Chapter 9

Molecular Geometry & Bonding Theories

I) Molecular Geometry (Shapes)

Chemical reactivity of molecules depends on the nature of the bonds between the atoms as well on its 3D structure

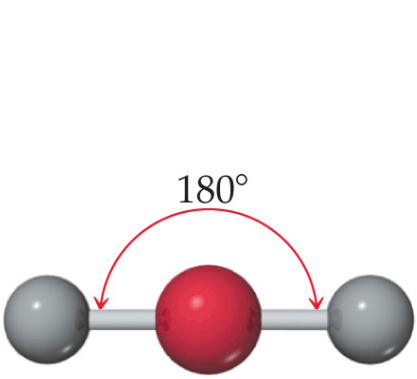
Molecular Geometry

Arrangement or positions of atoms relative to each other

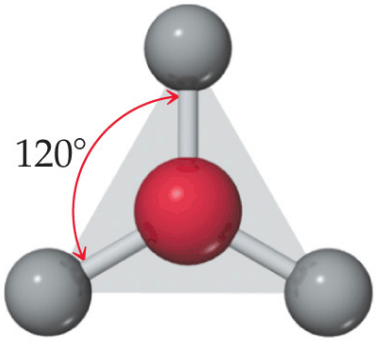
Bond Angles

Angles made by lines joining the nuclei of atoms bonded

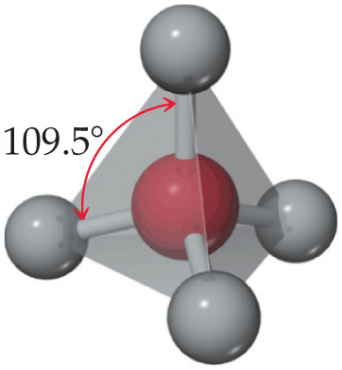
A) Basic AB_n Arrangements



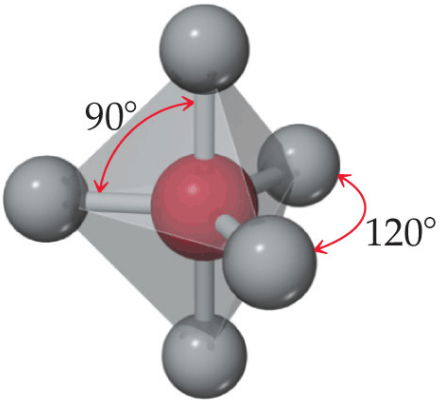
AB_2 linear



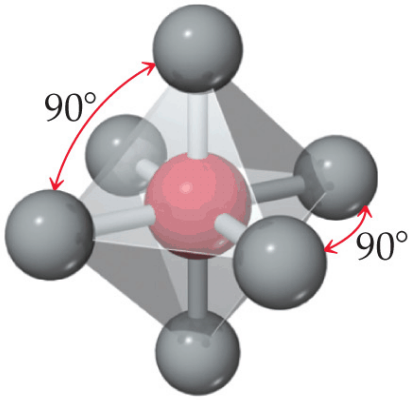
AB_3 trigonal planar



AB_4 tetrahedral

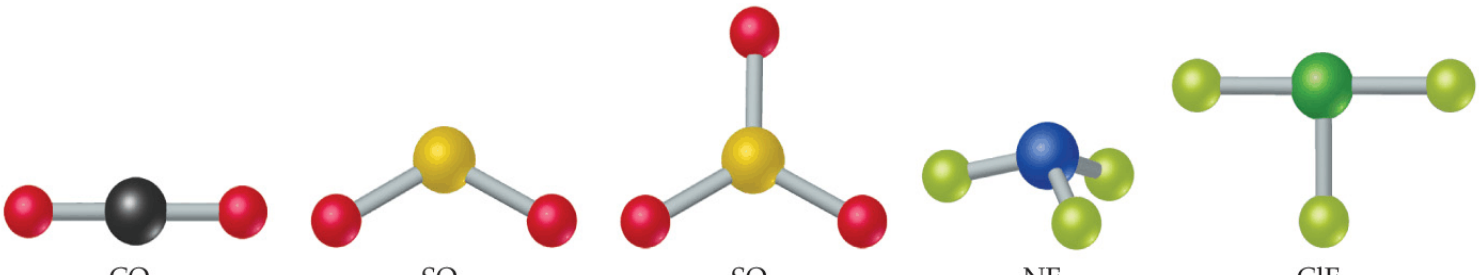


AB_5 trigonal bipyramidal



AB_6 octahedral

Various molecular shapes can arise from the 5 basic AB_n shapes.



CO_2
AB_2 linear

SO_2
AB_2 bent

SO_3
AB_3 trigonal planar

NF_3
AB_3 trigonal pyramidal

ClF_3
AB_3 T-shaped

II) VSEPR Theory

Valence-Shell Elecron-Pair Repulsion

e^- pair: lone pair e^- or bonding e^-
(single, double & triple
bonds treated same)

- really considering

regions of e^- density (domains)

VSEPR: e^- pairs arrange
themselves as far apart
as possible to minimize
repulsions between them

- controls geometry
around central atom

A) Types of Geometry

1) Electron-Domain Geom.

arrangement of bonding and nonbonding e^- pairs (domains) about the central atom

2) Molecular Geom. (Shapes)

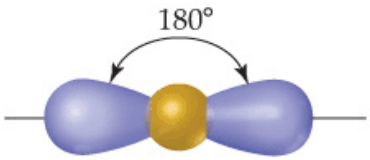
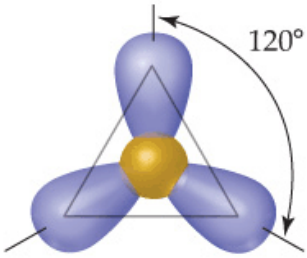
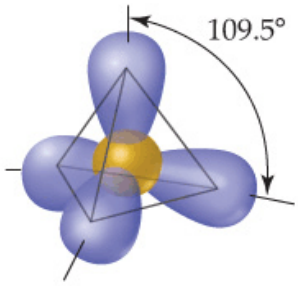
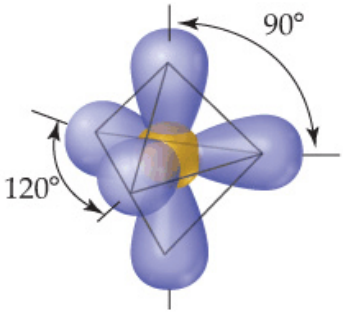
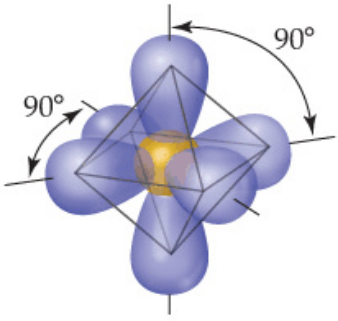
arrangement of bonded atoms about the central atom

described using ONLY the ATOMS

Distinction is very important!

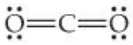
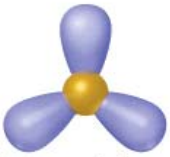
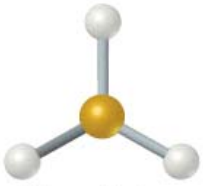
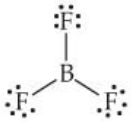
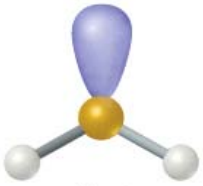
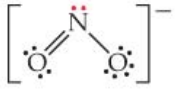
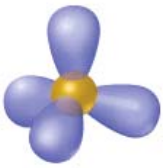
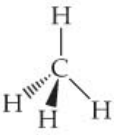
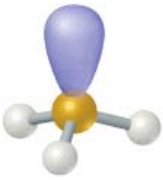
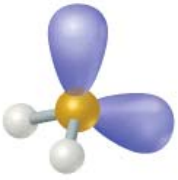
Electron-Domain Geom

TABLE 9.1 • Electron-Domain Geometries as a Function of Number of Electron Domains

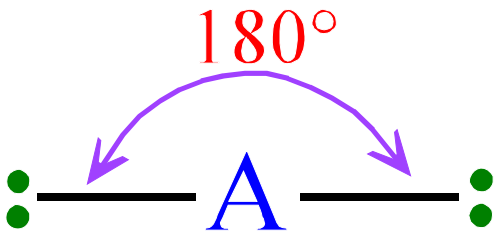
Number of Electron Domains	Arrangement of Electron Domains	Electron-Domain Geometry	Predicted Bond Angles
2		Linear	180°
3		Trigonal planar	120°
4		Tetrahedral	109.5°
5		Trigonal bipyramidal	120° 90°
6		Octahedral	90°

ED and MG for AB_2, AB_3 & AB_4 EDs

TABLE 9.2 • Electron-Domain and Molecular Geometries for Two, Three, and Four Electron Domains around a Central Atom

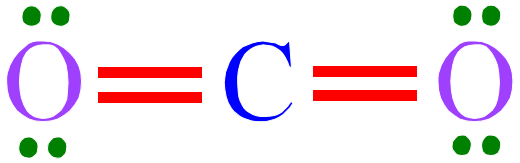
Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
2	 Linear	2	0	 Linear	
3	 Trigonal planar	3	0	 Trigonal planar	
		2	1	 Bent	
4	 Tetrahedral	4	0	 Tetrahedral	
		3	1	 Trigonal pyramidal	
		2	2	 Bent	

B) 2 e^- Pairs

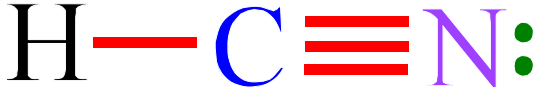


LINEAR

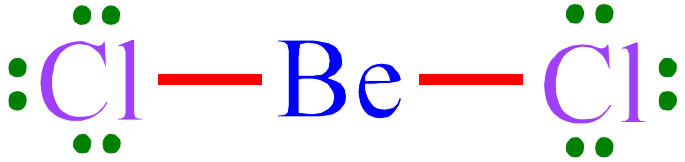
1) CO_2



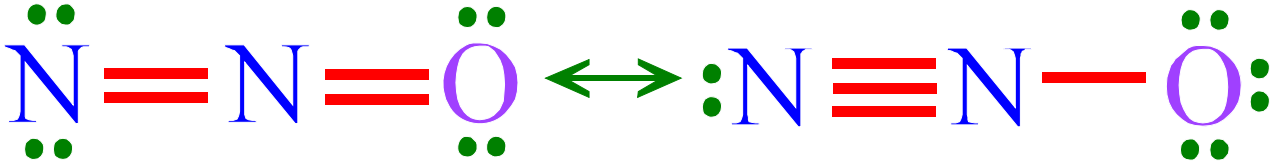
2) HCN



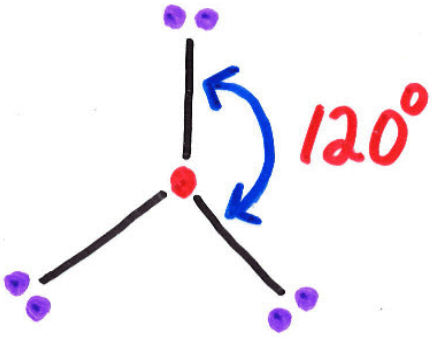
3) $BeCl_2$



4) N_2O



C) 3 e^- Pairs



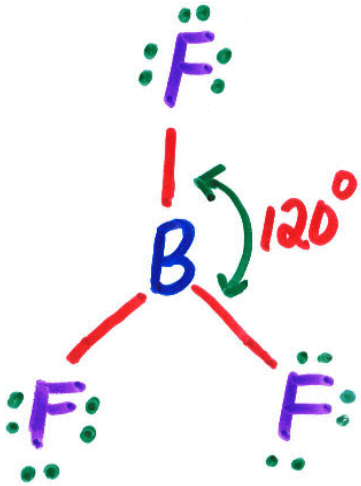
Trigonal Planar

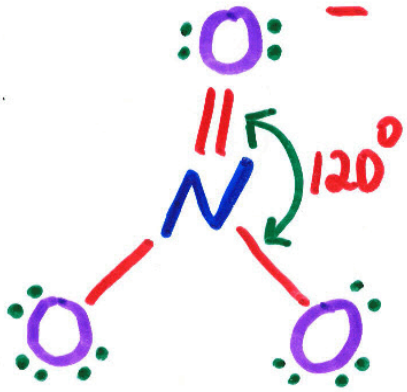
Basic e^- pair geometry

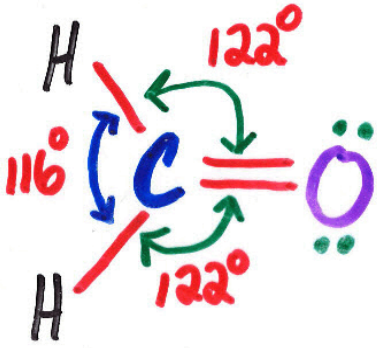
⇒ 2 possible molecular geom. or shapes

1) 3 bonding pairs

BF_3 NO_3^- H_2CO



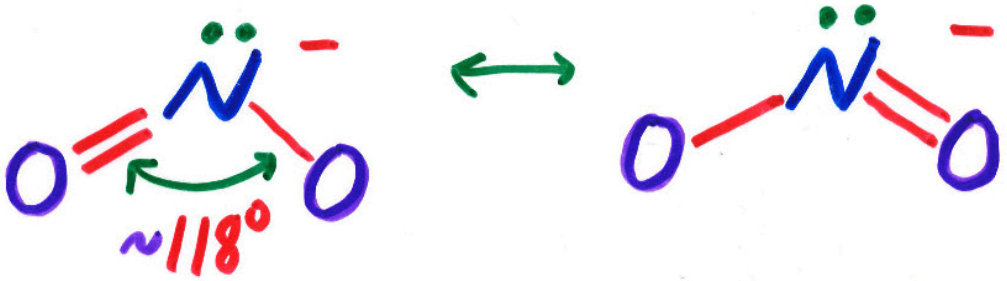




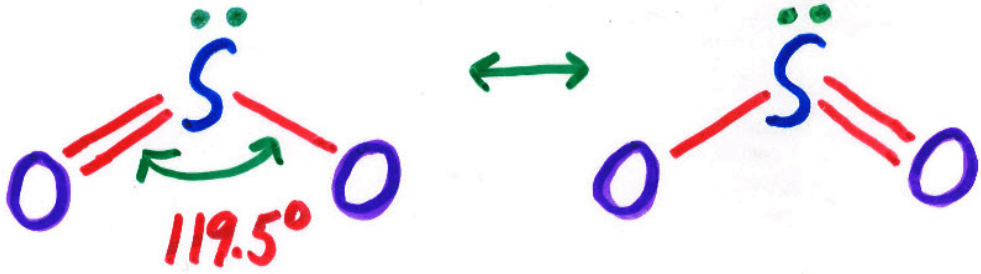
2) 2 bonding & 1 nonbonding

BENT (angular); Angle < 120°

NO_2^-



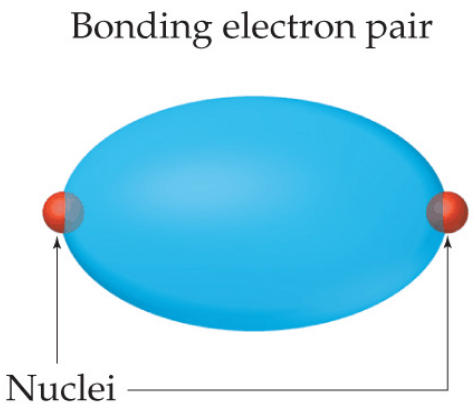
SO_2

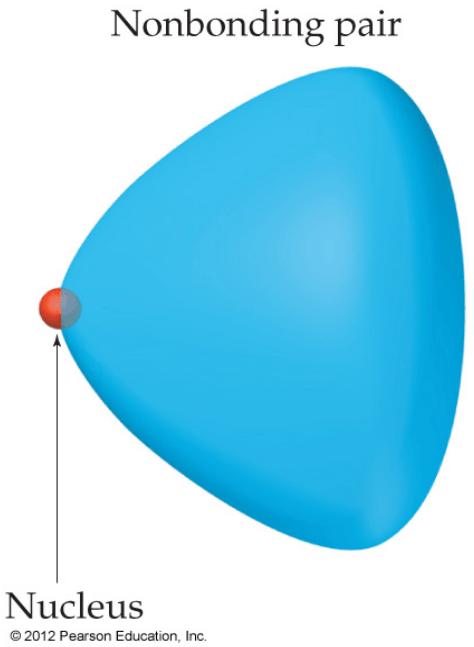


Molecular geom. is determined by arrangement of e⁻-pairs but is described by positions of the nuclei.

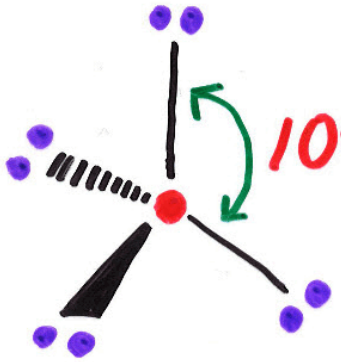
Why is the bond angle not exactly 120° ?

Lone-pair e^- (nbe) not trapped between two atoms and thus spread out and take up more space. Repulses bonding pairs and reduces the bond angles.





D) 4 e^- Pairs

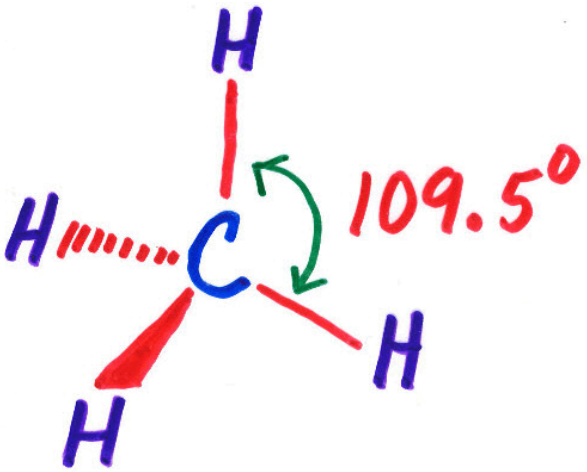


Tetrahedral

3 possible molecular geom. or shapes

1) 4 bonding pairs

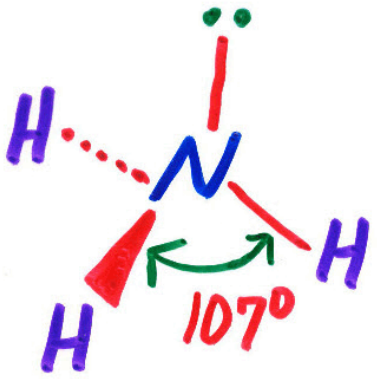
CH_4 PH_4^+ NH_4^+ SO_4^{2-}



Tetrahedral

2) 3 bonding & 1 nonbonding

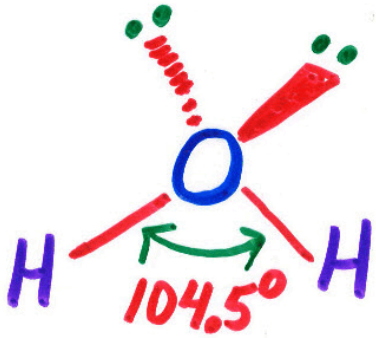
$:NH_3$ $H_3O:^+$ $:AsO_3^{3-}$



Trigonal pyramidal

3) 2 bonding & 2 nonbonding

$H_2O:$ $:\ddot{N}H_2^-$



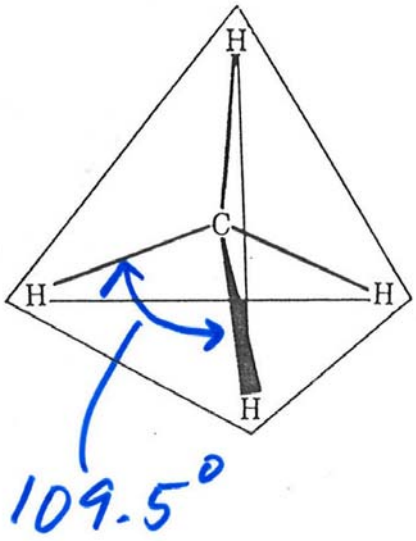
Bent

Note: bond angle dec. by ~ 2° for each lone pair of e⁻

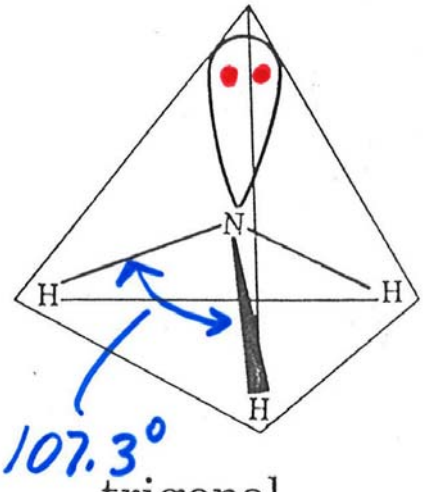
Arrangement of Electron Pairs and Geometry of Some Simple Molecules

Tetrahedral arrangement of electron pairs

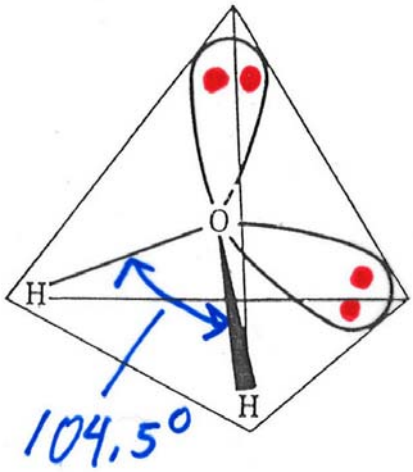
Molecular geometry:



tetrahedral



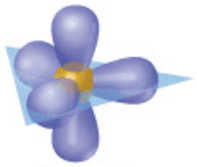
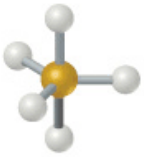
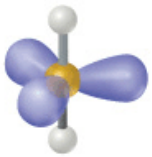
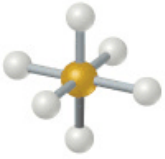
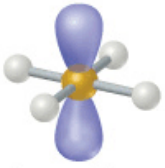
trigonal pyramidal



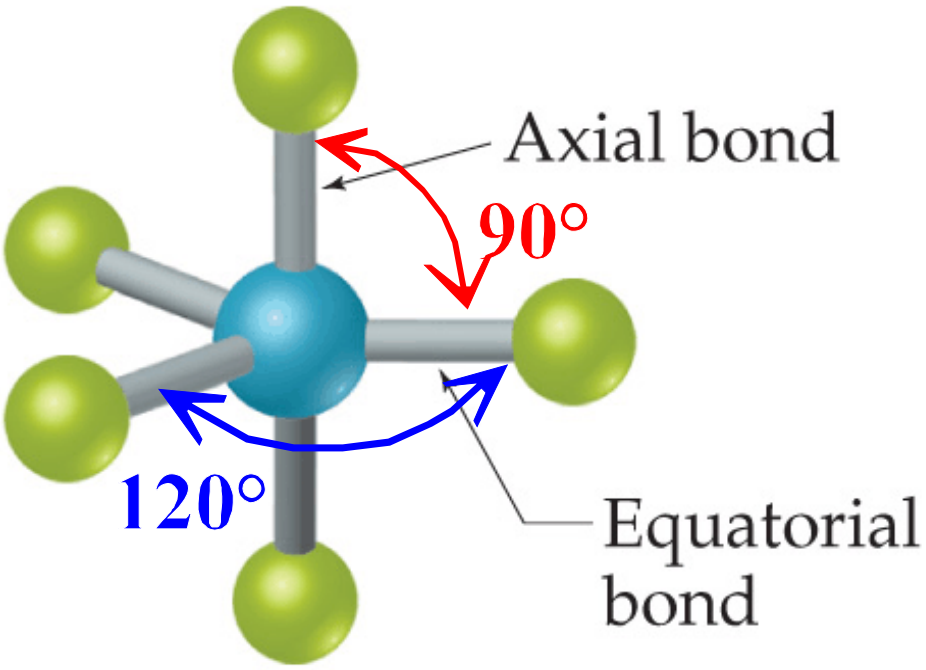
angular

ED and MG for AB_5 & AB_6 EDs

TABLE 9.3 • Electron-Domain and Molecular Geometries for Five and Six Electron Domains around a Central Atom

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
5	 Trigonal bipyramidal	5	0	 Trigonal bipyramidal	PCl_5
		4	1	 Seesaw	SF_4
		3	2	 T-shaped	ClF_3
		2	3	 Linear	XeF_2
6	 Octahedral	6	0	 Octahedral	SF_6
		5	1	 Square pyramidal	BrF_5
		4	2	 Square planar	XeF_4

E) 5 e^- Pairs Domains



Two "different" bonds.

3 equatorial bonds forming a trigonal planar arrangement w. 120° angles

2 axial bonds which are perpendicular to the trigonal planar equatorial bonds (90° angles)

4 Molecular Geometries

1) trigonal bipyramidal

   Angles: 120° & 90°

2) seesaw

   Angles: ~ 120° & ~ 90°

3) T-shaped

   Angles: ~ 90°

4) linear

   Angle: 180°

a) Lone-pair e^- & Bonding Pairs

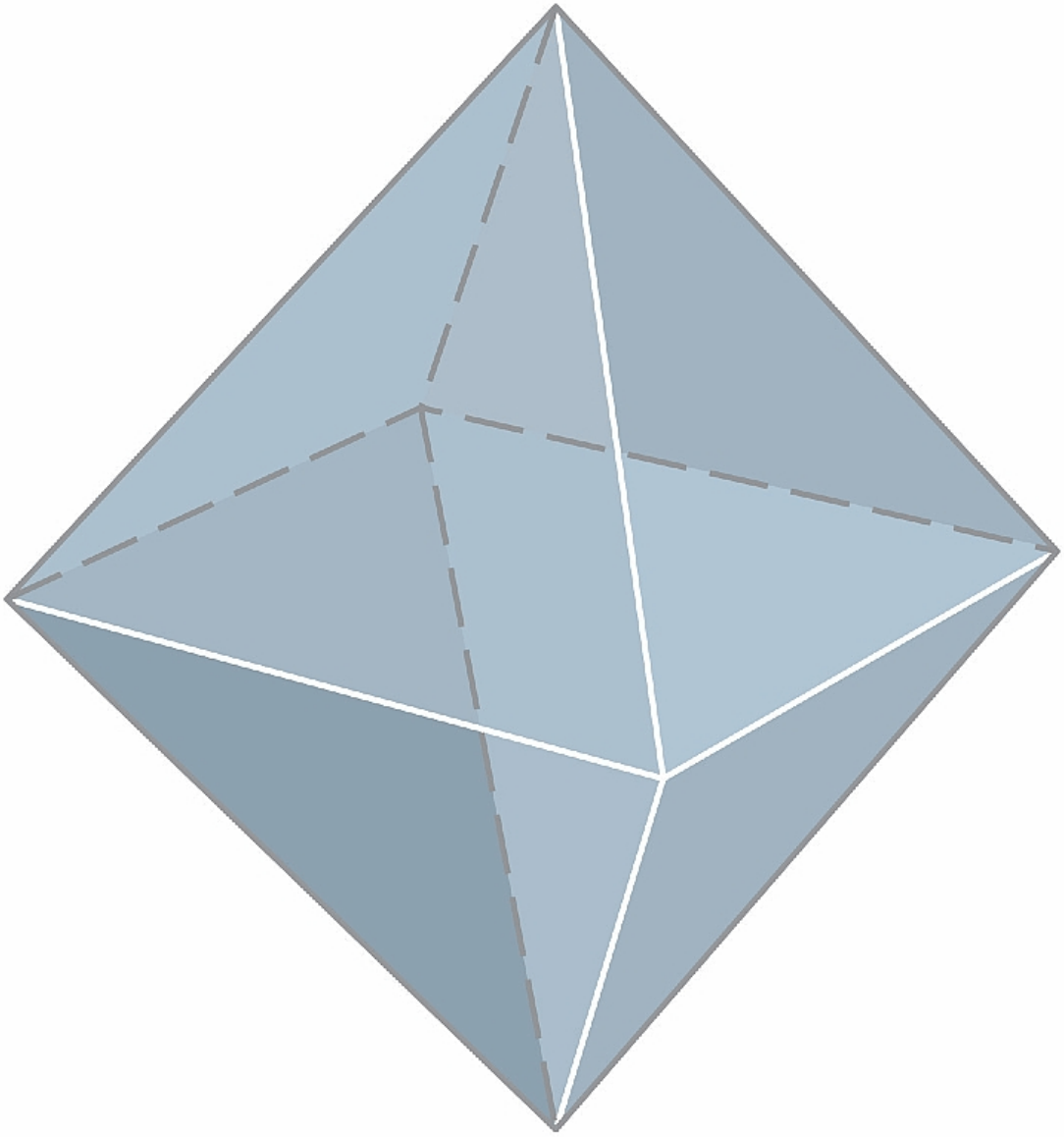
In 2, 3 and 4:

lpe^- wind up in the equatorial positions to maximize separation and reduce repulsions.

In 2 & 3 lpe^- pushes bonding pairs closer together and reduces angles

F) 6 e^- Pair Domains

Octahedral structure



3 Molecular Geometries

1) octahedral

Angles: 90°

2) square pyramidal

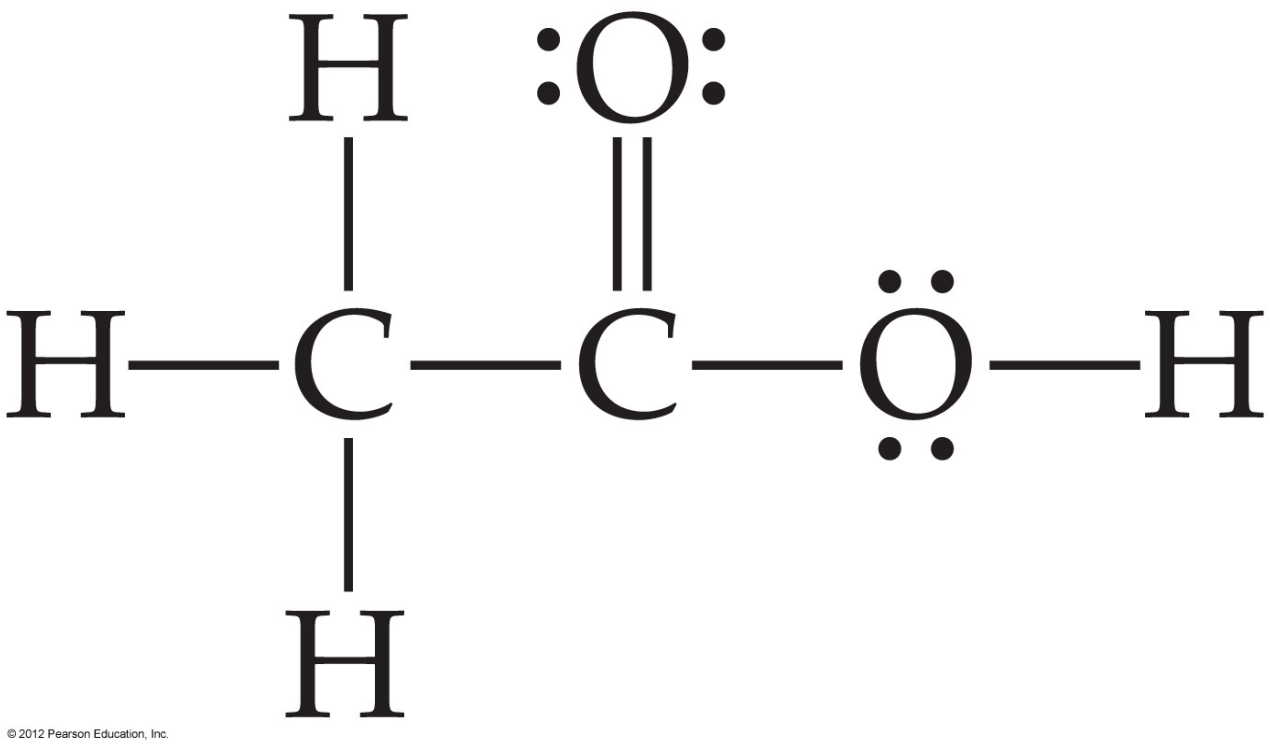
Angles: ~ 90°

3) square planar

Angles: 90°

G) Shapes of Larger Molecules

Same rules apply to individual atoms in larger molecules.



III) Molecular Shape and Polarity

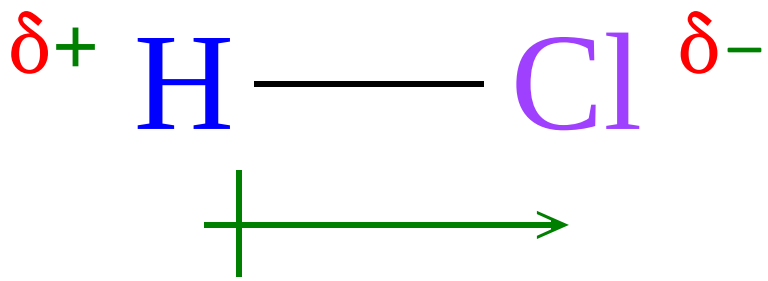
MUST have polar bonds

MUST consider shape

If the centers of + and – charges do not coincide, the molecule is polar.

A) Diatomic Molecules

A diatomic molecule w. a polar bond is polar



B) Polyatomic Molecules

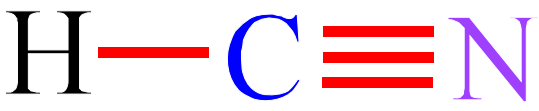
For polyatomic molecules geometry is very important in predicting if the centers of + and – charges coincide.

The dipole moment is for the entire molecule

vector sum of ALL of the individual bond dipole moments.

1) $BeCl_2$ 

2) CO_2 

3) HCN 

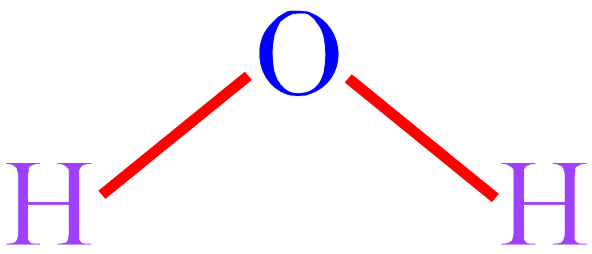
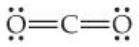
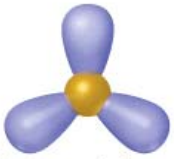
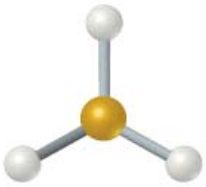
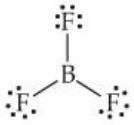
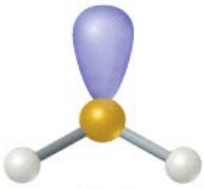
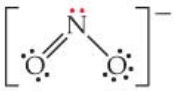
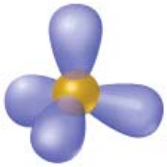
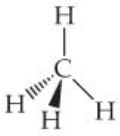
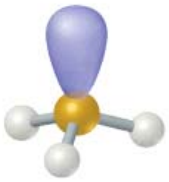
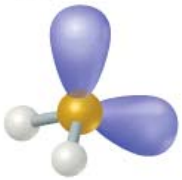
4) H_2O 

TABLE 9.2 • Electron-Domain and Molecular Geometries for Two, Three, and Four Electron Domains around a Central Atom

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
2	 Linear	2	0	 Linear	
3	 Trigonal planar	3	0	 Trigonal planar	
		2	1	 Bent	
4	 Tetrahedral	4	0	 Tetrahedral	
		3	1	 Trigonal pyramidal	
		2	2	 Bent	

5) PCl_5

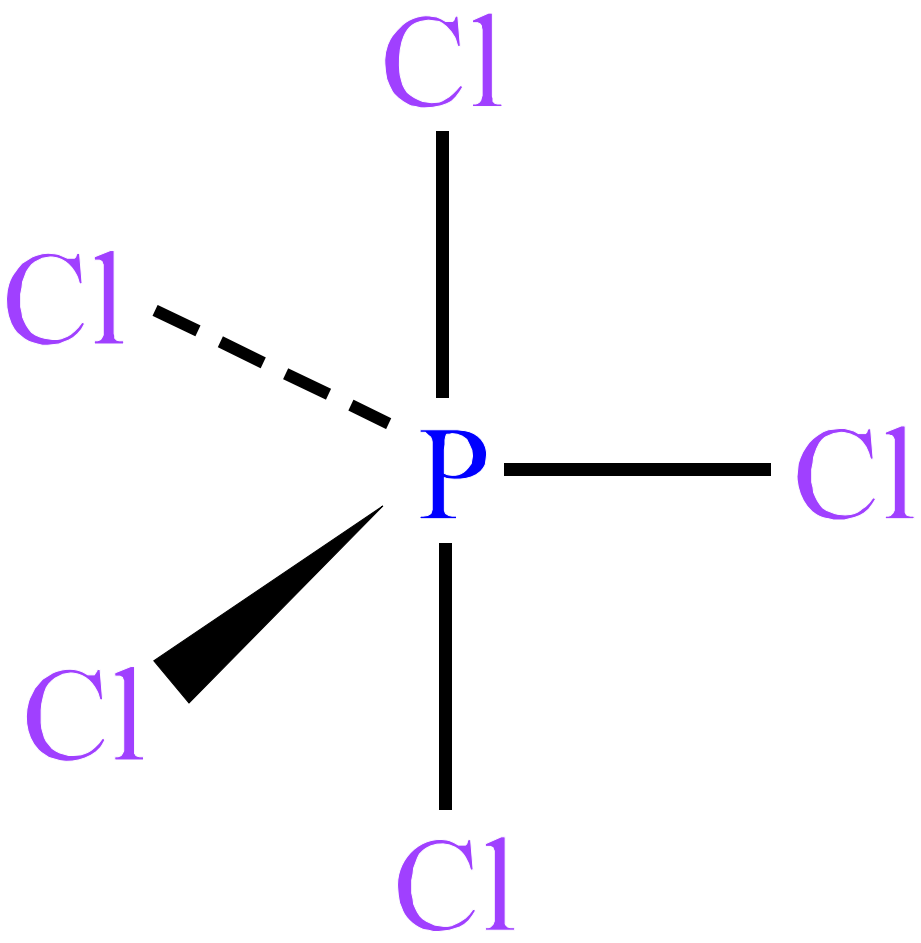
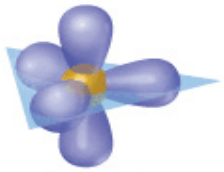
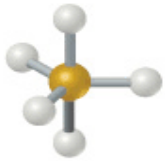
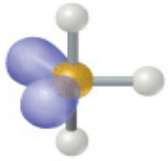
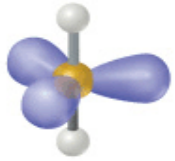
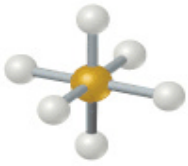
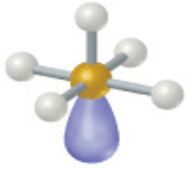
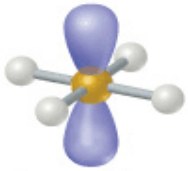


TABLE 9.3 • Electron-Domain and Molecular Geometries for Five and Six Electron Domains around a Central Atom

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
5	 Trigonal bipyramidal	5	0	 Trigonal bipyramidal	PCl_5
		4	1	 Seesaw	SF_4
		3	2	 T-shaped	ClF_3
		2	3	 Linear	XeF_2
6	 Octahedral	6	0	 Octahedral	SF_6
		5	1	 Square pyramidal	BrF_5
		4	2	 Square planar	XeF_4

IV) Covalent Bonding and Orbital Overlap

Wave Interference:

e^- behave like any other wave & when 2 waves meet they can interact constructively or destructively.

Constructive interference:

waves add together and
get a bonding orbital

Destructive interference:

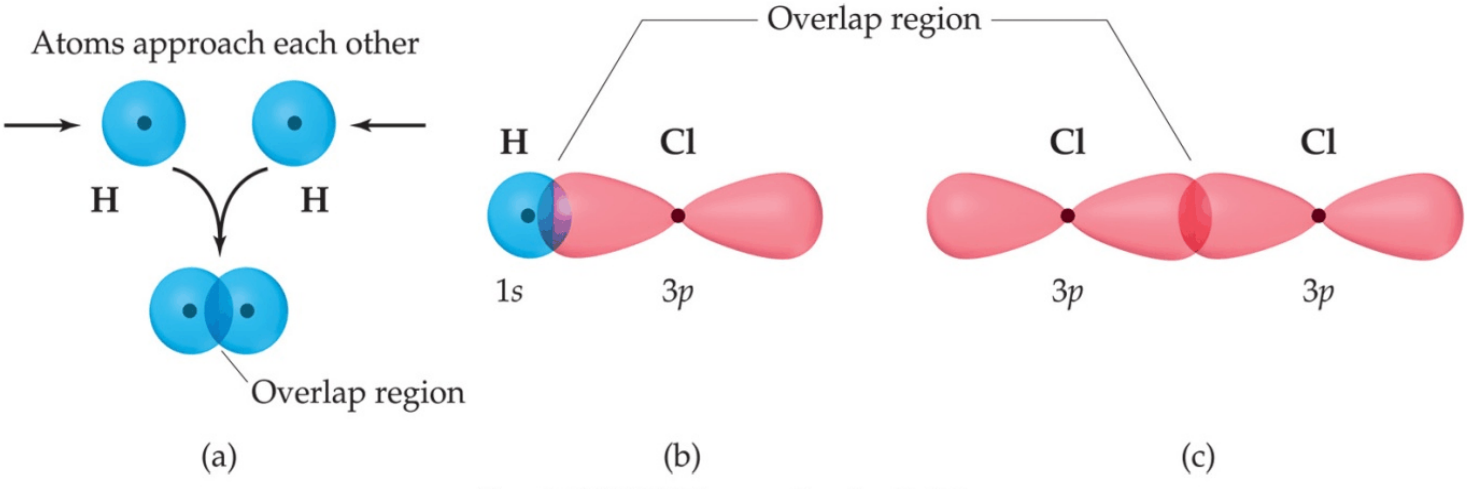
waves subtract from each other
and get an antibonding orbital

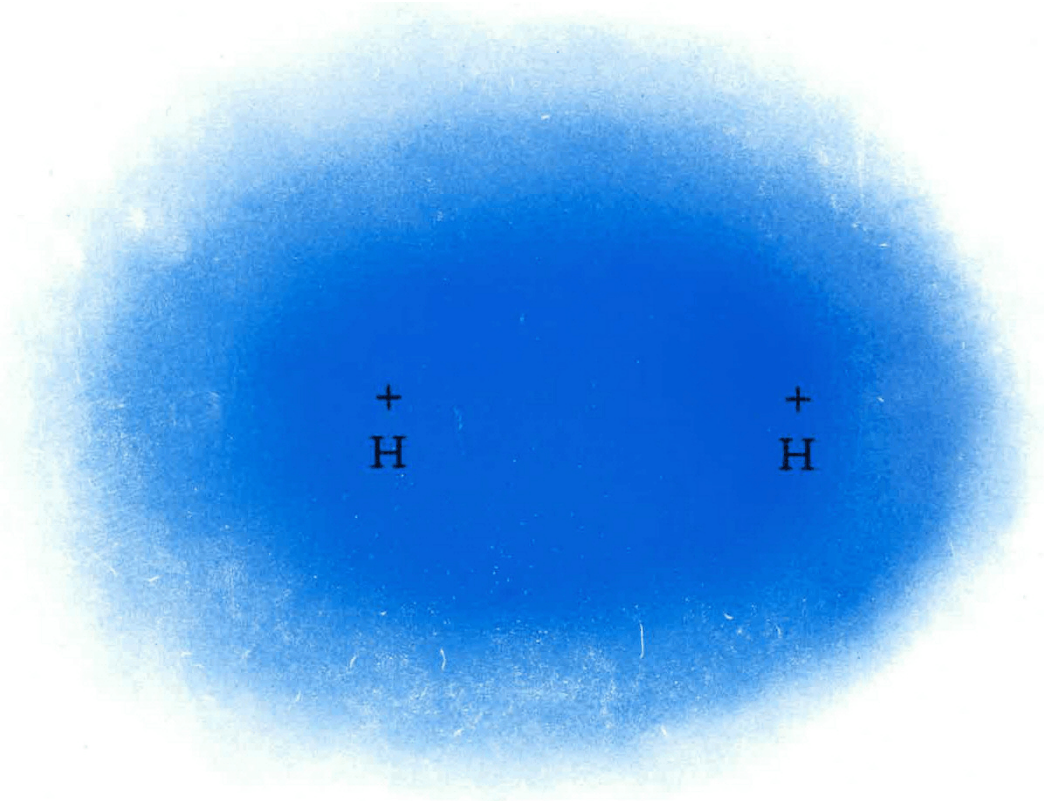
A) Sigma (σ) Bonds

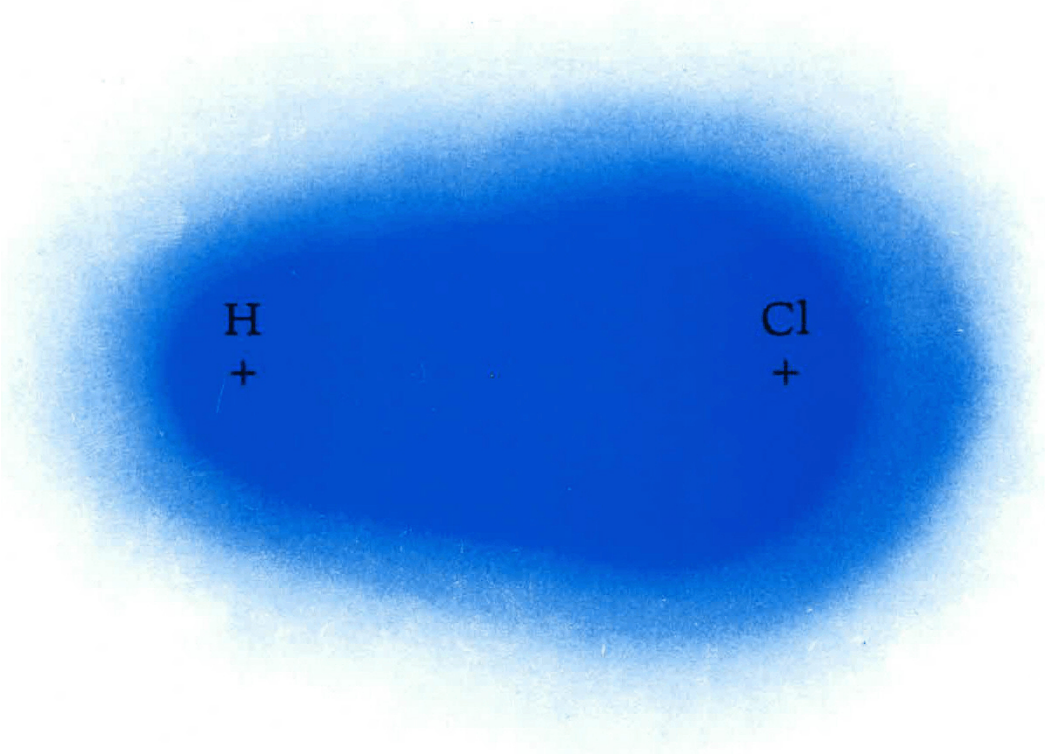
e^- density concentrated between nuclei along the internuclear axis

Results from overlap of 2 "*s*" orb., "*s*" & "*p*" orb., 2 "*p*" orb. end-to-end, "*s*" & hybrid orb., 2 hybrid orb (end on)

$$s + s \Rightarrow \sigma$$
$$s + p \Rightarrow \sigma$$
$$p + p \Rightarrow \sigma$$



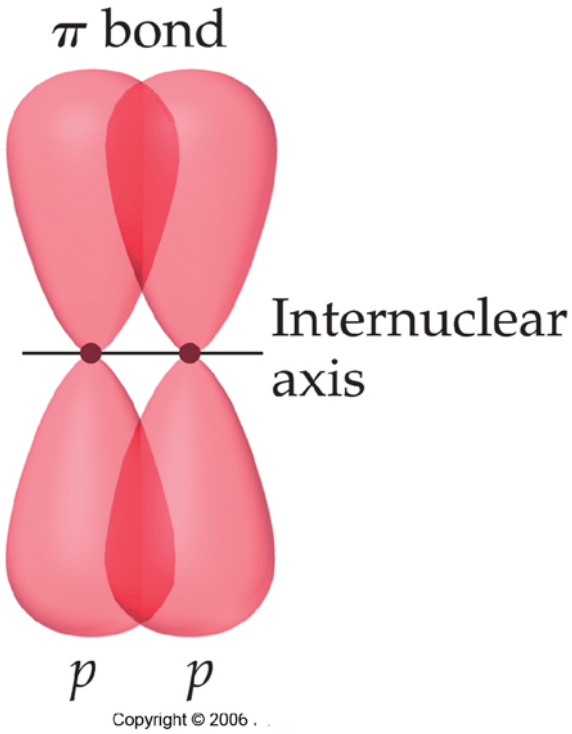

+
H
+
H

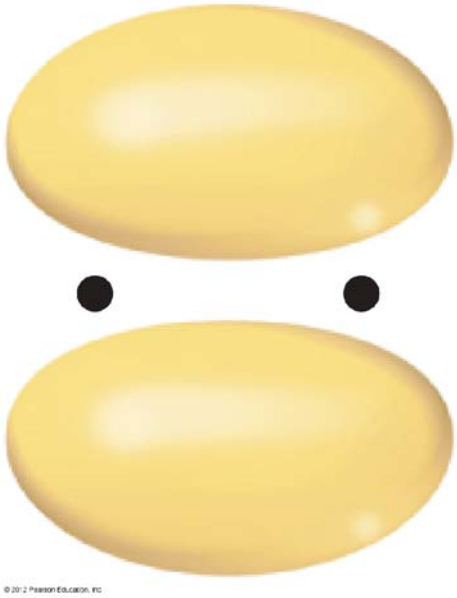

H
+
Cl
+

A) Pi (π) Bonds

e^- density above and below internuclear axis

Results from sideways overlap of parallel ***p*** orbitals





V) Hybrid Orbitals - Valence Bond Theory

Bonds are created by orbital overlap to produce **σ** or **π** bonds

To explain many observed molecular geometries, pure "s" and "p" atomic orbitals are combined to produce a set of "hybrid" orbitals on atoms.

These hybrid orbitals then form bonds between atoms producing the correct geometry.

A) *sp* Hybrid Orbitals

BeF_2 linear with 2 single bonds

Be atom:

[He] $\underline{\uparrow\downarrow}$ $\underline{\quad}$ $\underline{\quad}$ $\underline{\quad}$

2s 2p

Should not form bonds

- no singly occupied orbitals

As it forms bonds it can absorb enough energy to "promote" one 2*s* e^- to a 2*p* orbital.

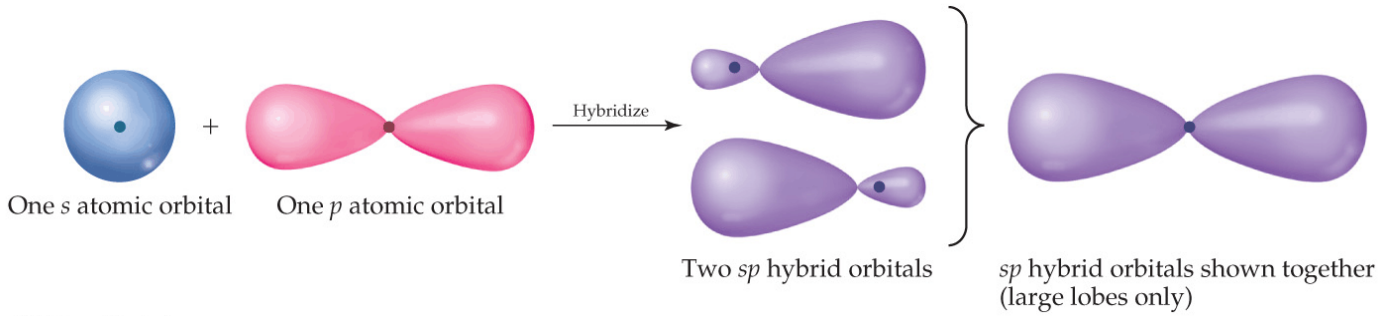
[He] $\underline{\uparrow}$ $\underline{\uparrow}$ $\underline{\quad}$ $\underline{\quad}$

2s 2p

The *s* and *p* orbitals then mix or "hybridize" to form two degenerate ***sp*** *hybrid* orbitals.

These ***sp*** *hybrid* orbitals have two lobes like a p orbital.

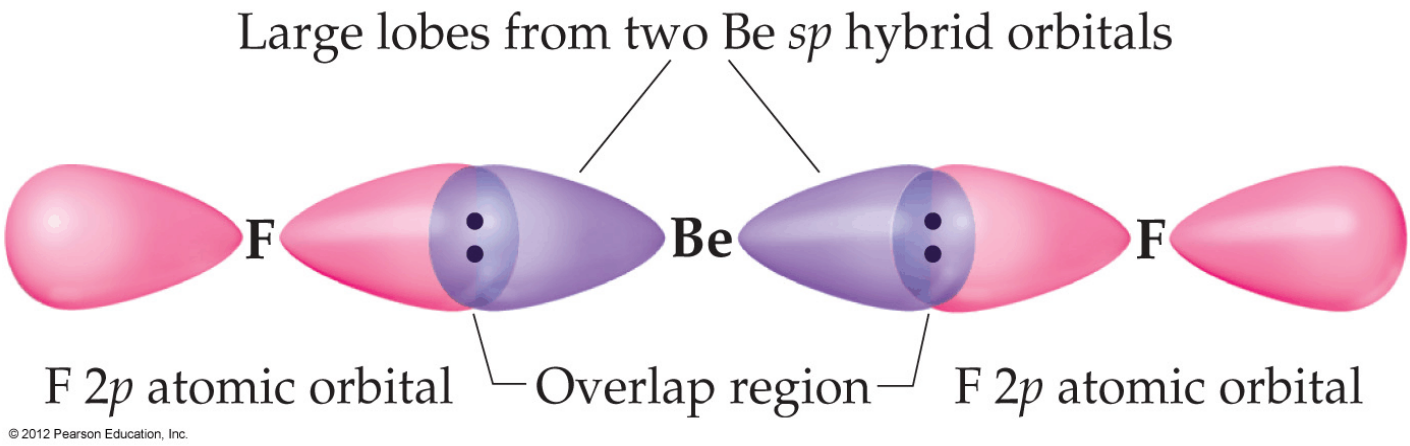
One of the lobes is larger and more rounded as is the *s* orbital.



These two degenerate orbitals align themselves 180° from each other:

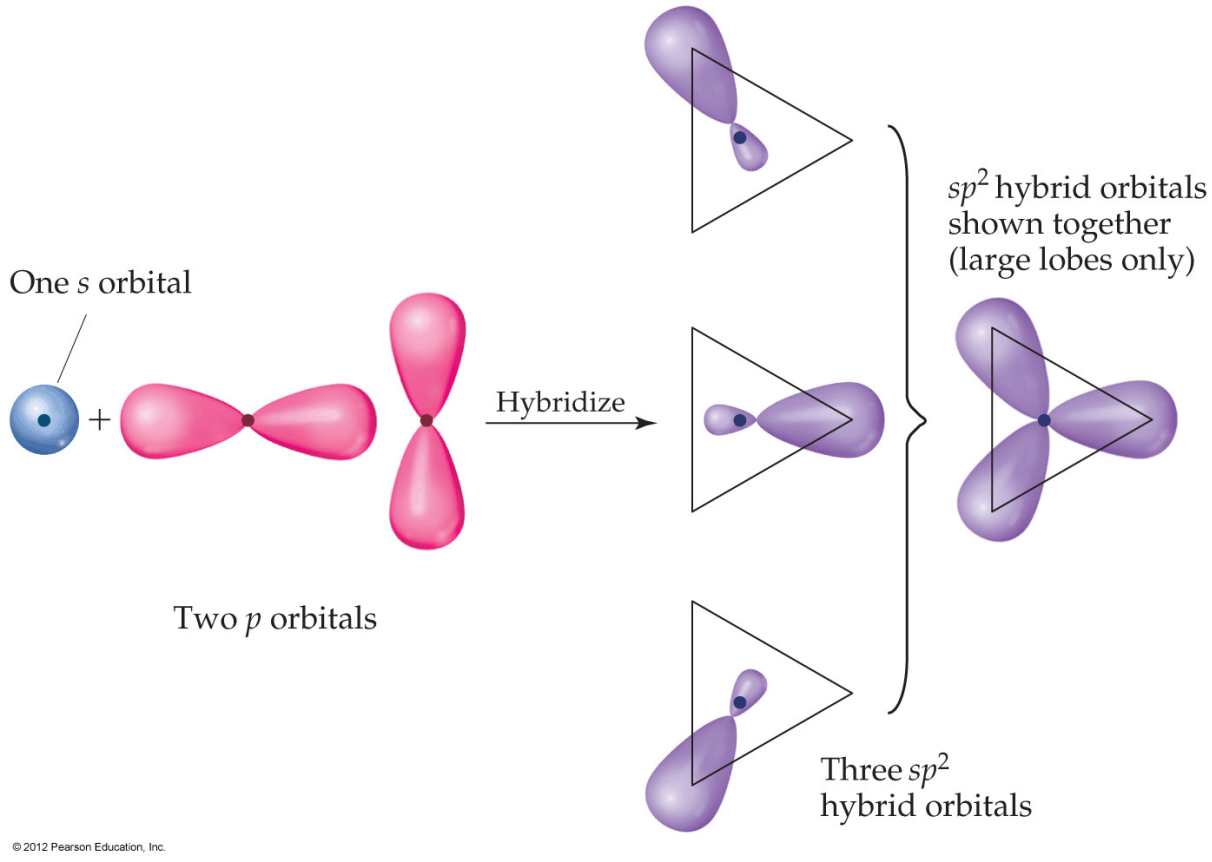
linear

Consistent with the observed geometry of Be compounds.



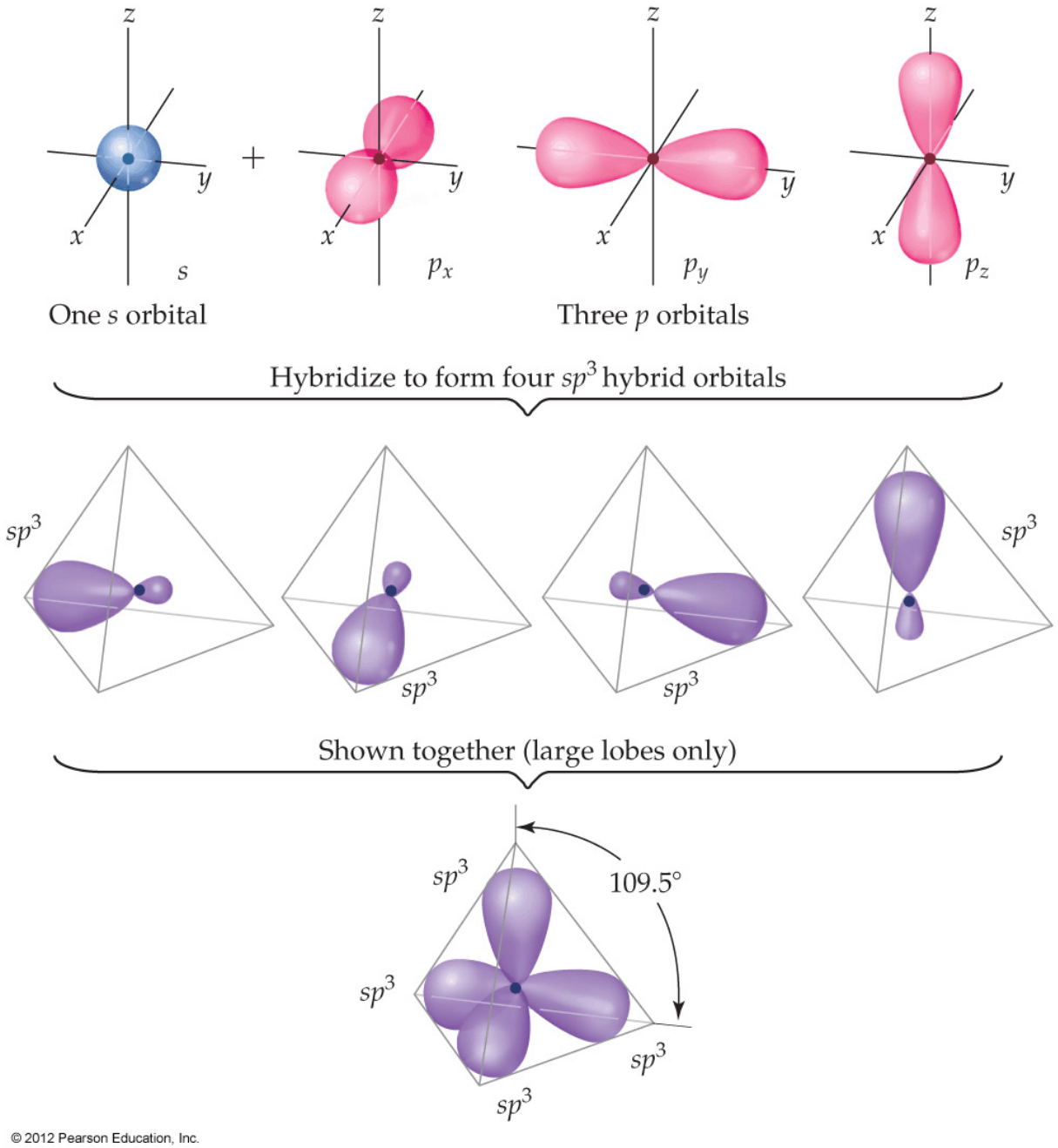
B) sp^2 Hybrid Orbitals

BF_3: trigonal planar, 120°



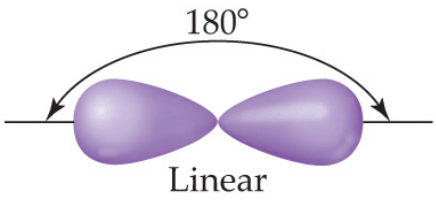
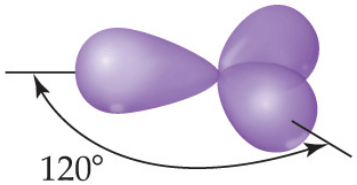
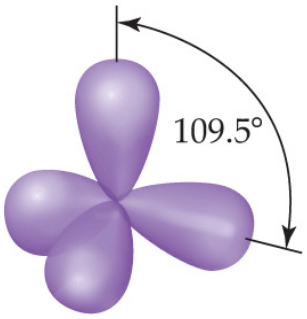
C) sp^3 Hybrid Orbitals

CH_4: tetrahedral, 109.5°



D) Hybrid Orbitals - Summary

TABLE 9.4 • Geometric Arrangements Characteristic of Hybrid Orbital Sets

Atomic Orbital Set	Hybrid Orbital Set	Geometry	Examples
s,p	Two *sp*	 Linear	BeF_2, $HgCl_2$
s,p,p	Three sp^2	 Trigonal planar	BF_3, SO_3
s,p,p,p	Four sp^3	 Tetrahedral	CH_4, NH_3, H_2O, NH_4^+

VI) Multiple Bonds

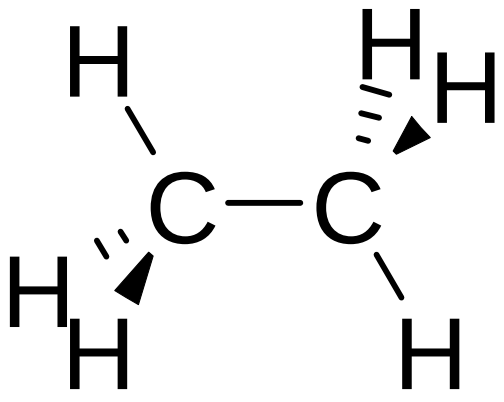
Overlap of hybrid orbitals with *s* or *p* or other hybrid orbitals (end-to-end):

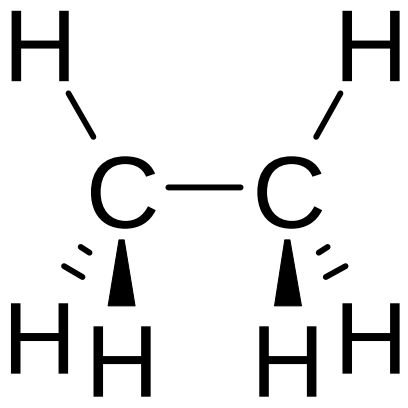
σ bonds.

e^- density is symmetric about the internuclear axis of **σ** bond, groups can rotate about the bond without breaking it.

- free rotation about **σ** bonds

Single bonds are **σ** bonds





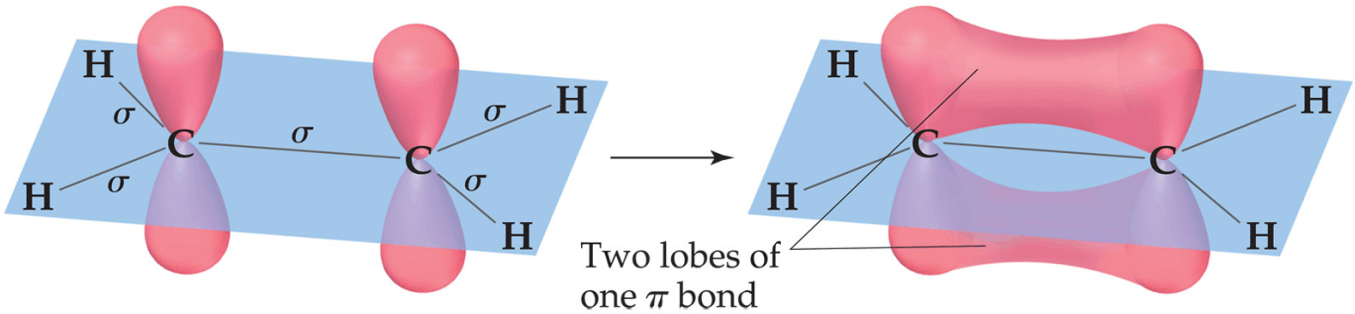
Multiple bonding requires π bonds

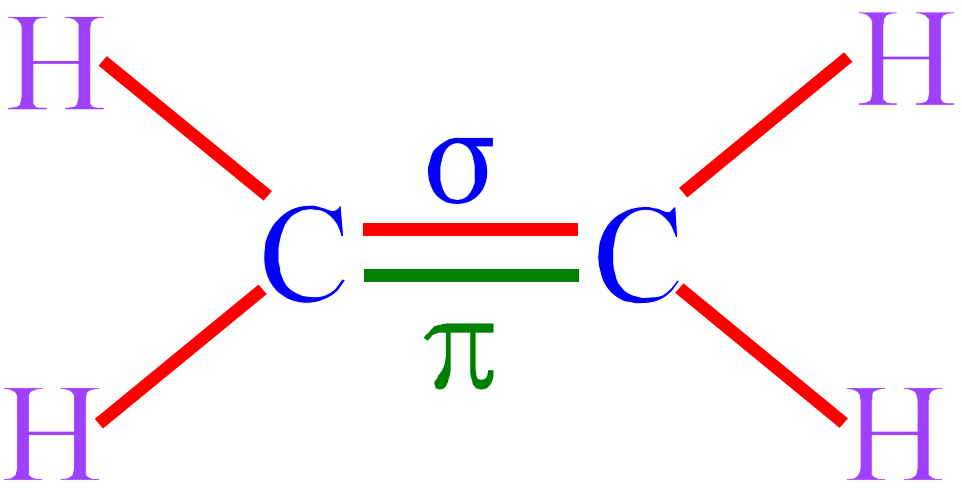
A) Double Bonds

Look at ethylene: C_2H_4

σ bonds between C and H and both C atoms using ***sp***^{2} hybrid orbitals

leaves "***p***" orbitals on each C which can overlap sideways to form **π** bonds





Trigonal planar around each C atom
- whole molecule is planar

π bond is perpendicular to plane

No free rotation between C atoms

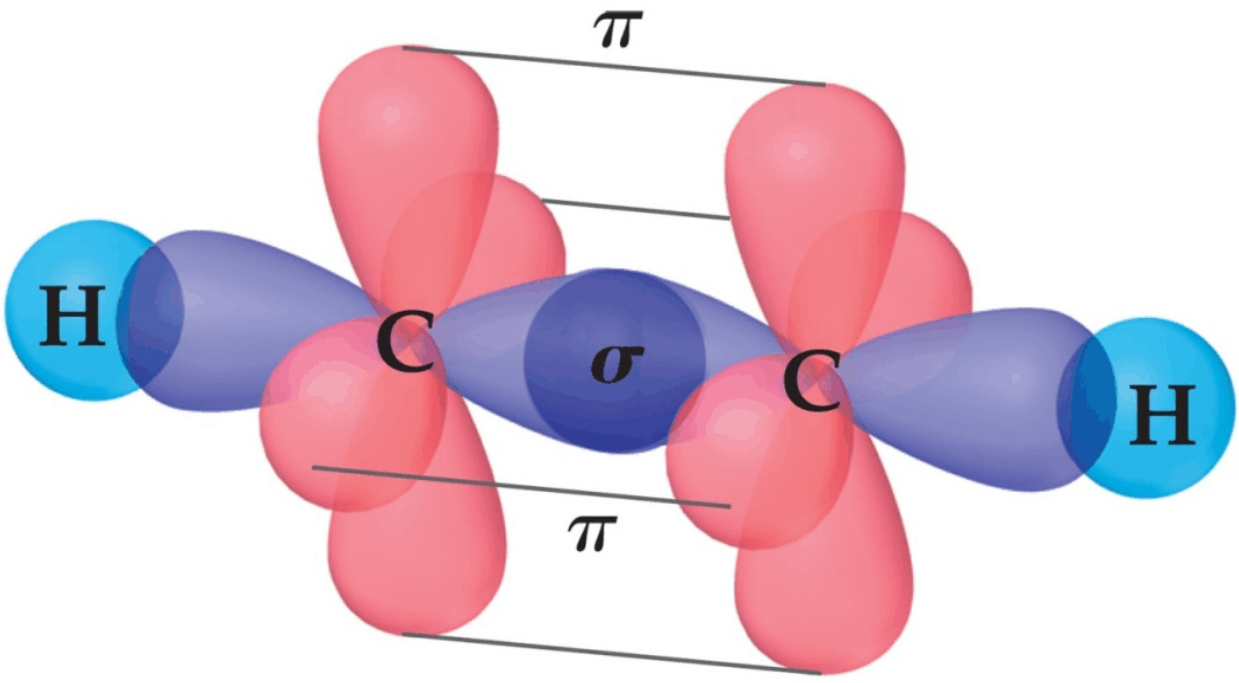
Double bond ≡ 1 σ + 1 π

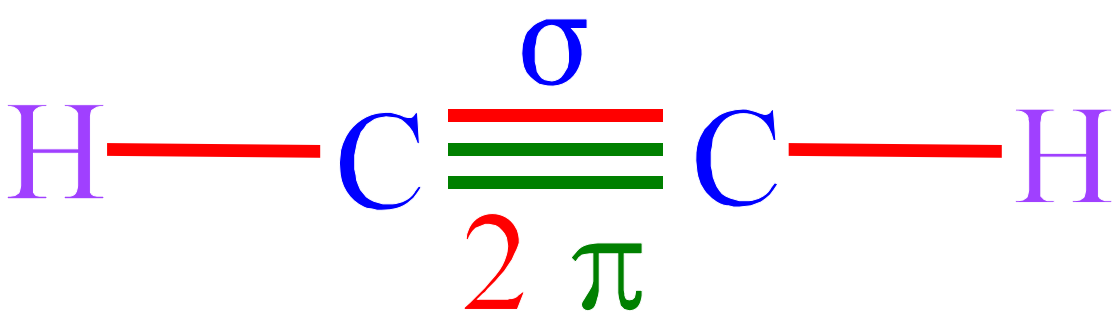
B) Triple Bonds

Look at acetylene: C_2H_2

σ bonds between C and H and both C atoms using ***sp*** hybrid orbitals

leaves 2 sets of "***p***" orbitals on each C which can overlap sideways to form 2 sets of **π** bonds





Linear around each C atom

Triple bond ≡ 1 σ + 2 π

C) Resonance & Delocalized Bonding

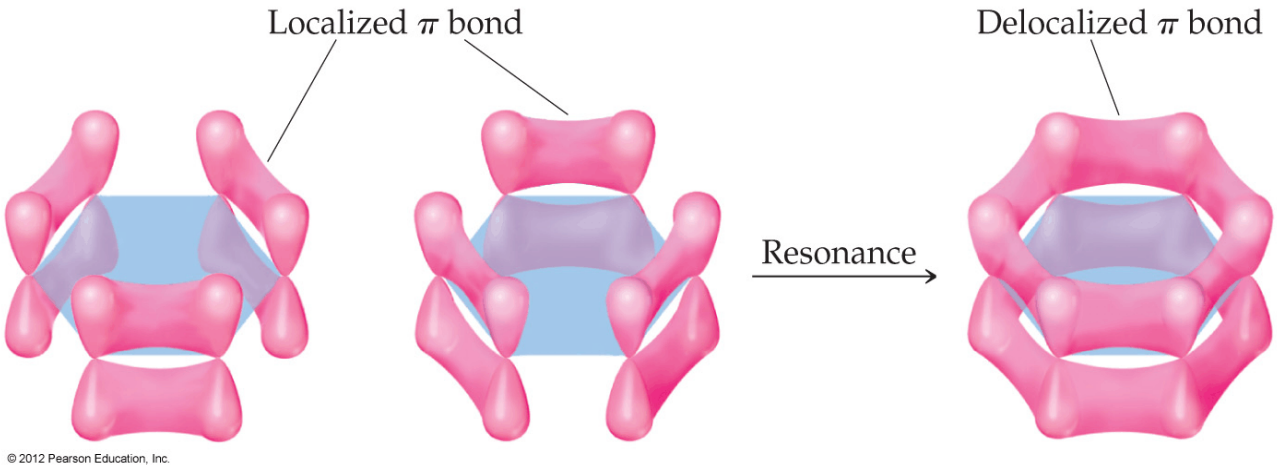
Localized σ and π bonds can't explain resonance.

Instead can think of atoms forming delocalized π bonding.

Benzene:

Each C atom is sp^2 hybridized and has 1 atomic *p* orbital left over

- form a delocalized π bond



VII) Molecular Orbitals

Some things not explained by VB theory

In MO theory orbitals are constructed as combination of AOs from **ALL** atomsin the molecule.

The MO can span more than 2 atoms.

Each MO can still only contain 2 e^-

In VB theory orbitals are mixed on individual atoms 1st then bonded together as needed

In MO theory the orbitals of all atoms mix and are then used to form the lowest energy molecular orbitals.