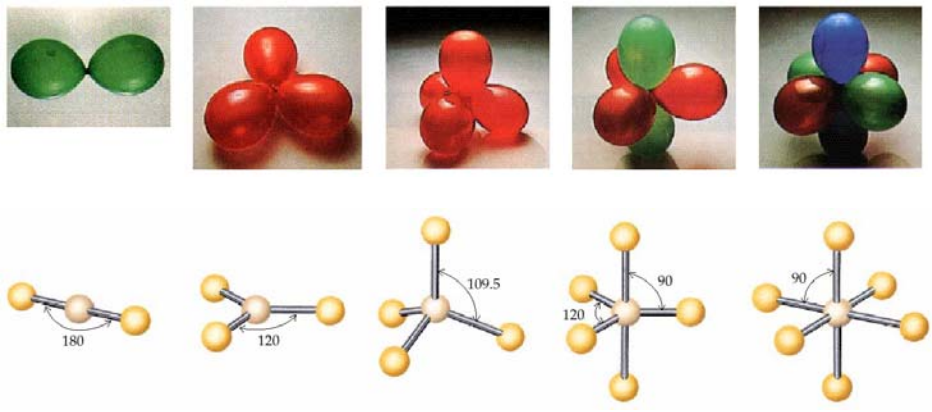
Chemical Bonding II: Molecular Geometry and Hybridization of Atomic Orbitals

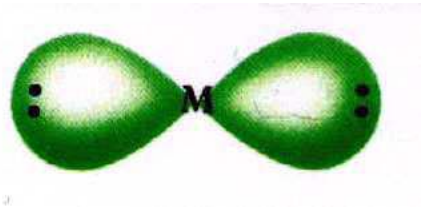
Chapter 10

Electron Pair Geometries in VSEPR Theory

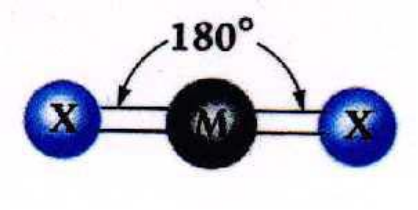


Linear	Trigonal planar	Tetrahedral	Trigonal Bipyramidal	Octahedral
180°	120°	109.5°	120 and 90°	90°

Electron Pair Geometry Molecular Geometry

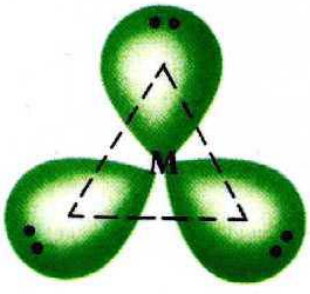


linear

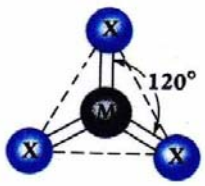


Linear
(AB_2)

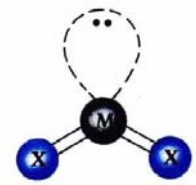
Electron Pair Geometry Molecular Geometry



Trigonal planar

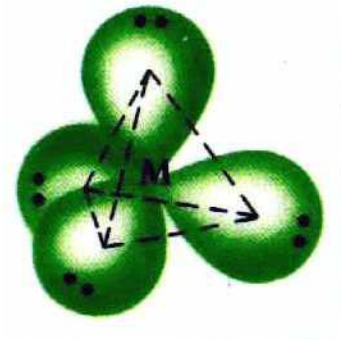


Trigonal planar
(AB_3)

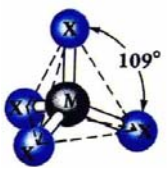


Bent
(AB_2E)

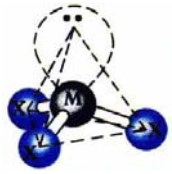
Electron Pair Geometry — Molecular Geometry



Tetrahedral



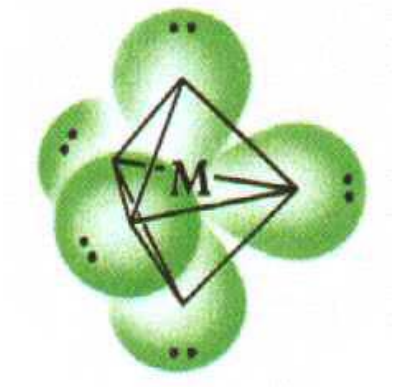
Tetrahedral
(AB_4)



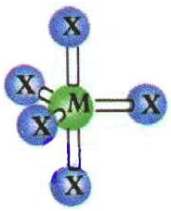
Pyramidal
(AB_3E)

Bent
(AB_2E_2)

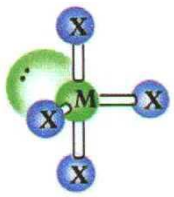
Electron Pair Geometry — Molecular Geometry



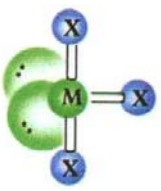
Trigonal Bipyramidal



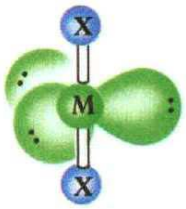
Trigonal Bipyramidal (AB_5)



Unsymmetrical Tetrahedron (AB_4E)



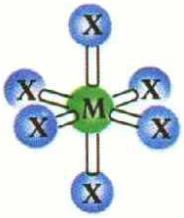
T-shaped (AB_3E_2)



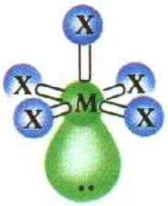
Linear (AB_2E_3)

Electron Pair Geometry Molecular Geometry

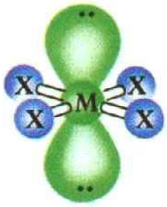
Octahedral



Octahedral
(AB_6)

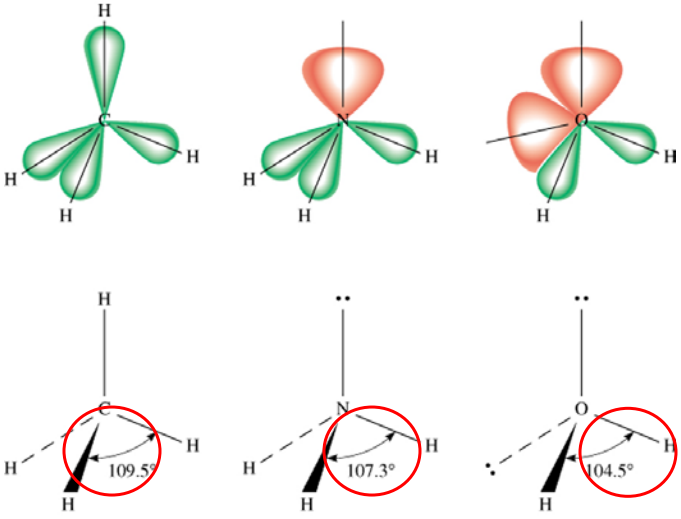


Square
pyramidal
(AB_5E)



Square planar
(AB_4E_2)

Lone Pairs Distort Bond Angles



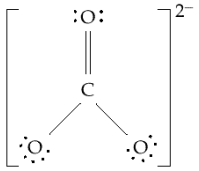
bonding-pair vs. bonding pair repulsion < **lone-pair vs. bonding pair repulsion** < **lone-pair vs. lone pair repulsion**

Applying VSEPR Theory

1. Determine the Lewis structure
2. Determine the number of electron pairs (or clouds) around the CENTRAL ATOM – multiple bonds count as ONE CLOUD (see next slide).
3. Find out the appropriate VSEPR geometry for the specified number of electron pairs, both bonding and lone pairs.
4. Use the positions of <u>atoms</u> to establish the resulting molecular geometry.

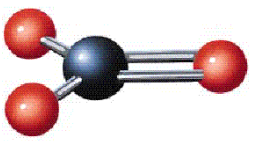
Multiple Bonds and Molecular Geometry

Multiple bonds count as one -

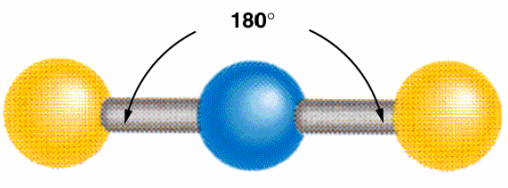


Lewis structure

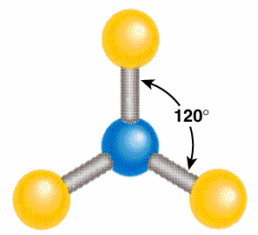
e.g. 4 bonding pairs around C, but trigonal planar instead of tetrahedral.

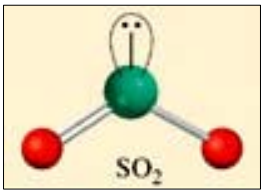


LINEAR - AB_2 e.g. $BeCl_2$

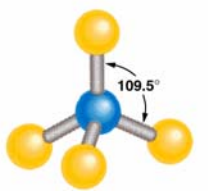


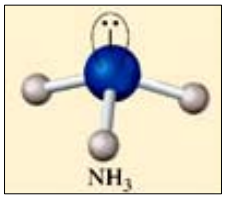
TRIGONAL PLANAR - BF_3 (AB_3)
- SO_2 (AB_2E)

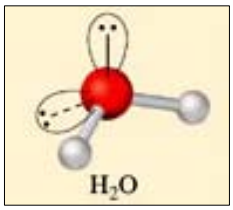




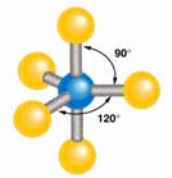
TETRAHEDRAL - CH_4 (AB_4)
- NH_3 (AB_3E)
- H_2O (AB_2E_2)

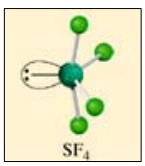


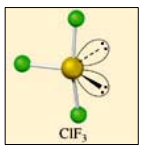


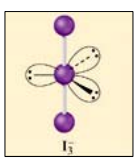


TRIGONAL BIPYRAMIDAL - PCl_5 (AB_5)
- SF_4 (AB_4E)
- ClF_3 (AB_3E_2)
- I_3^- (AB_2E_3)

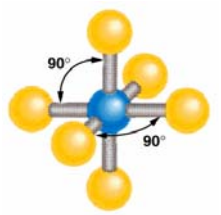


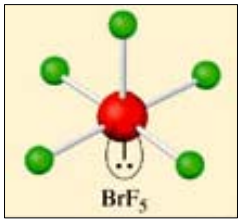


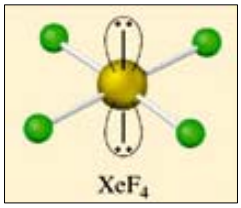




OCTAHEDRAL - SF_6 (AB_6)
- BrF_5 (AB_5E)
- XeF_4 (AB_4E_2)

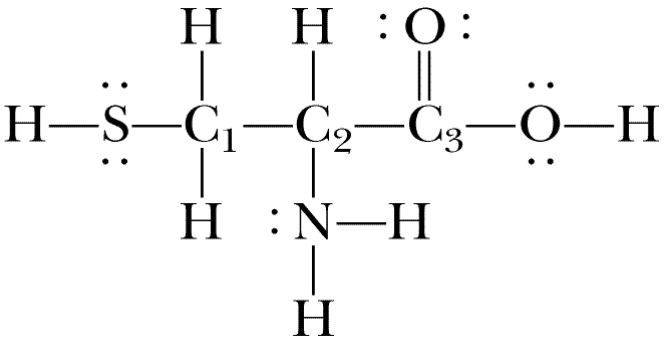






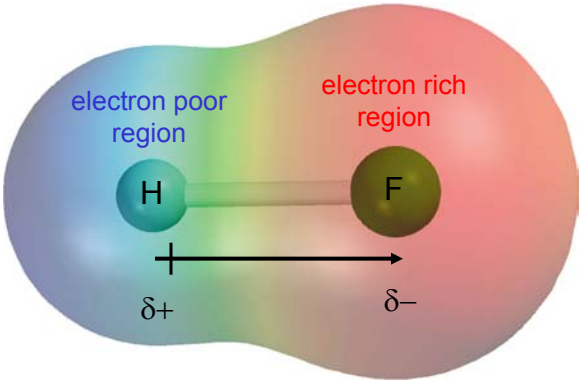
Example 10.1 Use the VSEPR model to predict the geometry of the following molecules and ions: (a) AsH_3, (b) OF_2, (c) $AlCl_4^-$, (d) I_3^-, (e) C_2H_4

Molecular Geometries of Molecules with more than 1 Central Atom

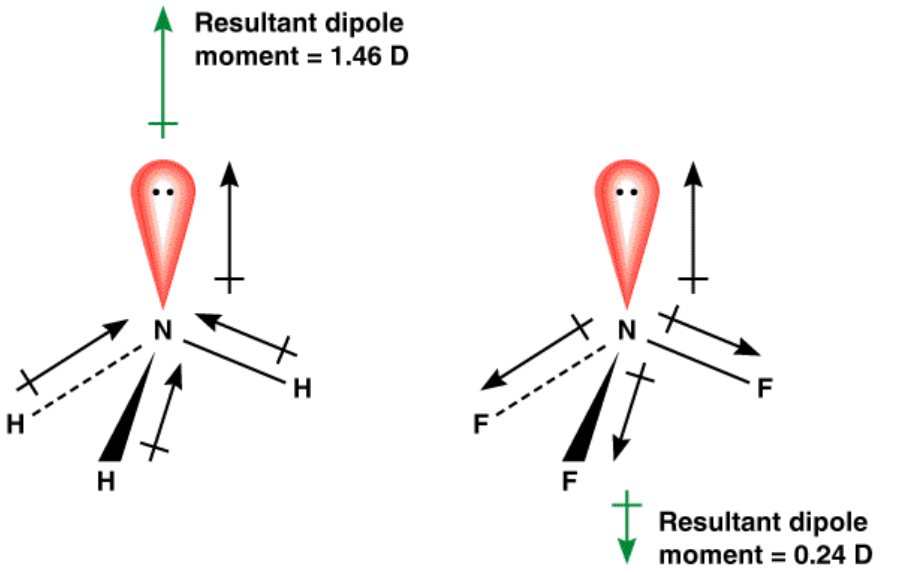


cysteine

Dipole Moments and Polar Molecules

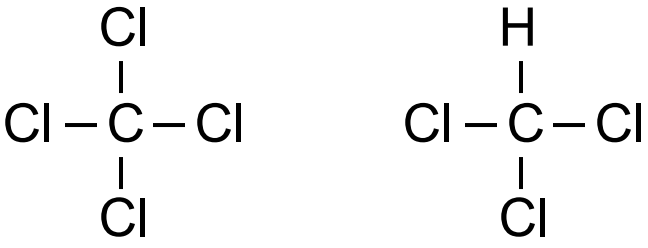


Bond Moments and Resultant Dipole Moments

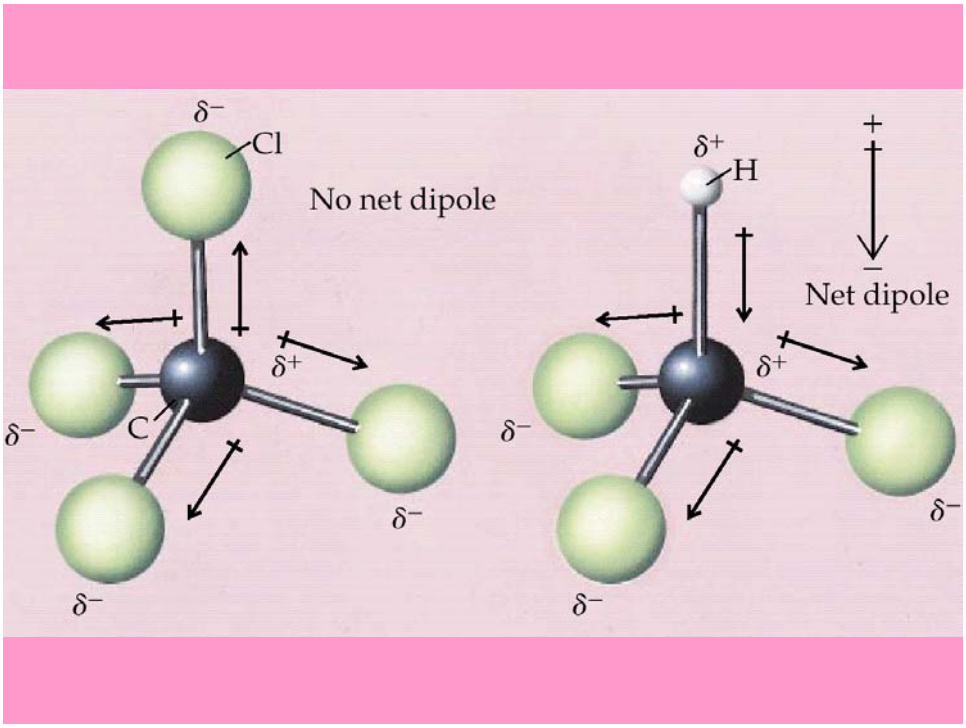


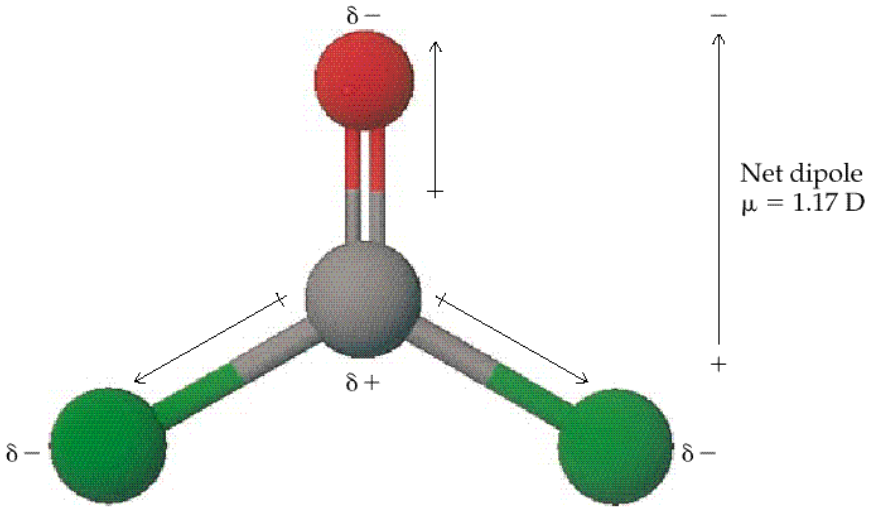
10.2

CCl_4 vs $CHCl_3$

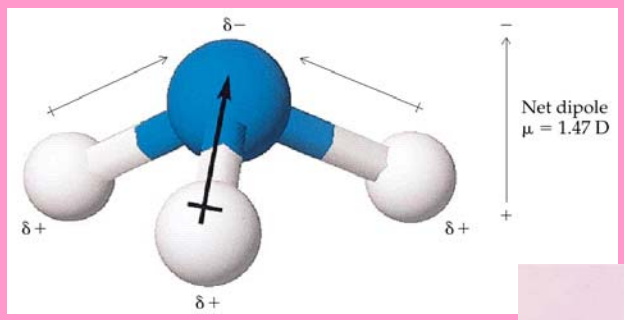


Which molecule is polar? You must look at the geometry to decide.

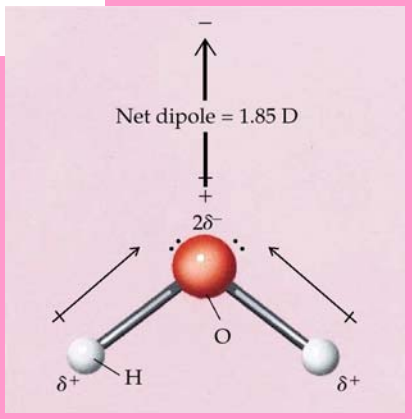

δ−
Cl
No net dipole
δ+
δ−
C
δ+
δ−
δ−
δ+
H
+
−
Net dipole
δ+
δ−
δ−
δ−


δ −
Net dipole
μ = 1.17 D
δ +
δ −
δ −

Cl_2CO

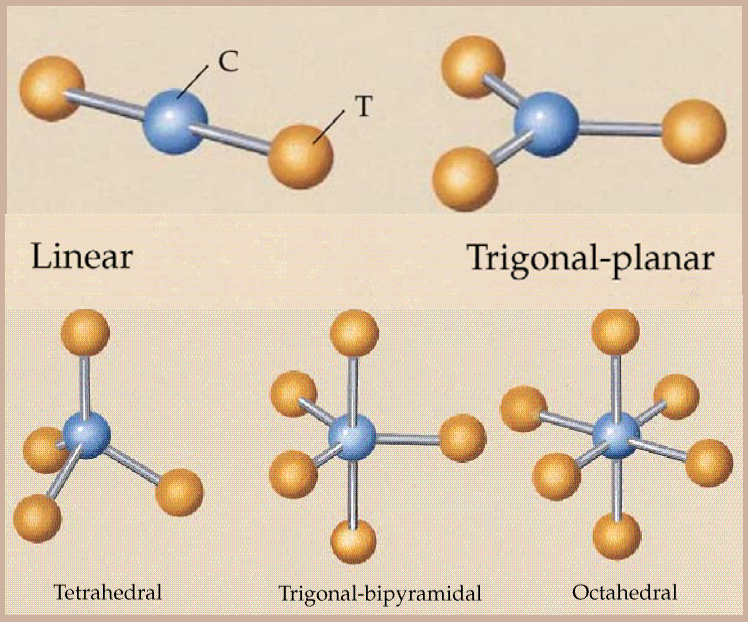


NH_3



H_2O

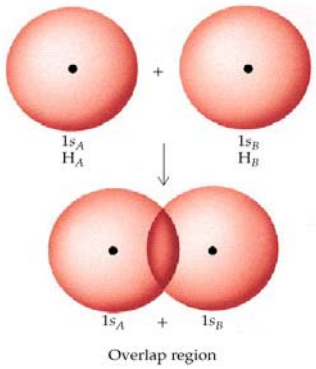
These types of molecules, where C = central atom and T = terminal atoms of the same type, are never polar.



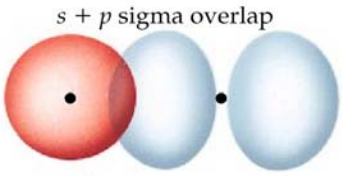
Valence Bond Theory (hybrid orbitals)

The Orbital Overlap Model of Bonding

H-H

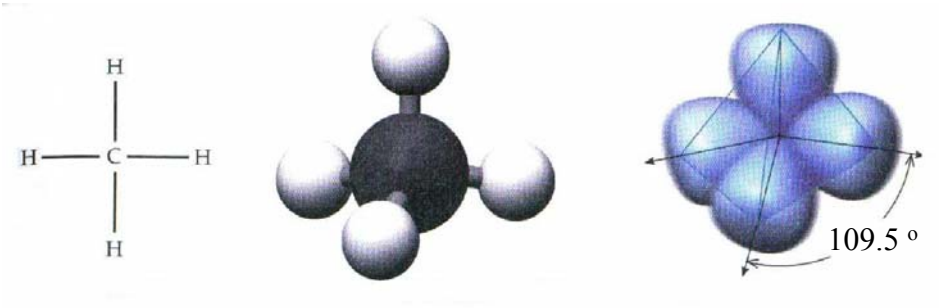


H-F



End to end overlap = sigma (σ) bond

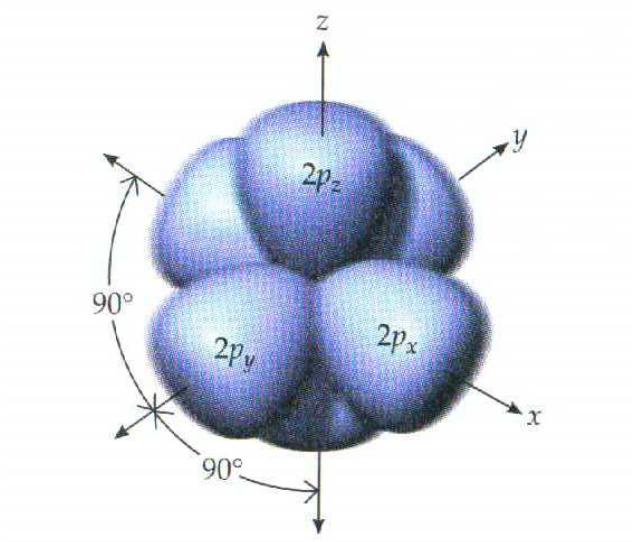
Predicted Bonding and VSEPR Geometry for CH_4



Lewis Structure

Electron pairs around C

Problem: the available s and p-orbitals are at 90° angles, not at the predicted 109.5°!



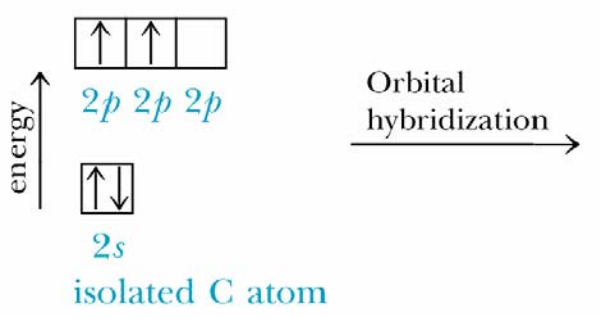
Orbital Hybridization

New orbitals are constructed from pre-existing s, p, and d-orbitals = hybrid orbitals

1. Hybridize the CENTRAL ATOM ONLY (others as needed)
2. Only use valence shell electrons
3. The number of hybrid orbitals formed = number of atomic orbitals used

sp3 Hybridization

For CH_4, we need 4 hybrid orbitals, so 4 atomic orbitals are required as follows: (s + p + p + p) = sp^3



Needed to form 4 sigma bonds

Fig. 10.7

Formation of sp^3 Hybrid Orbitals

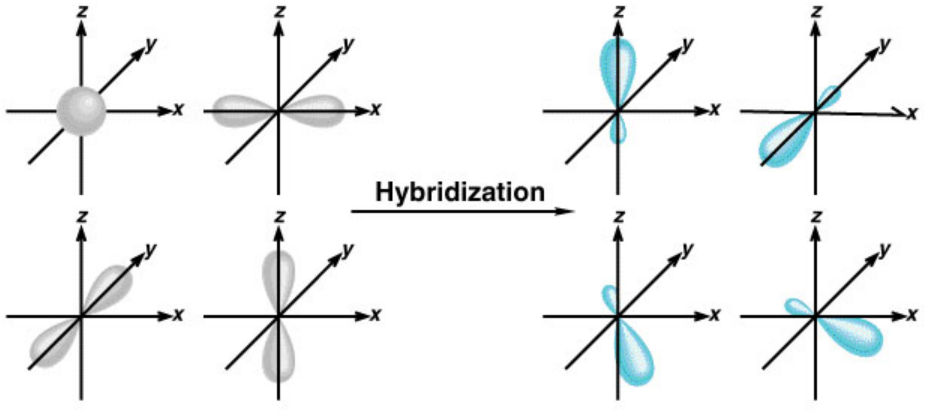
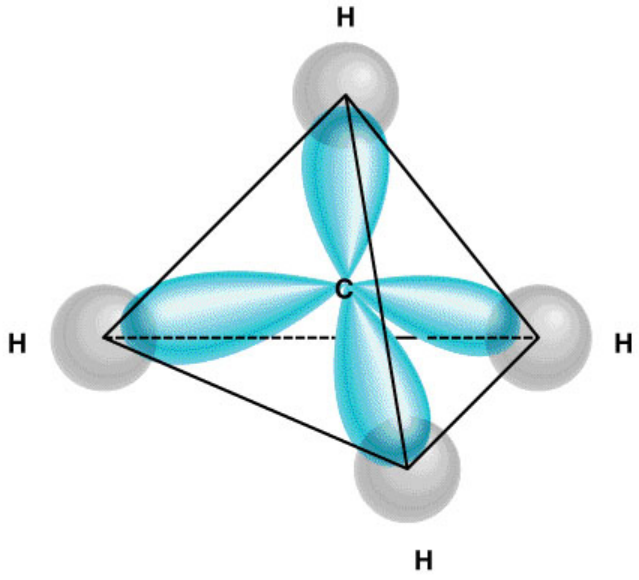
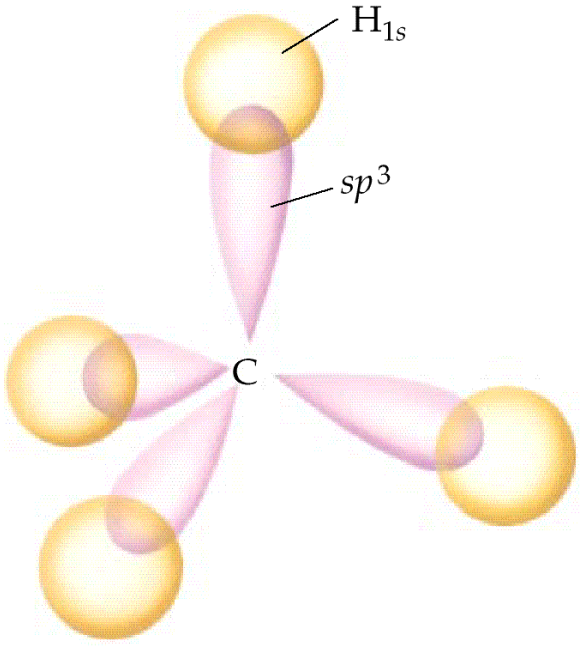


Fig. 10.8

Formation of Covalent Bonds



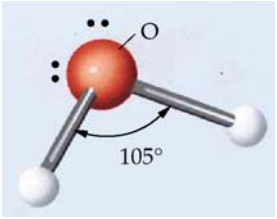


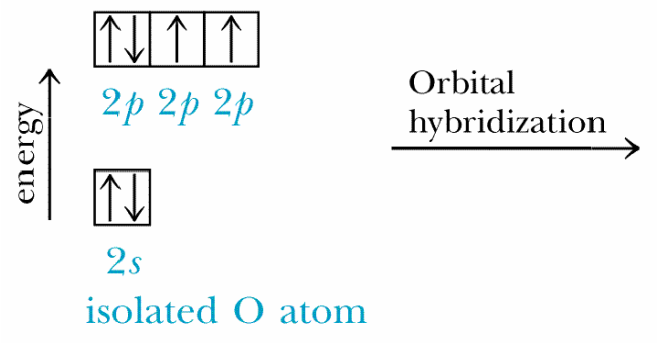
Hybridization Rules

(will be upgraded as we proceed)

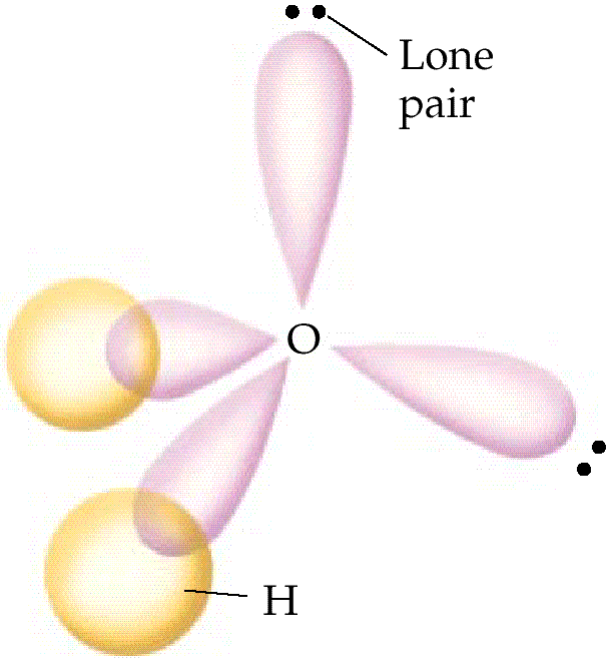
1. Hybrid orbitals get 1 electron for a σ-bond, 2 electrons for a lone pair.

sp^3 hybridization for H_2O



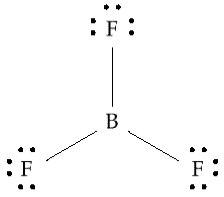


Needed to form 2 sigma bonds and 2 lone pairs

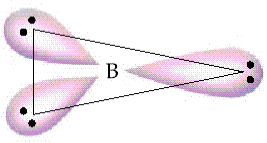


sp2 Hybridization

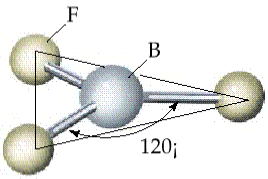
BF_3 - trigonal planar according to VSEPR Theory
(incomplete octet exception)



Lewis dot structure

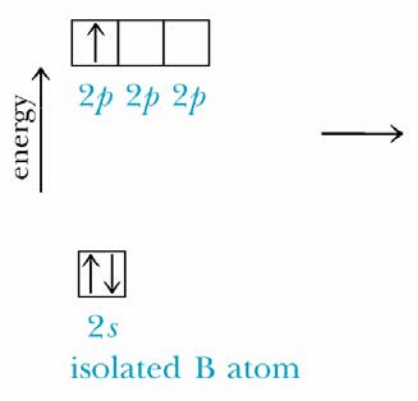


Electron-pair geometry



Molecular geometry

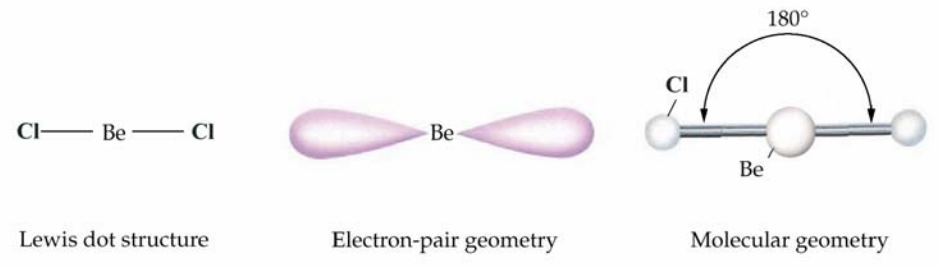
For BF_3, we need 3 hybrid orbitals, so 3 atomic orbitals are required as follows: $(s + p + p) = sp^2$



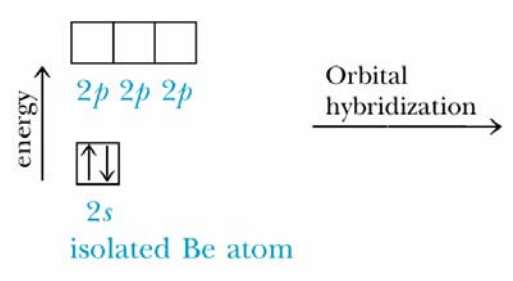
Needed to form 3 sigma bonds

sp Hybridization

$BeCl_2$ - linear according to VSEPR Theory



For $BeCl_2$, we need 2 hybrid orbitals, so 2 atomic orbitals are required as follows: (s + p) = sp

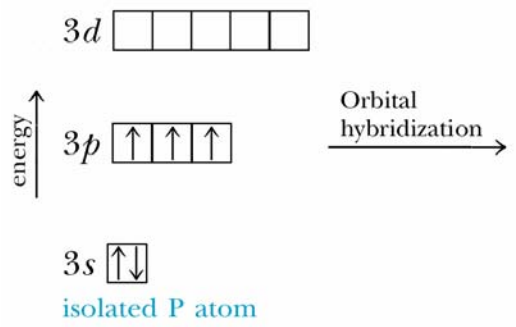


Needed to form 2 sigma bonds

sp3d Hybridization

Ex 10.4 Describe the hybridization state of phosphorus in PBr_5

For PBr_5, we need 5 hybrid orbitals, so 5 atomic orbitals are required as follows: (s + p + p + p + d) = sp^3d

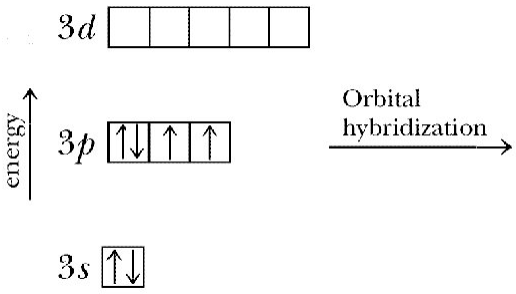


Needed to form 5 sigma bonds

sp3d2 Hybridization

e.g. SF_6

For SF_6, we need 6 hybrid orbitals, so 6 atomic orbitals are required as follows: (s + p + p + p + d + d) = sp^3d^2

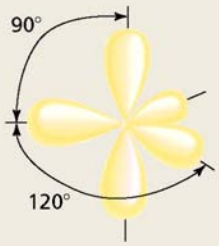
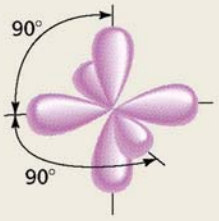


Isolated S atom

Needed to form 6 sigma bonds

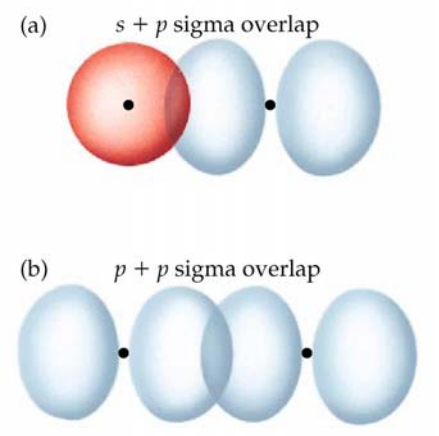
Table 10.4 Important Hybrid Orbitals and Their Shapes

Pure Atomic Orbitals of the Central Atom	Hybridization of the Central Atom	Number of Hybrid Orbitals	Shape of Hybrid Orbitals	Examples
s, p	*sp*	2	180° Linear	$BeCl_2$
s, p, p	sp^2	3	120° Planar	BF_3
s, p, p, p	sp^3	4	109.5° Tetrahedral	CH_4, NH_4^+

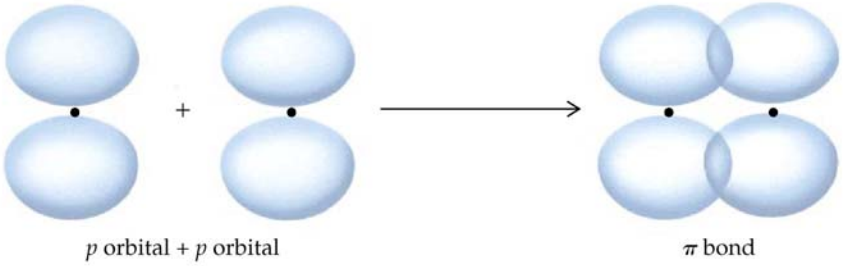
s, p, p, p, d	sp^3d	5	 Trigonal bipyramidal	PCl_5
s, p, p, p, d, d	sp^3d^2	6	 Octahedral	SF_6

Multiple Bonds

Sigma (σ) bonds = end-to-end overlap



Pi (π) bond = side-by-side overlap



C - C 1 σ bond

C = C 1 σ bond
1 π bond

C≡C 1 σ bond
2 π bonds

Hybridization Rules

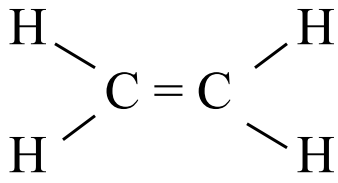
(upgraded – more will be added)

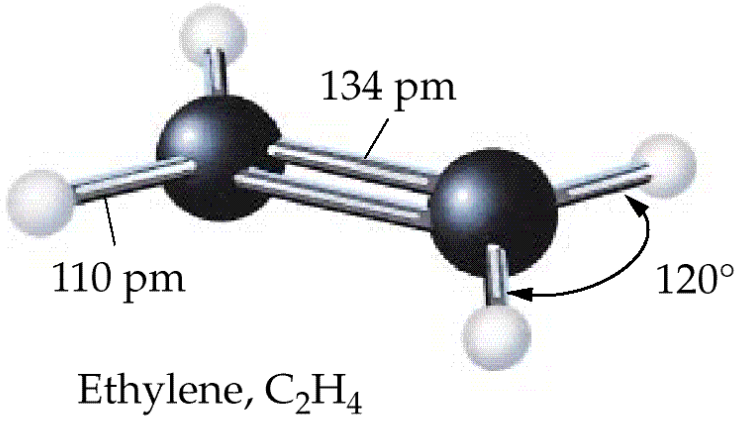
1. Hybrid orbitals get 1 electron for a σ-bond, 2 electrons for a lone pair.
2. Remaining electrons go into unhybridized orbitals = π bonds

DOUBLE BONDS: Ethylene, CH_2CH_2

Lewis Structure:

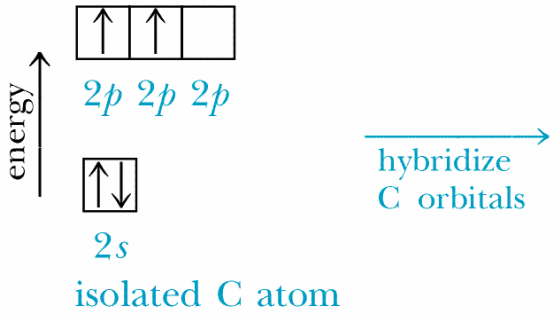
Apply VSEPR Theory and Determine Hybridization



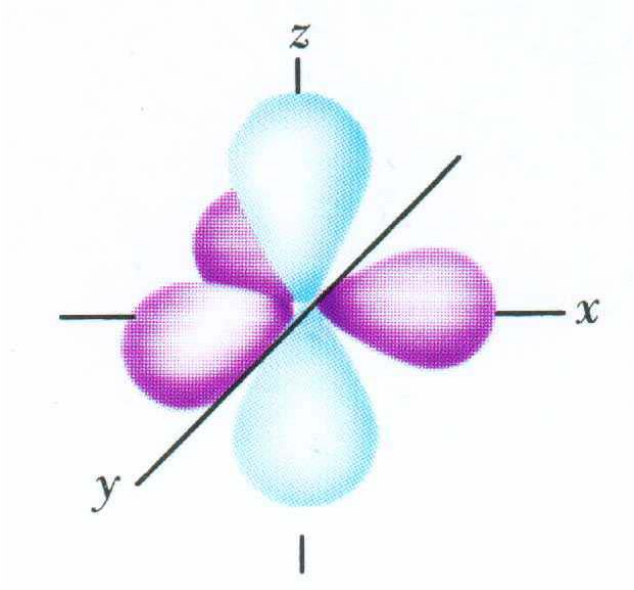


Ethylene, C_2H_4

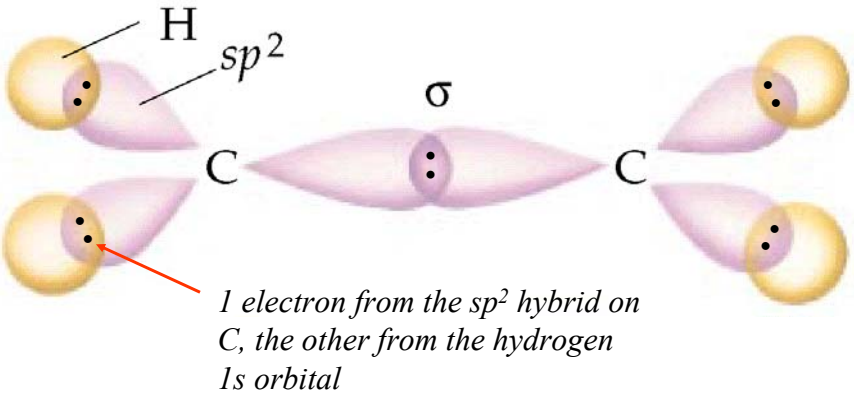
sp^2 hybridization on each C atom -



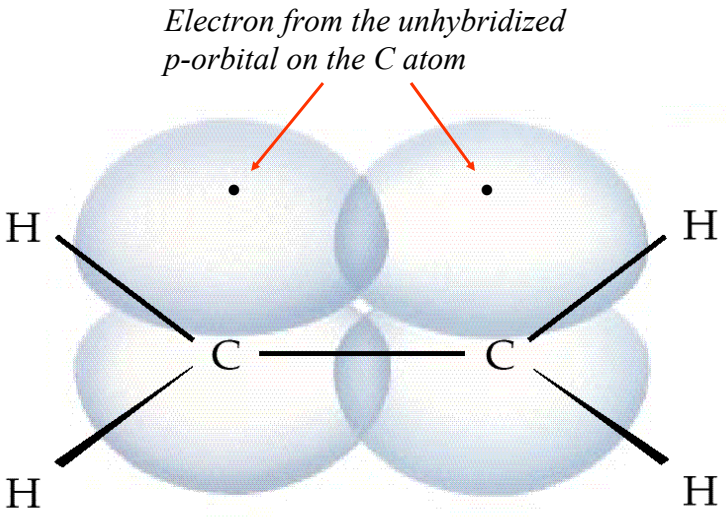
sp^2 hybrids and unhybridized p-orbital



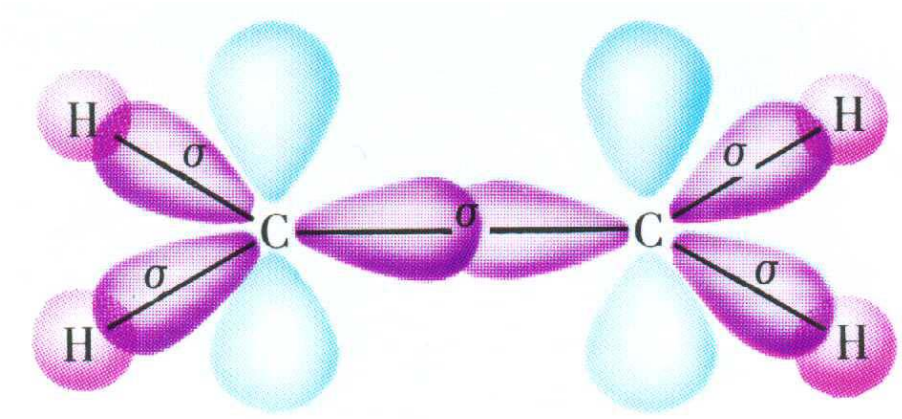
σ bond = end-to-end overlap of the sp^2 hybridized orbitals



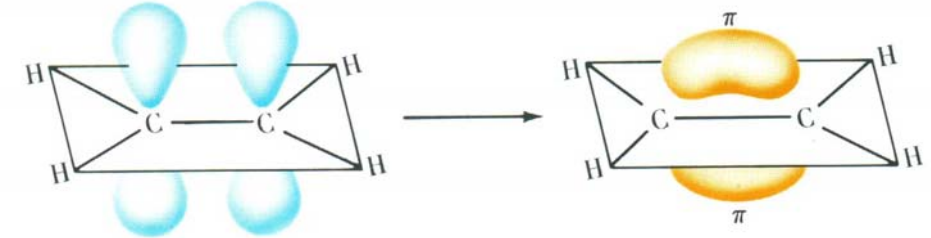
π bond = side-by-side overlap of the unhybridized p-orbitals



Sigma (σ) Bonding in Ethylene



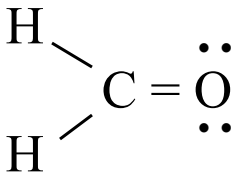
Pi (π) Bonding in Ethylene

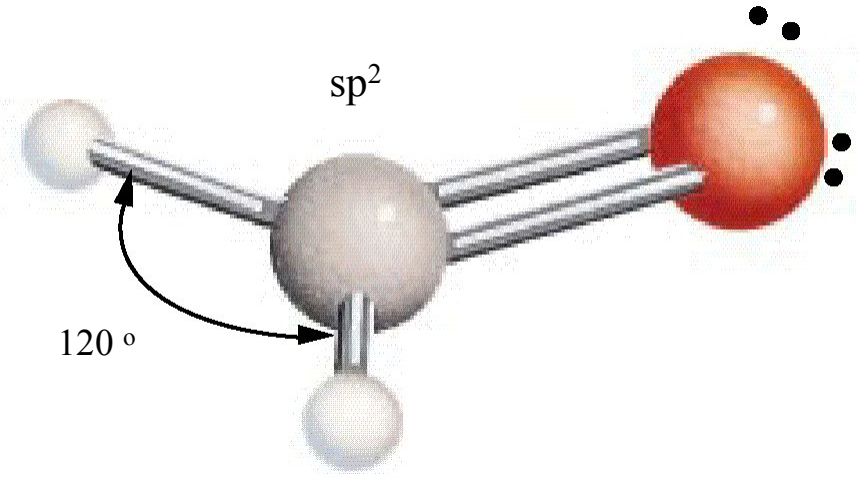


DOUBLE BONDS: Formaldehyde, CH_2O

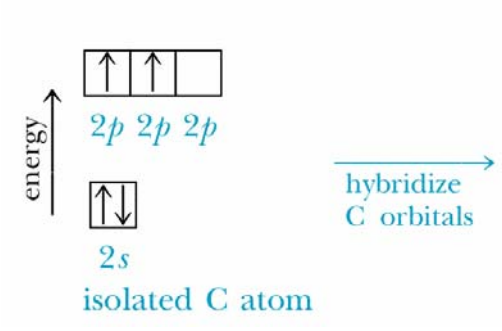
Lewis Structure:

Apply VSEPR Theory and Determine Hybridization

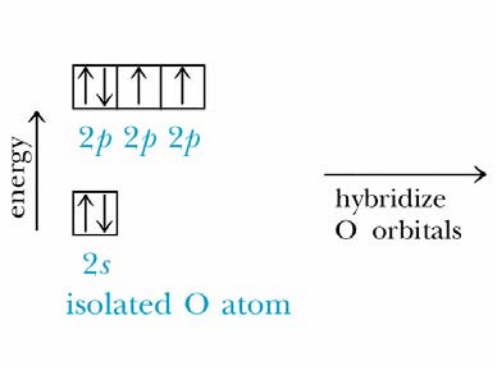




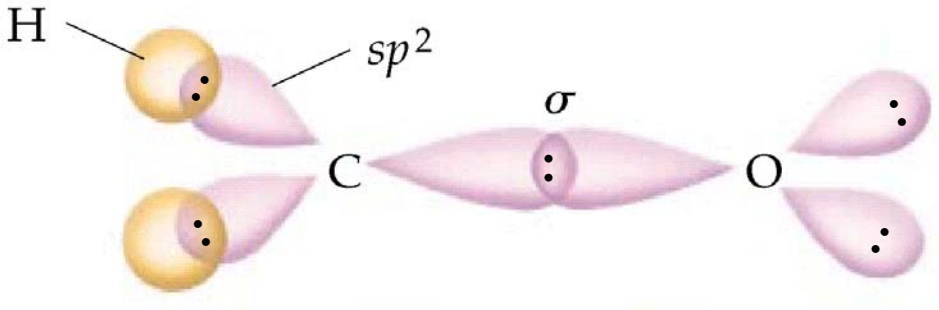
sp^2 hybridization on C -



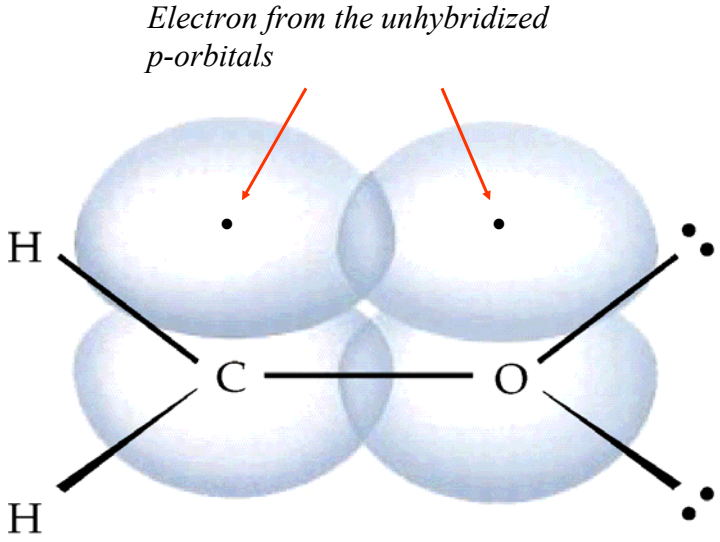
sp^2 hybridization on O -



Sigma (σ) Bonding in Formaldehyde



Pi (π) Bonding in Formaldehyde



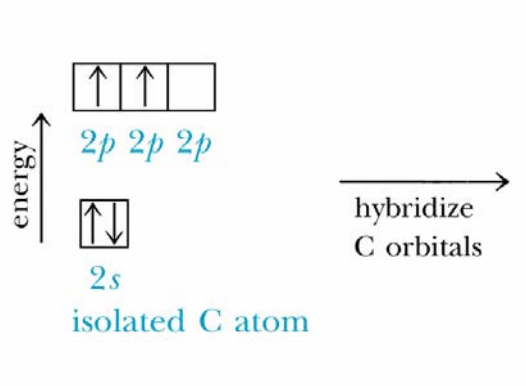
TRIPLE BONDS: Acetylene, C_2H_2

Lewis Structure:

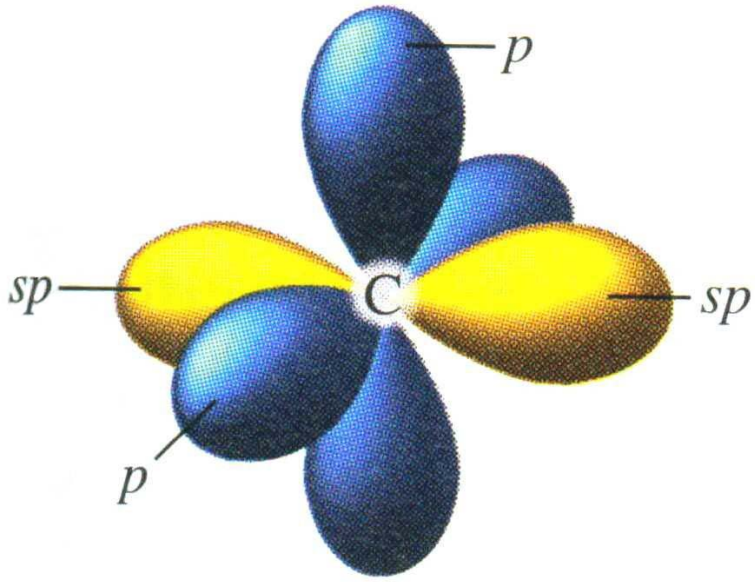
Apply VSEPR Theory and Determine Hybridization

$$H - C \equiv C - H$$

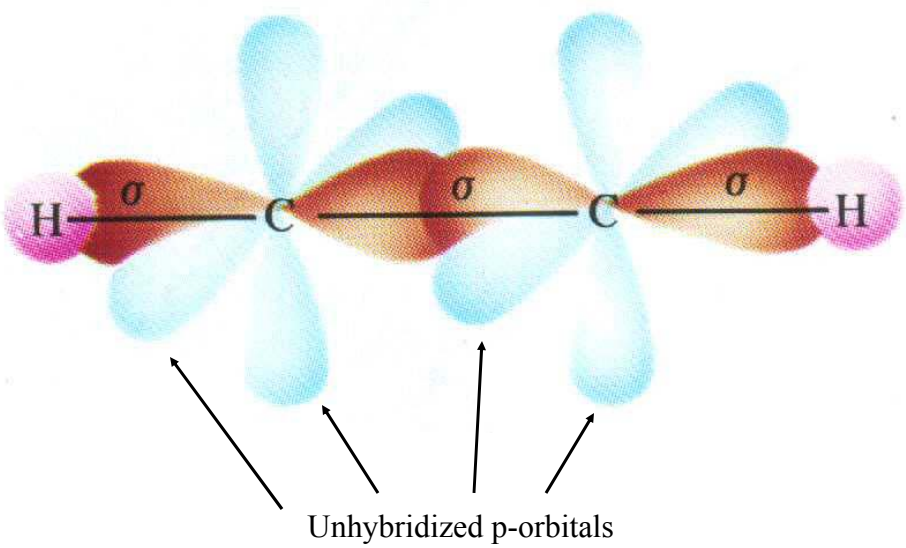
sp hybridization on each C atom -



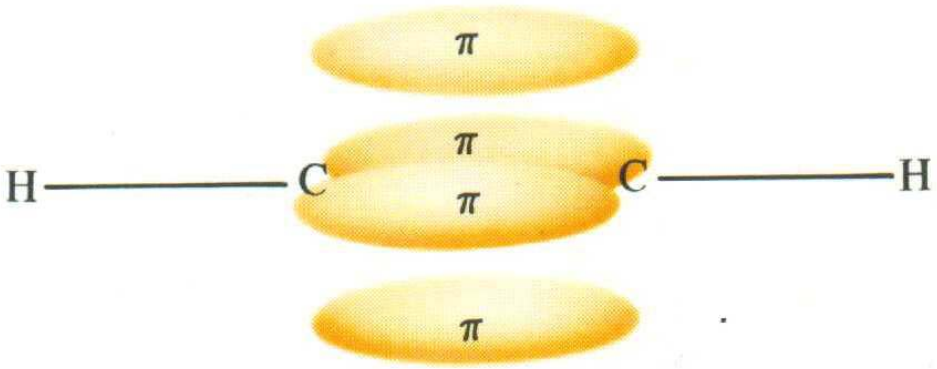
sp hybrids and unhybridized p-orbitals



Sigma (σ) Bonding in Acetylene



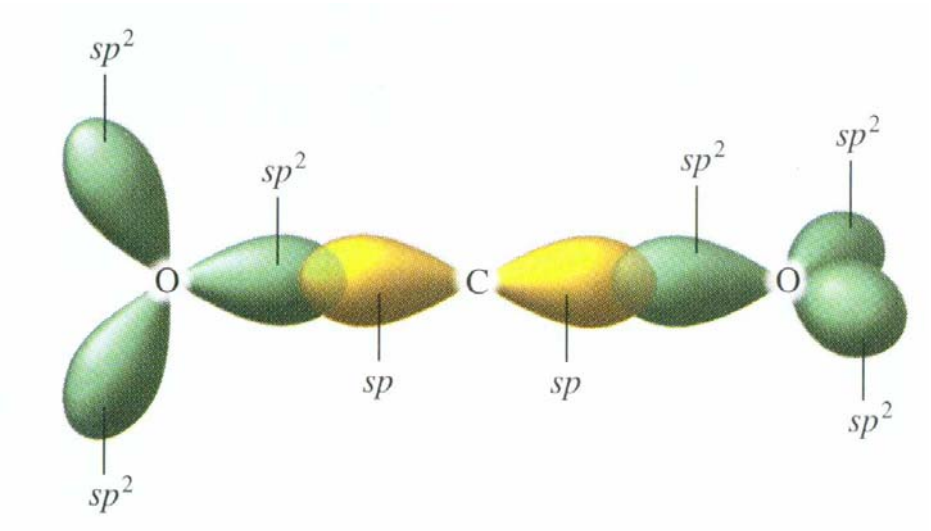
Pi (π) Bonding in Acetylene



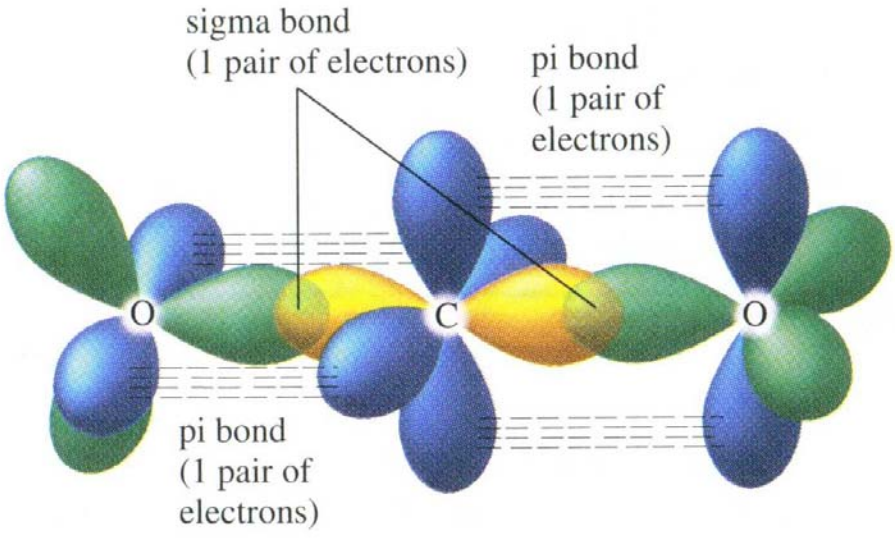
Explain the Bonding Using Valence Bond Theory

CO_2

Sigma Bonding in CO_2



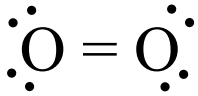
Pi Bonding in CO_2

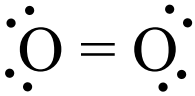


VSEPR Theory - electron pair repulsions influence molecular shape

Valence Bond Theory - atoms form bonds by overlapping atomic and/or hybrid orbitals

Applied to O_2 - 2(6) = 12 valence electrons or 6 pairs



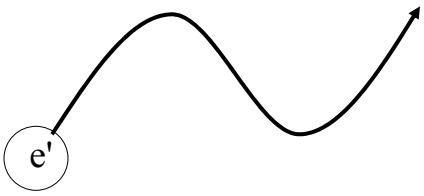


This prediction is WRONG! Since all of the electrons are paired up, the molecule should be diamagnetic, but experiments prove that it is PARAMAGNETIC!

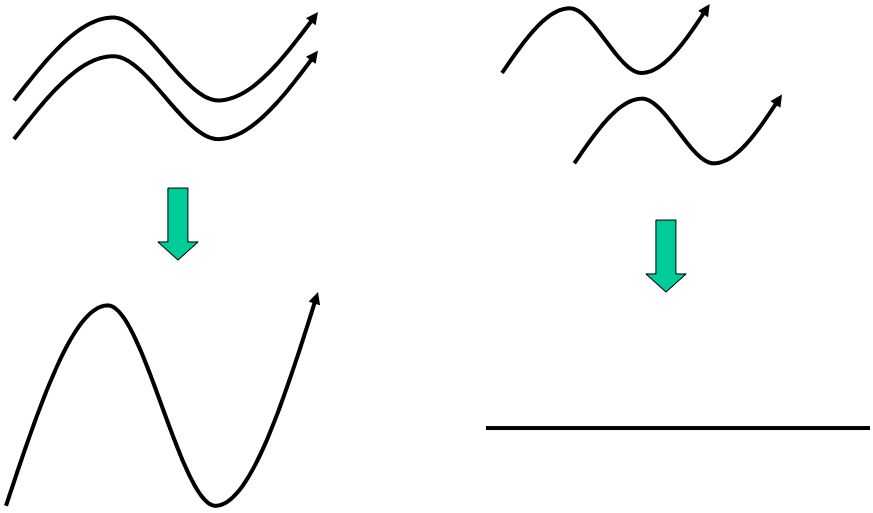
An additional refinement in bonding theory is necessary =

Molecular Orbitals - Preliminary Ideas

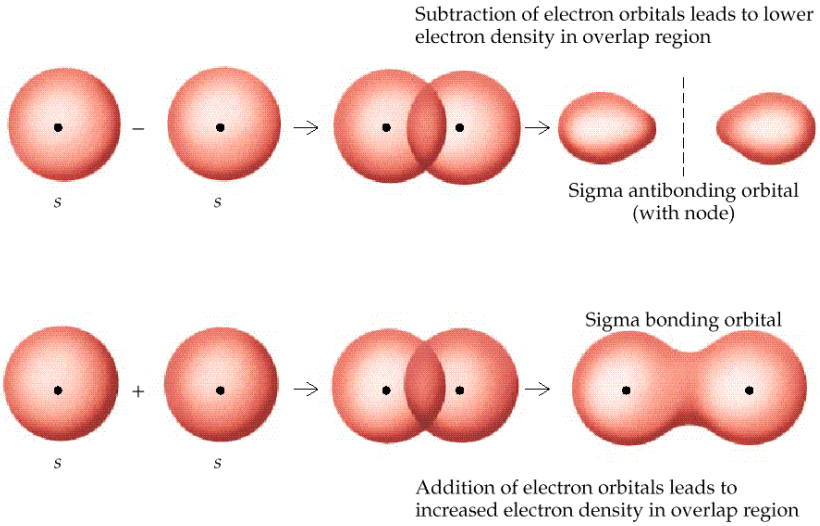
Don't forget that electrons behave like WAVES, and there are WAVE FUNCTIONS (ψ) that describe the electron position in space = ATOMIC ORBITALS (ψ^2)



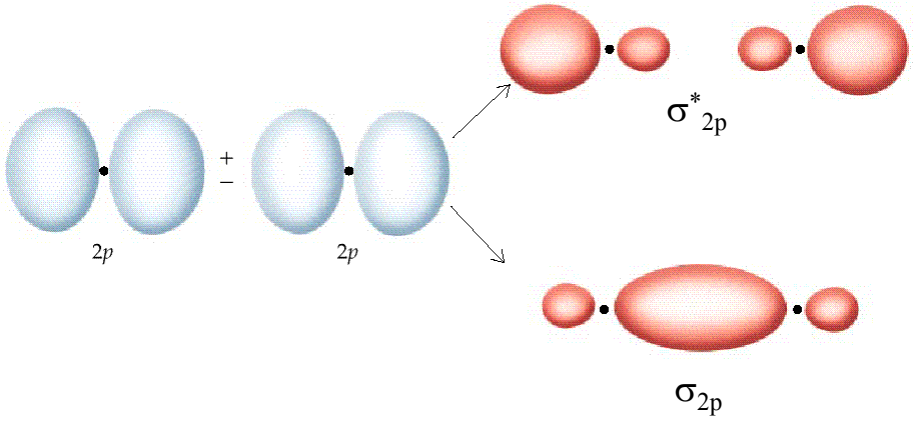
Waves (electrons) can interfere with each other, either CONSTRUCTIVELY or DESTRUCTIVELY



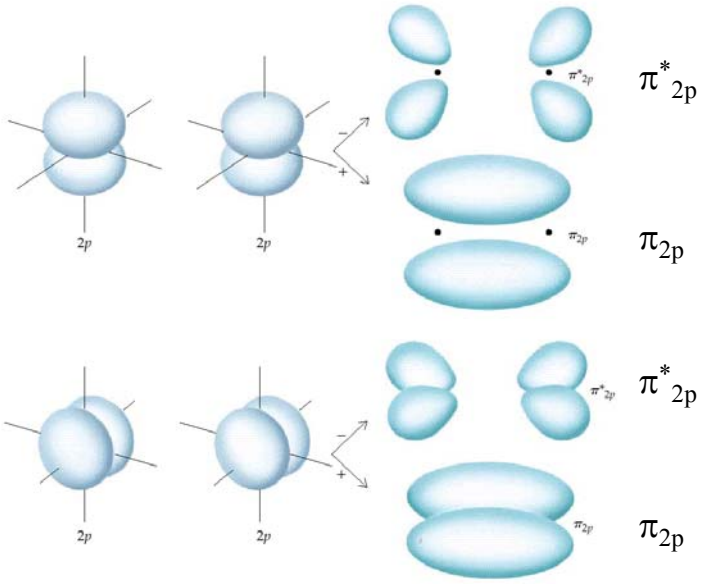
Molecular Orbitals - destructive and constructive interference of atomic orbitals



Sigma bond formation involving p-orbitals



Pi bond formation involving p-orbitals



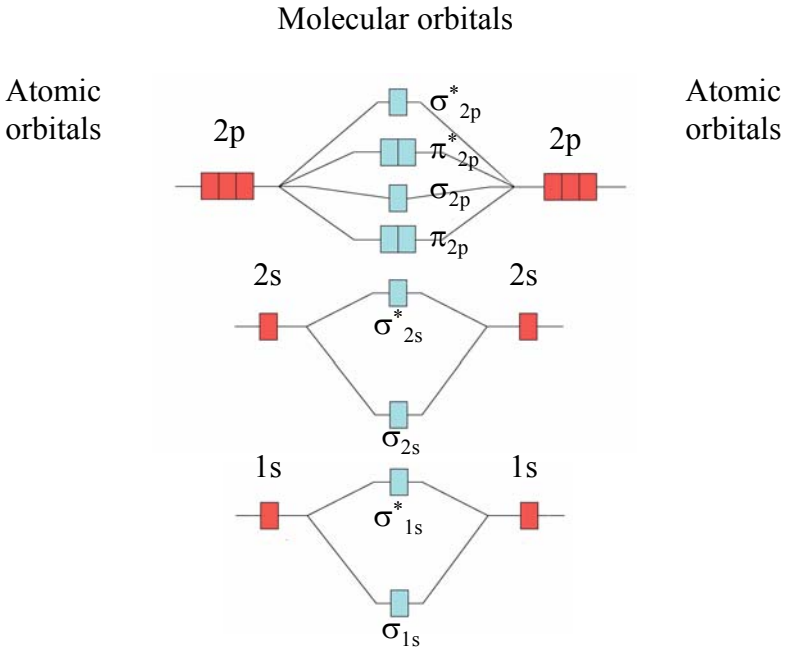
Principles of Molecular Orbital Theory

1. The total number of molecular orbitals = total number of atomic orbitals contributed by the bonding atoms

2. Bonding MO's are lower in energy (more stable) than antibonding MO's

3. Electrons occupy molecular orbitals following the Pauli Exclusion Principle (spins pair up) and Hund's Rule (remain unpaired as long as an empty orbital is available of the same energy)

Energy Levels of Molecular Orbitals for Homonuclear Diatomics - H_2, O_2, etc



Molecular Orbital Electron Configurations

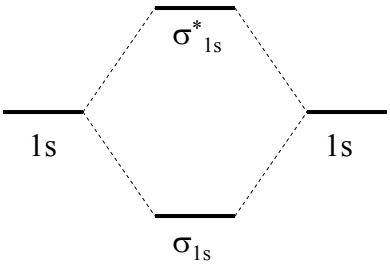
e.g. O_2

Bond Order

Order = ½ [# electrons bonding MO's -
# electrons antibonding MO's]

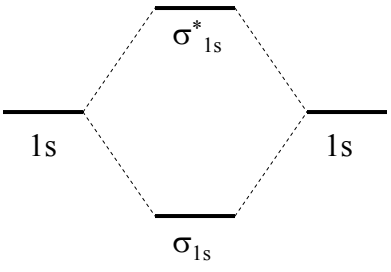
1. The greater the bond order, the more stable the molecule
2. A high bond order means higher bond energies and shorter bond lengths.
3. Fractional bond orders are possible

H_2^+



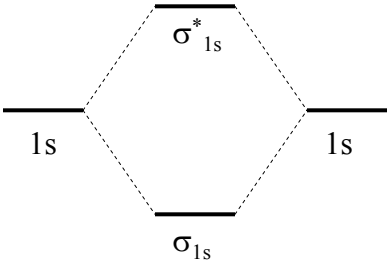
Bond order =

H_2



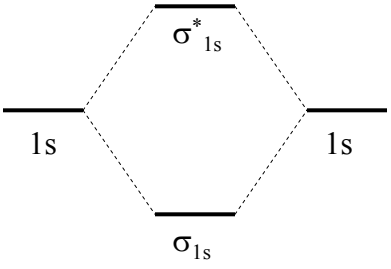
Bond order =

He_2^+



Bond order =

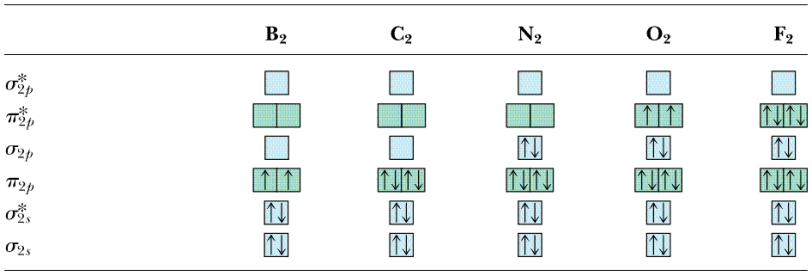
He_2



Bond order =

Homonuclear Diatomic Molecules of Second Row Elements

(the inner MO's formed from overlap of the 1s orbitals aren't shown)

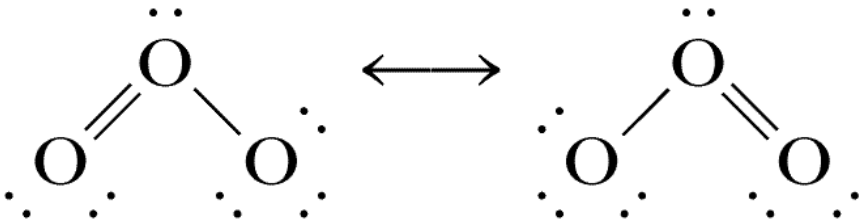


	B_2	C_2	N_2	O_2	F_2
σ_{2p}^*					
π_{2p}^*					
σ_{2p}					
π_{2p}					
σ_{2s}^*					
σ_{2s}					
Bond order	One	Two	Three	Two	One
Bond-dissociation energy (kJ/mol)	290	620	946	498	159
Bond distance (pm)	159	131	110	121	143
Observed magnetic behavior (paramagnetic or diamagnetic)	Para	Dia	Dia	Para	Dia

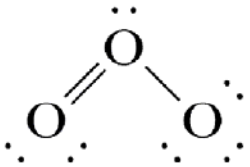
Resonance and MO Theory

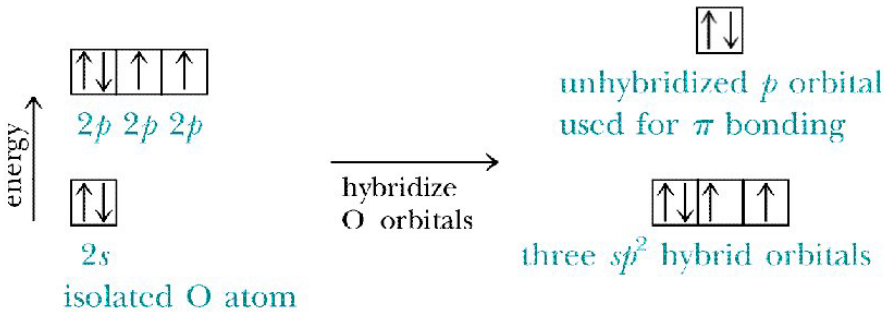
Let's take a look at the molecule ozone - O_3

Lewis structure: 3(6) = 18 or 9 pairs

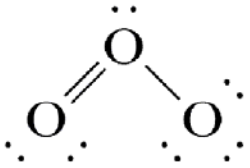


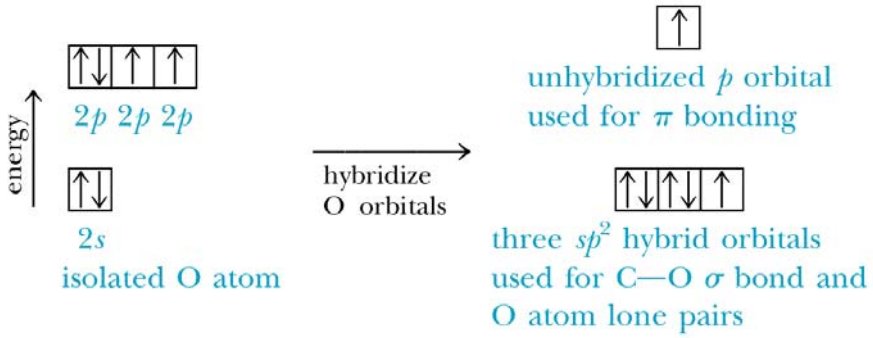
sp^2 hybridization of the central oxygen -





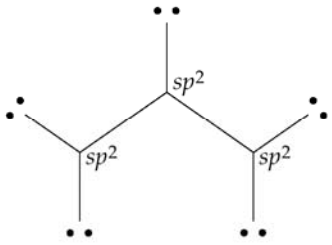
sp^2 hybridization of the terminal oxygens -

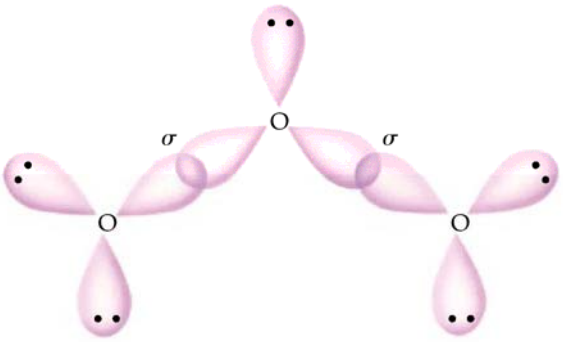




Sigma Bonding in O_3

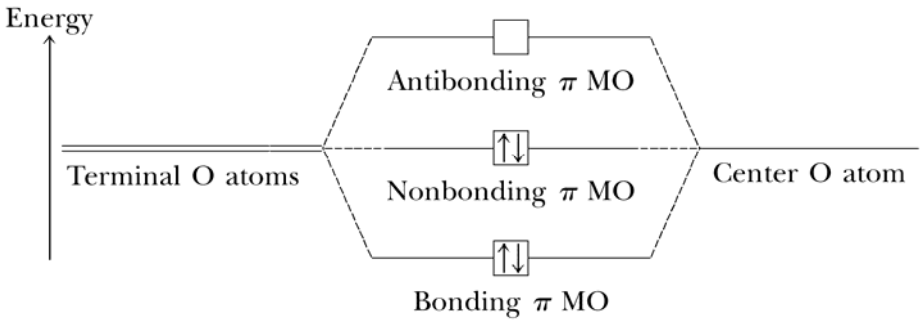
Explain using Valence Bond Theory



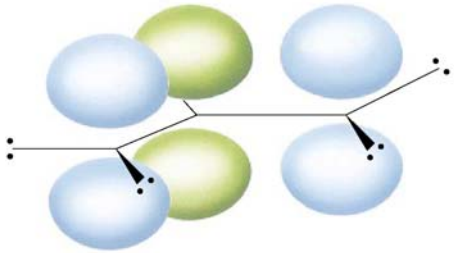


Pi Bonding in O_3

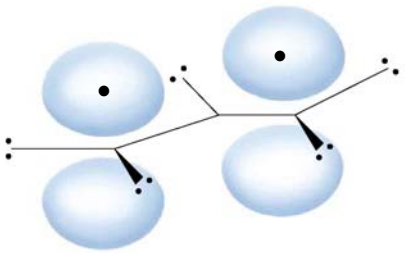
Combine 3 p-orbitals = 3 molecular orbitals



Pi Bonding in O_3

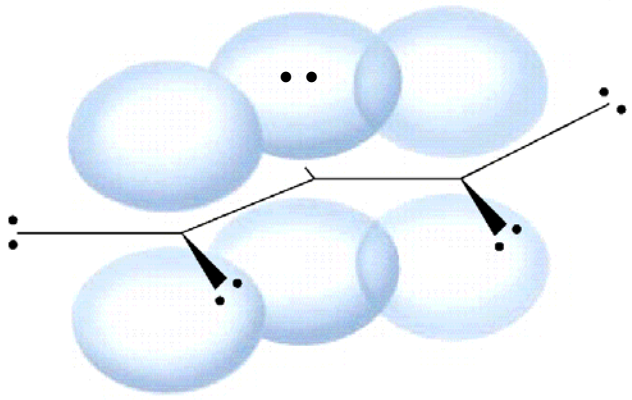


Antibonding π orbital



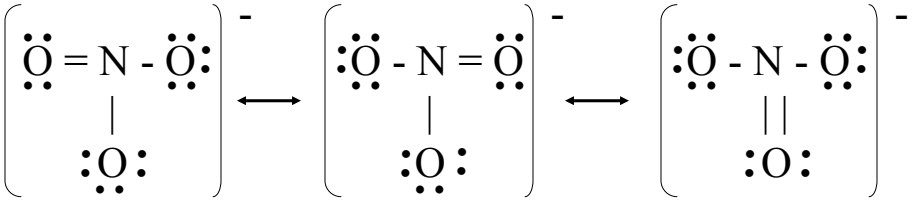
Nonbonding π orbital

Electrons in the bonding MO are free to move along the length of the molecule = delocalization

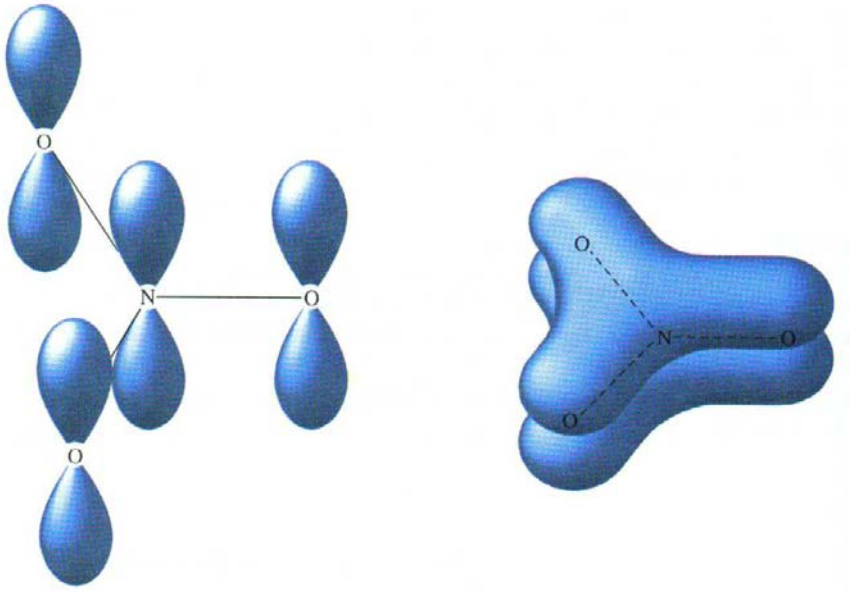


Bonding π orbital

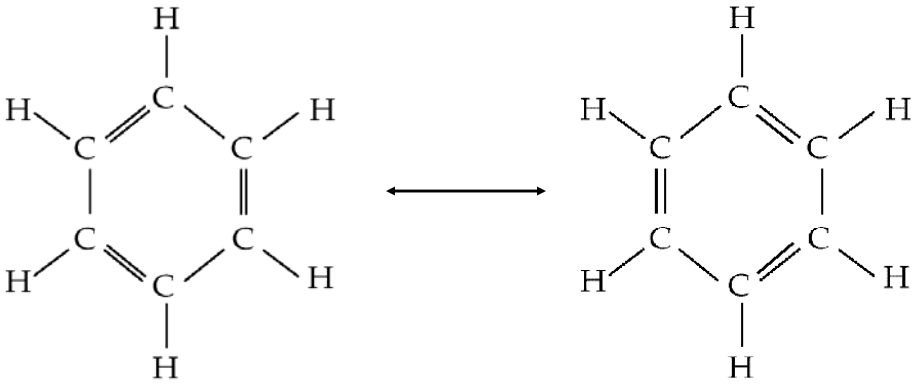
Another example - NO_3^-



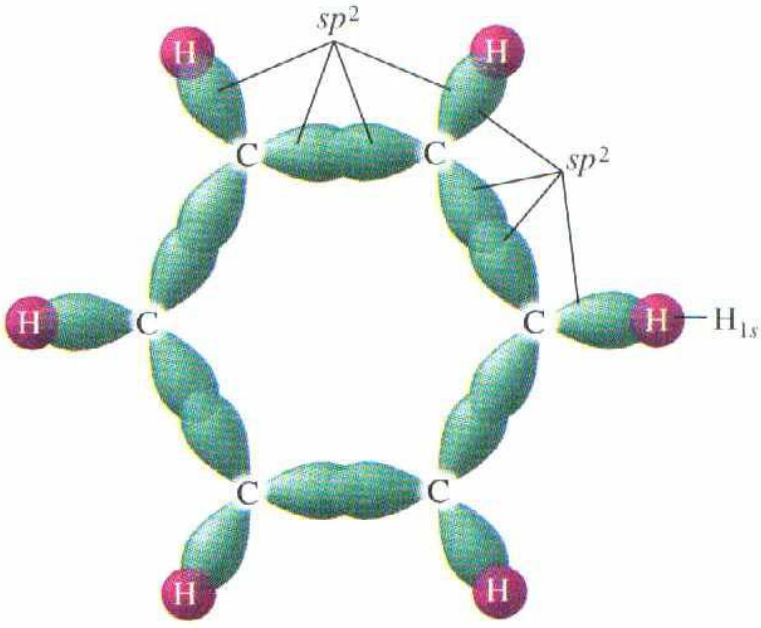
Hybridize all of the atoms to sp^2 and combine the unused p-orbitals into molecular orbitals.

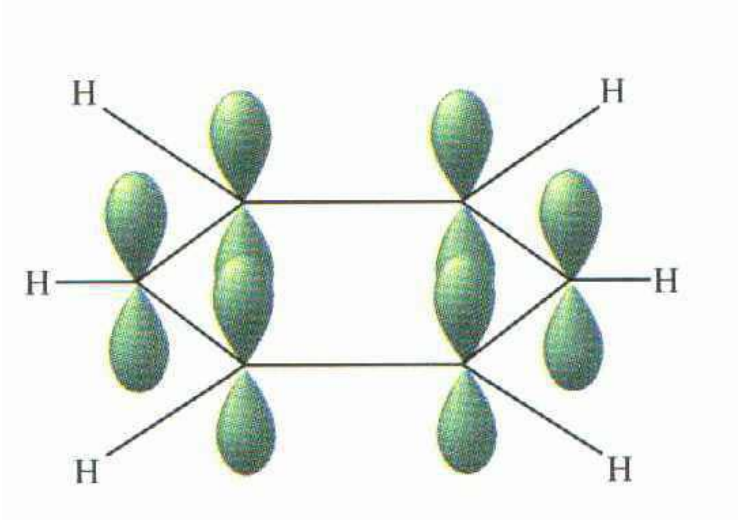


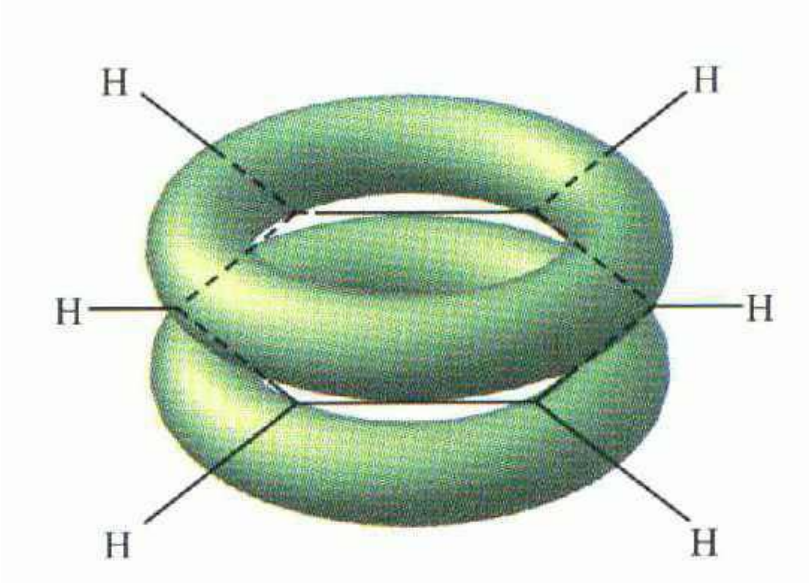
Benzene - C_6H_6

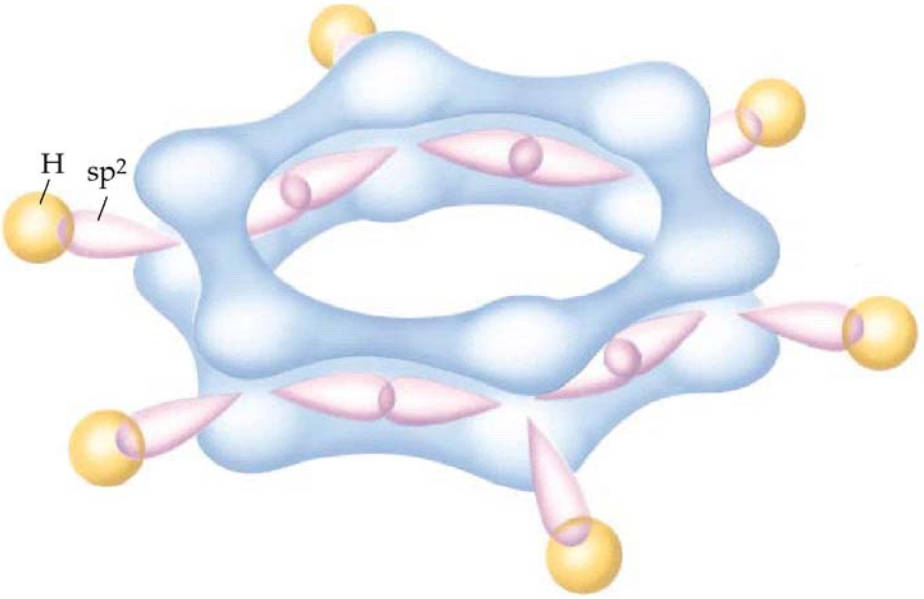


sp^2 hybridize the C atoms and combine the unused p-orbitals into molecular orbitals.


sp^2
sp^2
H
H
C
C
H
C
C
H
H_{1s}
C
C
H
H


H
H
H
H
H
H


H
H
H
H
H
H


H
sp2