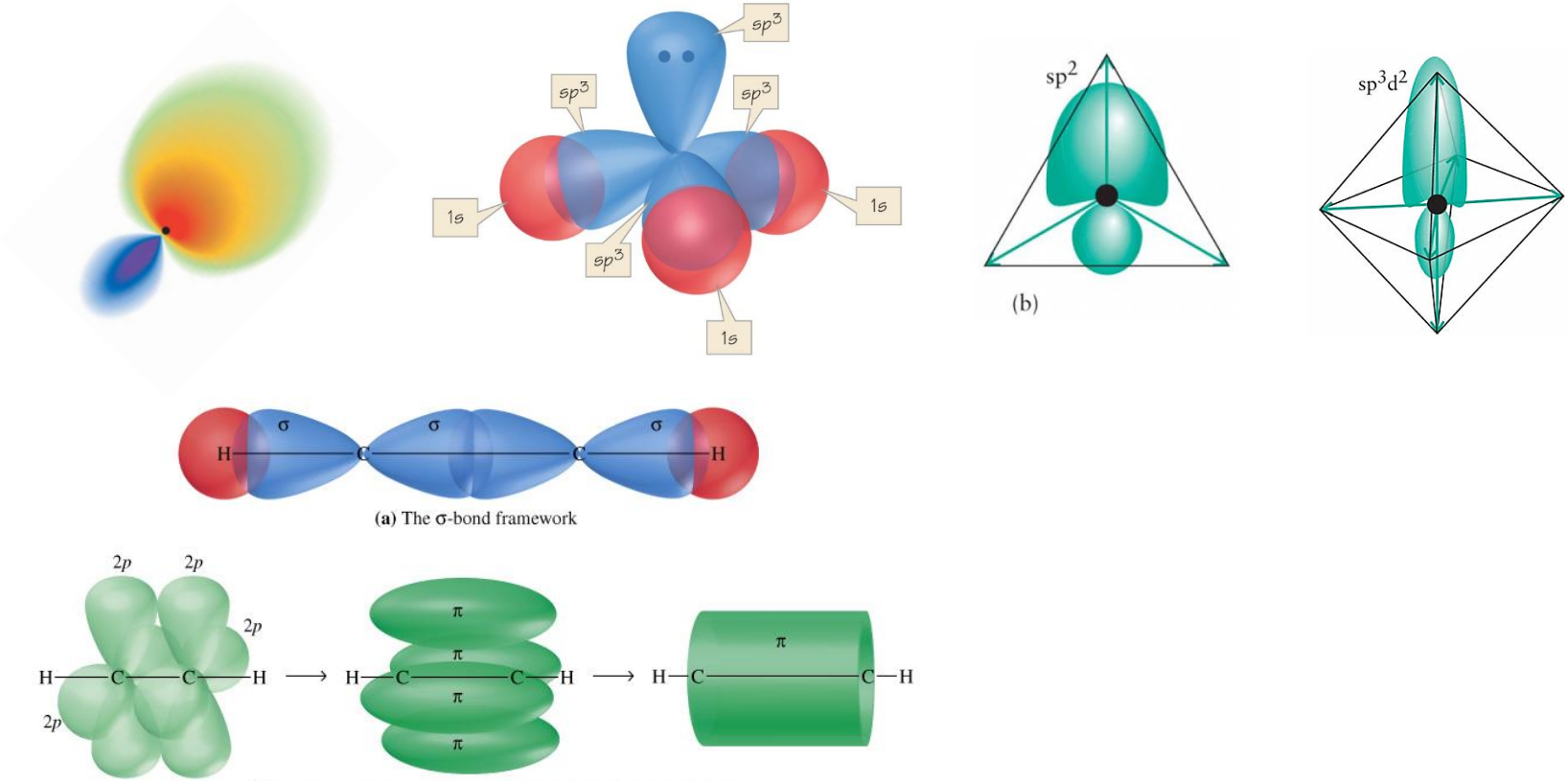
Hybridization Schemes

Electron arrangement around the central atom	Hybrid orbitals (number)	Angle(s) between σ-bonds	Example(s) [underlined atom]
Linear	sp (two)	180°	$\underline{Be}Cl_2$, $\underline{C}O_2$
Trigonal planar	sp^2 (three)	120°	$\underline{B}F_3$, $\underline{C}H_3^+$
Tetrahedral	sp^3 (four)	109.5°	$\underline{C}Cl_4$, $\underline{N}H_4^+$
Trigonal bipyramidal	sp^3d (five)	120°, 90°, and 180°	$\underline{P}Cl_5$
Octahedral	sp^3d^2 (six)	90° and 180°	$\underline{S}F_6$


3d
3p
3s
Isolated P atom
mix
five sp^3d
Hybridized P atom
One of five sp^3d orbitals
One Cl 3p orbital
Cl
P
Isolated S atom
six sp^3d^2
Hybridized S atom
One of six sp^3d^2 orbitals
One F 2p orbital
F
S

Q) Hybrid orbital only for sigma bonding?

: The shape/directionality of the hybrid orbitals allows only sigma bonding.



Q) What is the orbital of the Nitrogen in N_2?

: Again, use the hybrid orbital only when it is necessary.

In fact, we rarely use the hybrid orbital for the terminal atoms and diatomic molecules.

Egg and Chicken probem:
How do we know which hybrid scheme to use?

- Hybridization in itself CANNOT predict molecular shape. It can only explain which atomic orbital contributes to the bond.

Example)

Known tetrahedral shape of methane

→ sp^3 hybrid → bonding of sp^3 and H atoms